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SOME REFLECTIONS ON THERMAL ANALYSIS

ROBERT C. MACKENZIE

Department of Chemistry, University of Aberdeen, Aberdeen (Gt. Britain)

ABSTRACT

Although most of the changes that have occurred in thermal analysis over the past 20 years have been beneficial, some give cause for concern. Thus, the continuing popularity of thermoanalytical techniques in some fields is partially counterbalanced by its general decline in importance in others and increasing awareness of the value of some of the less-common techniques by waste of effort in studies that merely repeat earlier work. Even the present sophistication of data-handling facilities has dangers for the unwary. These aspects, the possible reasons behind them, and what can be done by way of rectification is considered.

INTRODUCTION

Two particularly striking aspects that are noticeable at 8th ICTA are (a) the developments that have occurred in thermal analysis, its applications and instrumentation and (b) the changes that have taken place in the outlook of thermal analysts in the twenty years that have elapsed since the first International Conference in 1965. At that Conference the formation of an international body was first mooted and it is noteworthy that many of the advances have been the product of the activities of that body—namely, ICTA—itself, which has taken a lead in aspects relating to nomenclature, standardization and the provision of literature guides. Other developments, such as the increasing use of what are usually referred to as less-common techniques, have been the result either of the activities and enthusiasm of individuals or of a general appreciation that certain methods can give unique information in specific studies. It is noteworthy, too, that manufacturers of thermoanalytical equipment have been very active in producing advanced instrumentation and in providing information on applications through the research or consultancy departments they maintain.

As always, however, advances bring with them further problems and the remainder of this article is devoted to discussion of some aspects relating to the future of thermal analysis, to less-common techniques, to publications and to instrumentation.

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RISE AND FALL OR RISE AND RISE?

An oft-repeated, and somewhat disturbing, pattern in the history of thermal analysis has been a steady increase in thermoanalytical activity in a particular application followed by a fairly sudden drop to a low but reasonably stable minimum. Sometimes, too, superposed on this is a geographical pattern resulting in the final level of activity in certain regions being higher than in others. The striking part of this cycle is the rapidity and magnitude of the drop in activity: normally, one would expect a rise as the applicability of a method is being assessed to be followed by a gradual decrease to a stable level of employment. The sudden drop and the low final level tend to indicate that the technique involved has little to contribute to the discipline concerned. Several questions therefore arise: namely, does this explanation apply, is the same pattern likely to be followed in fields where activity is still increasing, and what are the reasons for geographical differences? As the answers to these questions are important to the future of thermal analysis, not only to those involved and to those arranging future meetings but also to manufacturers of equipment, let us examine them briefly, using mineralogy as an example of the pattern detailed.

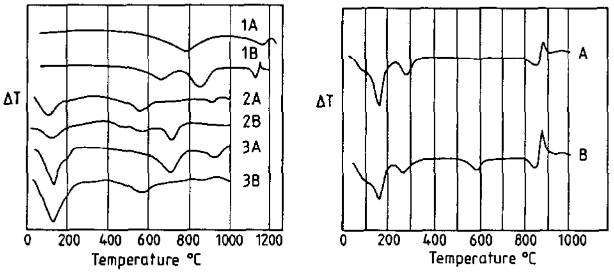
Minerals were among the earliest materials to be investigated thermoanalytically [1,2] and the use of thermal methods increased markedly until it reached a peak about the 1950s: indeed, the development of DTA from a purely empirical to a soundly based technique took place in mineralogy over that period [3]. However, activity then dramatically decreased, particularly in America and western Europe, although a higher level of activity was maintained in eastern Europe and Japan. Even at present, it is particularly noticeable that the description of virtually every new mineral published in the U.S.S.R. includes thermoanalytical data, whereas descriptions published in the West rarely, if ever, do. Moreover, the fact that relatively few mineralogists in the West appear to have access to thermoanalytical equipment indicates that the above observations on utilization are authentic and are not artifacts caused by, for example, the performance of much routine work not recorded in the literature.

