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APPLICATIONS OF NEW METHODS AND INSTRUMENTATION IN THERMAL ANALYSIS

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SUMMARY

Thermal analysis techniques are non-specific in that they do not identify particular chemical species. The use of evolved gas analysis (EGA) overcomes this limitation and opens up new dimensions to the extent that the combination of thermal methods and EGA can be regarded as a novel and very powerful group of techniques for analysing complex mixtures and for studying thermally induced reactions.

INTRODUCTION

Thermal analysis (TA) techniques are being used in an increasingly wide range of applications, including qualitative and quantitative analysis, the determination of important physical and mechanical properties of materials, and fundamental studies of the nature of chemical reactions. To accommodate the demand for new types of information, and in order to solve complex problems, a great many innovative techniques have been developed in recent years.

This paper will concentrate on one of these developments which has a potential for major growth. The family of techniques in question is evolved gas analysis (EGA). Such is the power of EGA that a case can be made to consider it not merely as an adjunct to conventional TA methods,

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but as a new area of immense promise. The combination of a knowledge of the mass and energy changes occurring in a material, together with full information on the gas-phase products, as the temperature is slowly scanned, gives a hitherto unobtainably detailed insight into the system. The result is a very powerful 'new' tool in the armoury of the analytical chemist. It is hoped that the applications mentioned at the end of this paper will begin to substantiate the claim that TA-EGA deserves a much greater coverage and recognition than accorded to it currently as a minor off-shoot of DTA and TG.

The mass of data produced by TA-EGA is complemented by the increasing use of on-line computer systems to enhance the precision of data acquisition, to perform calculations in seconds which would otherwise take hours, or to analyse results in ways which are so time consuming that they would not normally be attempted. Of course, computer-based processing of data is available for most commercially produced thermal analysis equipment, but there is still a place for the custom-designed system which meets specific requirements.

Classical thermal analysis techniques are generally non-specific i.e. they do not respond to particular chemical species, but give, in the form of a DSC or TG curve, an indication that some undefined thermally induced event has occurred. It is a consequence of this almost universal response that TA methods find such an immense range of applications. However, while this may be satisfactory for the analysis of simple, well-characterised systems, there is often a requirement for more specific information. This may arise from the need to understand the processes revealed by DTA/TG etc. or because the material being analysed is a complex mixture which gives a series of unresolved, or at least partially resolved TA curves. For these reasons it is often necessary to employ a variety of ancillary techniques to provide the extra information required.

THE USE OF ANCILLARY TECHNIQUES - ANALYSIS OF THE SOLID PHASE

There are two approaches to the problem. One can study the solid material remaining at various stages in the thermal analysis experiment. However, although such an approach can be very useful, there are certain disadvantages. Frequently the samples are rather too small for accurate chemical analysis and so various instrumental methods are often employed. One commonly used technique is that of X-ray diffraction. However, although of great value, this approach is not without potential difficulties. For example, high temperature phase changes, if reversible, will not be detected after cooling to room temperature, unless the sample can be quenched sufficiently quickly to freeze in the high temperature form. A decomposition process might well reduce the crystallite size to a point where the products appear amorphous to X-rays. Further,it has been found that some materials do not immediately crystallise into the product structure after the reaction has been completed, as indicated by TA, thus causing uncertainty in the interpretation of the XRD results.

The solids produced by thermal decomposition often possess a large surface area and hence a high degree of reactivity, making them susceptible to attack by oxygen, carbon dioxide or water in the atmosphere. Unless rigorous precautions are taken to exclude even traces of these gases, the products observed on subsequent analysis may well be different from those produced in the original reaction.

In addition to these difficulties there are always the problems arising from non-simultaneous techniques, i.e. those associated with the unambiguous association of two measurements made at different times and under possibly very different conditions. There will always be some uncertainty regarding any processes which may occur while the sample is being cooled to room temperature, prior to analysis.

A further problem is that the analysis of a sample at various stages in a TA experiment is very time consuming and is therefore not suitable for producing results rapidly, as is often required in indusrial operations.

Of course, some of the objections to this approach can be overcome by employing the ancillary analytical techniques simultaneously and indeed some workers have developed equipment for simultaneous TA-XRD and TA-IR. However the approach is rather specialised, expensive and is not readily available.