Closer examination of available data shows that the "golden age" of thermal analysis in mineralogy coincided with a time when methods of characterizing and classifying minerals, and particularly clay minerals (which defied identification by classical mineralogical methods), were being actively sought. Certainly, X-ray diffraction was available, but equipment was much more expensive than anything mineralogists were accustomed to and it could take up to 24 h to obtain a good powder photograph. As equipment for DTA could be constructed relatively cheaply and a trace could be obtained in less than 2 h, its advantages, if it could be used, were obvious. Despite some promise [4–8], and some success in specific instances in trained hands, it was soon clear that mineral identification was not the strong point of

DTA, either for clay minerals or for other classes that yield thermal effects, as curves can vary because of experimental factors (instrumental and procedural), mineral variation (exchangeable cations, isomorphous substitution, etc.) and/or reaction between components of a mixture. At about the same time, X-ray diffractometry came to the fore, rendering the time of investigation comparable with DTA and, theoretically at least, enabling all crystalline components to be detected. Moreover, X-ray diffraction gave fundamental data based on crystal structure and not affected by factors relating to instrumentation and technique. It is interesting to speculate whether the general and rapid drift away from thermal analysis that occurred when mineralogists gained more ready access to X-ray diffraction equipment would have happened had commercial thermoanalytical instrumentation, which obviates many of the irregularities likely to occur with home-made equipment, been readily and cheaply available. It is indeed possible that the drift away would have been much smaller, as many scientists realized that thermal analysis could yield mineralogical information that cannot, even yet, be obtained by any other method—to mention but three examples [9,10]: (a) the identification and estimation of small amounts (< 1%) of certain hydrate and carbonate minerals, (b) the separation of some dioctahedral minerals into "normal" and "abnormal" types and (c) the detection of a small number of randomly interstratified layers in some apparently pure minerals (Fig. 1).

The higher level of thermoanalytical activity in countries like the U.S.S.R. and Japan seems to be related to the fact that mineralogists in these countries were deeply versed in, and accustomed to, using thermal analysis and therefore maintained activity at a level more commensurate with its true value. Such an explanation fits in with the tradition they inherited from Kurnakov in the U.S.S.R. and Sudo in Japan and their collaborators [3].

Mineralogy, therefore, provides a clear instance of "rise and fall" in thermoanalytical activity; is the same pattern likely to be followed in other



(a) (b)

Fig. 1. (a) DTA curves for "normal" (A) and "abnormal" (B) varieties of 1, pyrophyllite; 2, illite; 3, montmorillonite. (b) DTA curves for vermiculite without (A) and with (B) some randomly interstratified brucite layers [10].

disciplines where today we see a "rise and rise" situation? The most prominent discipline in this position at present is probably polymer science. Arising from early studies on natural and synthetic polymers in the 1930s and 1940s [3], thermoanalytical activity in this field took off in the 1950s and 1960s, following the pioneer work of Murphy [11] and Ke [12]. This more than compensated for the drop in mineralogical studies and, since then, thermal analysis has been ever increasingly used, demand being such that instrumentation has been specifically designed for dealing with such materials.

Polymers are quite different from minerals in that they are formed synthetically under the influence of moderate heat and their behaviour towards heat can be critical in relation to their eventual use. For such materials, thermal analysis is particularly suitable for determining such properties as, to take three simple examples: (a) degree of cure, (b) glass transition, crystallization and melting temperatures, and degradation and decomposition characteristics (Fig. 2) and (c) the effect of temperature on the damping characteristics of elastomers [13]. Here, therefore, thermal analysis is providing *primary* information on heat-dependent properties rather than essentially *secondary* information on constitution. Consequently, one would expect its use not to follow the trend described for mineralogy but rather to follow activity trends in research and production of polymers. Such geographical patterns as are discernible can also be broadly related to relative activity in research and production, thus tending to confirm this conclusion.

The "polymer pattern" can, in all probability, be extended to other materials formed under the influence of heat and whose uses are dependent on the effect of temperature on characteristics; e.g. electronic materials [14]. It might, therefore, be asked why the pattern in ceramics followed (apart from the use of thermodilatometry, which is a classical ceramic method) that in mineralogy rather than that in polymer science. The answer seems to lie in the fact that the high temperature behaviour of materials such as clays depends on bulk chemical composition (which is not obtainable thermoana-

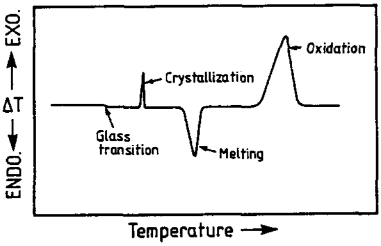


Fig. 2. Diagrammatic DTA curve for a polymer in air, showing the various processes detectable [10].

lytically) rather than on original mineralogical constitution. Yet it is interesting to note that thermoanalytical methods are now being used increasingly in assessment of specialist ceramics—a trend also observed in metallurgy and even in mineralogy. Perhaps the activity in fields that have for some time been "out in the cold" may yet reach the level at which the downward trend should have stopped had adverse factors not been over-operative.

LESS-COMMON TECHNIQUES

Many of what were classified as less-common techniques only a few years ago are now finding increasing use. To illustrate this, one need only consider the use of dynamic thermomechanical methods, which are now extensively employed in polymer science [13] or the position of emanation thermal analysis [15]. It may not be out of place here, however, to refer to three quite different methods, the use of which has been quietly growing but which still seem underrated.

In modern catalyst studies, temperature-programmed desorption is currently giving valuable information on the manner in which volatiles are adsorbed on catalysts. For example, the curves in Fig. 3 reveal that up to four different oxygen species can be adsorbed on a nickel oxide catalyst, depending on the pretreatment temperature [16]. The related method of temperature-programmed reduction, which measures the uptake of hydrogen on heating, can be equally as informative by revealing characteristics of the catalyst itself; for example, the existence of two types of copper species in impregnated alumina catalysts [17]. However, one has to guard against incorrect interpretation, as hydrogen can also be taken up in the formation of a new compound [18]. As with all thermoanalytical methods, experimental conditions must be rigidly controlled—a fact that is now, fortunately, being fully recognized [19]. Although the value of these techniques is mainly

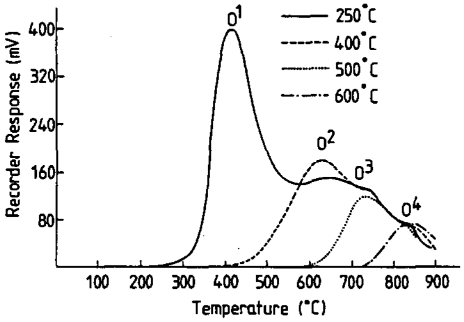


Fig. 3. Temperature-programmed desorption curves for oxygen desorption from a sample of NiO heated to the temperatures indicated; O^1–O^4 indicate the oxygen species—after [16].

appreciated in the catalysis field at present, it seems likely that they have much to contribute in other studies on surfaces and we can therefore expect considerable extension of their use over the next few years.

Another technique with a possibly exciting future is thermosonimetry, which also seems to have potentialities not yet fully exploited. This ingenious refinement by Lønvik [20] of the earlier rather crude method of 'decrepitation analysis' [21] enables accurate recording of rate or amplitude of sound emission during heating. The strong sound emissions associated with phase transitions and decomposition reactions [20,22] are now believed to be associated with release of strain, as they seem to cease fairly abruptly just as the transition or reaction commences [23]. In addition to these processes, however, sound emission is also associated with microcrack propagation in glass, where the intensity of sound emitted is related to both critical microcrack length and to surface microcrack density [24], and with the number of dislocations occurring in crystals [25]. Moreover, the frequency of the sound emitted depends on the process giving rise to the emission [26]. This technique may, therefore, have wide application in relation to the strength of materials.