ANALYSIS OF THE GASEOUS PHASE

Fewer problems are found in analysing the gases which are evolved during thermal analysis. Evolved gas analysis (EGA) is usually a coupled simultaneous method, in that the sample is heated in a separate (thermoanalytical) apparatus and the vapour-phase products carried into the gas analyser, often using an inert purge gas, via a suitable connecting line. Problems of identifying the evolved gas analysis results unambiguously with those of the thermoanalytical technique remain. However, the experimental design can be such that the time difference between the evolution of the gases and their detection is so small that it can be neglected. It is possible to reduce this time delay, for example, to less than one second.

Steps have to be taken to preserve the integrity of the evolved gases and to check that the measures adopted have been successful. This is particularly important with products which are readily oxidised or changed catalytically. Frequently the materials used in thermal analysis equipment possess excellent catalytic properties. For example, platinum and its alloys are widely found in both thermocouples and in furnace windings. It is necessary, therefore, to design the system so that contact between the evolved gases and the equipment is minimised or eliminated. The problem is exacerbated as, of course, the TA equipment is used at elevated temperatures.

Once the evolved gases have been extracted safely, they must be transferred intact to the gas analysis equipment. Less volatile materials will tend to condense and steps must be taken to prevent this, not only to preserve the original composition of the gas phase , but also to avoid the gas lines becoming blocked. This requires some form of heating for the lines carrying the gas-phase products from the point of their generation to the gas detector.

During the transit time the volatiles must be protected from degradation and this is often accomplished by using an inert covering on the interior of the gas line. A short transit time further reduces the possibility of reaction with the walls of the line and also minimises the risk of any gas-phase chemical processes.

TYPES OF EGA DETECTOR

A great many detectors and analysers have been used in EGA. They can be classified as either specific or general in their mode of operation.

Specific devices are of great value as there can be no doubt as to the identity the gas being detected. However this virtue rather limits the range of possible applications as each detector responds to one and only one gas. Examples include hygrometers, oxygen meters, infra-red gas analysers and, for gases which can be dissolved in a suitable solvent, selective ion electrodes.

However, because of the restrictive nature of such techniques, much work has been done to develop methods of more general application. The simple katharometer is of use in detecting the evolution of a gas, but more sophisticated equipment is needed to identify its chemical nature. On-line IR can be very effective, provided sufficiently rapid scanning can be achieved and this requires rather specialised instrumentation. Similarly GLC potentially offers a great deal in terms of sensitivity and in its ability to deal with complex mixtures. Here again modifications to the technique are required if more than one analysis is to be carried out in the course of a weight-loss process. Desirably short retention times can only be achieved at the expense of resolution. Several workers have overcome this limitation by using automatic equipment to store the evolved gases on short, cooled lengths of tube, containing an adsorbent, which are changed at regular, brief intervals during the thermal analysis experiment. The material trapped in this way can be analysed by GLC subsequently under optimum conditions such that the maximum resolution of which the technique is capable can be achieved.

THERMAL ANALYSIS-MASS SPECTROSCOPY (TA-MS)

Perhaps the most powerful of all EGA techniques is mass spectrometry (MS), especially when combined with GLC to give TA-GLC-MS.

Amongst the pioneers of the use of MS in EGA were Langer and Gohlke (1,2). They established the two main techniques, the first of which, "Mass Spectrometric Thermal Analysis" (MTA) involves placing the sample in a specially designed mass spectrometer source. This has a number of advantages over other methods, as very small amounts of gas can be detected and, because the experiment is performed in the high vacuum of the spectrometer, there is no possibility of any gas-phases reactions before the evolved materials are detected. A similar technique was developed by Price et al. (3) who used a temperature-programmed solid insertion probe in a time-of-flight mass spectrometer to study the thermal decomposition of cadmium oxalate.

However, the very low pressure prevailing in the source of the mass spectrometer is also responsible for a number of serious limitations as it can greatly affect processes which are pressure dependent, causing problems with the control and measurement of the sample temperature. Further, not only are the peak temperatures reduced markedly, but the resolution and general shape of the curve is changed. This makes correlation with TA experiments carried out at atmospheric pressure very difficult. Nevertheless, in some instances the results of MTA, when the MS is set to read the ion current at fixed m/e ratio, rather than scan a range of masses, appear similar to those of DTA, so that the processes giving rise to the DTA peaks can be identified.

To avoid these problems an alternative approach was developed, in which the sample is heated in an external furnace, or DTA etc., at normal pressures and the evolved gases led into the MS where they are analysed at the low pressure prevailing in the source. In addition to the potential difficulties which this link may cause and which are outlined in the introduction, there is the new requirement that some way must be found to accommodate the two very different pressures at which the DTA and MS operate. Despite this extra difficulty, most workers have used this approach rather than MTA, as it is much easier to correlate the results of DTA etc. and MS. A further advantage is that a standard mass spectrometer can be used with the minimum of reconfiguration. Many reports are found in the literature of links of this type between TA equipment and mass spectrometers of various designs.