The third technique has no official name as yet. It depends on the use of the Guinier–Lenne X-ray diffraction camera (produced by Nonius), which enables the diffraction pattern to be continuously recorded on a vertically moving film as the sample is heated. The record so obtained gives very valuable information on the structural changes undergone on heating and can be correlated with other thermoanalytical, such as TG and DTA, data.

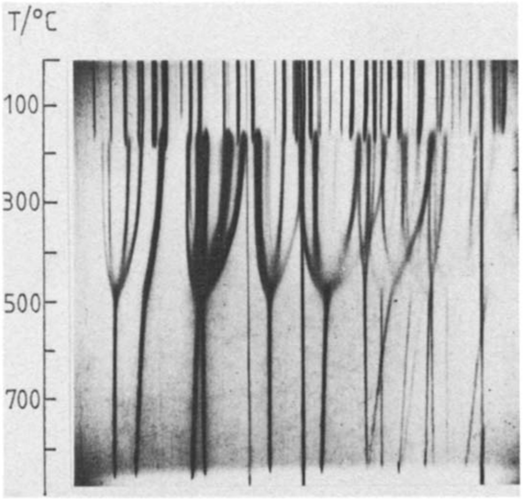


Fig. 4. X-ray diffraction pattern from a Guinier–Lenne camera showing the structural changes occurring in $NaHCO_3$ on heating.

The record for sodium bicarbonate (Fig. 4) is an excellent example, showing the sudden decomposition to sodium carbonate and the changes in the latter as it passes through the various polymorphic forms at about 400°C; the continuous "lines" come from the platinum holder and are useful for calibration. The reason this technique is not more widely used appears to be related to practical problems, as the camera is time-consuming to set up accurately and, once set up, is easily disturbed, necessitating re-alignment. Moreover, for some materials that give diffuse patterns, such as clays, the lines on the film can, at times, be difficult to follow. Surely, however, modern technology could overcome these impediments, the first by design improvements and the second by image enhancement. With such improvements, it seems reasonable to conclude that this camera could become a major thermoanalytical tool.

Clearly, therefore, there is still development potential in some less-common techniques and thermal analysts can look forward to an exciting future as more and more are fully exploited.

PUBLICATIONS

While editing Thermal Analysis Abstracts, the author has been rather surprised by the number of papers that repeat earlier work without adding anything new. Perhaps this is normal and perhaps as much duplication of effort occurs in other fields, but such squandering of resources makes one think of the reasons and of possible remedies. The reasons for unnecessary duplication seem to be: (a) unavailability of the literature in which the earlier work was described; (b) a large disparity in the disciplines to which the two studies related; (c) inadequate checking of the literature. Cause (c) indicates undue haste, but cause (b) raises some sympathy: however, both can be obviated by proper training: i.e. by emphasizing the necessity of checking standard texts for older studies and thermoanalytical journals and abstracts for more recent ones, always remembering that the same material can be used for quite disparate purposes in widely differing disciplines. Cause (a) arises from economic factors that little can be done about at present. Should the work have been done, however, there is one simple means of precluding the extra expense of unnecessary publication—namely, adequate and informed refereeing of papers before publication. Indeed, several journals would be vastly improved and scientists saved from large amounts of junk paper if more attention were paid to preliminary assessment of papers.

The problem of unavailability of literature causes great difficulties in countries with limited foreign exchange. Can anything be done to relieve this situation? It is interesting to note that chemists have recently set up, with the backing of several bodies, a Center for History of Chemistry at the University of Pennsylvania, U.S.A., to act as a central archival store. One wonders whether something similar could be done for thermal analysis. For example, it might be possible to establish a central international archive containing all books on the subject, complete runs of thermoanalytical journals and abstract services, together with such historical material as could be collected in the form of reprints or copies. One feels certain that many senior thermal analysts would be willing to donate much such material should anything eventuate. Not only would this be a valuable repository for historical research, but, if properly staffed, it could be consulted for information by those unable to obtain access to a wide range of literature. Unfortunately, the finance required to establish, maintain, staff and operate such an institution would be very considerable and, even should some sponsors come forward, the only practical solution would seem to be that it be set up as a section within a suitable university department. Despite its apparent impracticability at present, it might be useful for ICTA to look into the whole question of access to literature and maintenance of archival material to see what can be done. Unless action is taken soon, much will be lost.

INSTRUMENTATION

Enormous strides have been taken in thermoanalytical instrumentation over the past twenty years and manufacturers must be congratulated on the quality of instruments they now produce. There are still, however, some matters of concern.

All advances in instrumentation have essentially been in the areas of temperature control, data acquisition and data processing through the use of solid-state circuits and computerization. This has proved invaluable to numerous users by removing the drudgery associated with interpretation of recorder traces, but one wonders whether sufficient attention has always been paid to the system that produces the data—namely, the specimen holder. Certainly, there has been a general tendency to standardize on the flat-pan micro type of holder and systems of this type operable to about 1500°C are readily available. But, admirable as this system is for most investigations, it is not satisfactory for all and some thought should perhaps be given to improving specimen holders so that they yield raw data of a quality commensurate with the sophistication of the data-handling system. It is often forgotten that the quality of the output is no better than the quality of the input. One of the holders not now available is the gas-through-the-sample type, designed in the 1950s [27] but unobtainable since the Stone equipment ceased to be marketed, yet, in certain studies, this holder can yield invaluable data that cannot be obtained in any other way. Perhaps the time is ripe, therefore, for manufacturers to reassess the types of specimen holders they supply.

With the fully computerized equipment and software now available, raw data can be processed in a variety of ways, thus saving much time in situations where standard operations are required. To avoid error, however, such instruments should be operated by someone conversant with the theory of the process concerned and, although manufacturers take great trouble to instruct and train operators, there are circumstances over which they have no control. Thus, in the current climate, where a thermoanalytical technique such as DTA is only one of a whole battery of techniques that may be applied and is often a complementary technique, operators may change and the new one may be instructed only in the process being followed at the time. Moreover, in a large establishment, equipment may be moved from one department to another or even disposed of to a third party with only a sketchy understanding of the method. All these situations could lead to unsatisfactory results being obtained through erroneous use and to rejection of the method without proper testing. A great onus is, therefore, on the shoulders of all experienced thermal analysts to ensure that *all* those responsible for thermoanalytical equipment, irrespective of grade, are properly trained in the background of the various programs, so that they understand exactly what the "black box" is doing.

Two other aspects that give some cause for worry in connection with processing of DTA data relate to curve-smoothing and interpolation of the baseline. With regard to the first, one wonders whether it can be guaranteed that only noise is removed and that one will not miss a very small but highly significant effect and, with regard to the second, there must be some concern about the nature of the interpolated line. The answer to the first seems difficult to assess, but the answer to the second must be that, unless it conforms to the theoretical baseline of Šesták [28]—and this would be impossible for a standard program covering a wide range of materials—it must be a compromise. As a consequence, there must be some uncertainty in all calculated area-dependent parameters.

At this point, it should again be stressed that, used properly, fully computerized instruments are admirable, but that *every* operator requires instruction in what the machine does, the limits of the information available and the number of *significant* figures in a numerical output.

CONCLUSIONS

In general, the future of thermal analysis seems secure and it is unlikely that there will be sudden decreases of activity in some fields, as has happened in the past. Moreover, the less-common techniques have much more to offer than has probably been realized. Problems exist in relation to duplication of work and possible misuse of highly sophisticated equipment, but these can be overcome by better refereeing of papers and thorough education in the basics of thermal analysis as a whole. A case can be made for a central repository of thermoanalytical information, although funding would present a problem. Finally, so that common problems are fully realized, there is a strong case for ICTA retaining a strong interdisciplinal character and not becoming too compartmentalized.

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