ADVANCED TA-MS

The combination of TA and MS is undoubtedly powerful, but such is the wealth of information provided when complex gas-phase components are analysed that the task of interpretation is often impossible. The mass spectrometer is at its most efficient when analysing single components, for which it gives, when operated conventially, a large number of peaks, each due to one of the many fragments produced in the ionisation process. When mixtures are analysed, the cracking patterns of the individual components are superimposed, very considerably increasing the complexity of the spectrum.

To overcome this limitation several advanced methods of TA-MS have been devised. Chang and Mead (4) used a combination of TG, GLC, and high resolution MS in their study of the thermal degradation of polymers. By interposing a GLC before the MS, it was possible to effect a preliminary separation of the components in the evolved gases, so that the MS could operate under ideal conditions.

Baumgartner et al. (5) employed MS with chemical ionisation to reduce fragmentation of the sample within the source, so that only parent-ion peaks were recorded, thus greatly simplifying the mass spectrum.

Another approach has been developed by Gibson and Johnson (6) who used a computer to unravel the complex mass spectra produced from multi-component mixtures.

An interesting modern development is the use, by Dyszel (7) of an atmospheric pressure ionisation mass spectrometer, in conjunction with TG, in her work on the analysis of guar gums.

THE AUTHOR'S TA-MS SYSTEM

The work carried out in the author's laboratories has been aimed at developing a low-cost, versatile system which overcomes as far as possible the potential difficulties outlined above. A flexible multi-inlet TA-GLC-MS system is used (fig.1), in which the gases are evolved, at controlled pressure, from samples in DTA, TG equipment, or a special micro-furnace designed to permit very rapid heating rates whilst maintaining excellent contact with the thermocouple used to measure the sample temperature. The gaseous products are swept from the TA equipment into the gas analysis system by a flow of inert purge gas which is usually helium. The gases are carried by a tube of small bore to ensure a rapid transit time, and which is lined with glass to reduce or eliminate adsorption and catalytic effects. This glass-coated metal line can be heated to avoid blocking caused by condensation of the vapours evolved in the experiment. The end of the heated line, which is a few mm in diameter, protrudes into the crucible containing the sample, and this together with the high flow of purge gas minimises contact between the gases and the hot furnace components. By using a relatively high flow rate of purge gas, together with a small diameter tube, the time elapsed between the evolution of a gas and its detection in the mass spectrometer can be kept below 1 second. In turn this provides less scope for subsequent gas-phase reactions and thus helps to simplify the interpretation of the data.

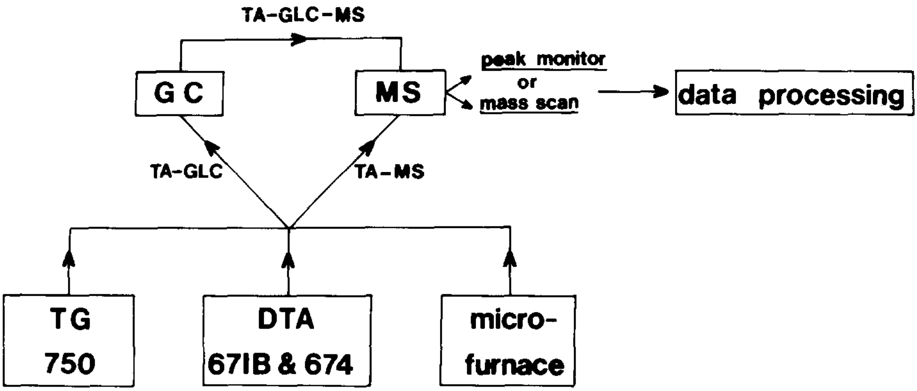

Fig.1 Schematic diagram of the TA-GLC-MS system

The pressure difference between the TA equipment and the MS is accommodated by means of an all-glass jet separator of the type used in GC-MS.

In practice, mass spectra are obtained during a TA run at points of interest on the TA curve. Once the prime species of interest have been identified, in a second experiment the MS can be set to the selected-ion mode (SIM) in which the MS gives a continous readout of selected m/e values. This produces a series of continuous curves, each corresponding to the evolution of a single compound, which are almost identical to the corresponding DTA or DTG peaks. These "evolved gas profiles" give specific information on the chemical reactions taking place and can be used for both qualitative and quantitative analysis. They are also particularly useful in studying the kinetics of thermal decomposition reactions as they enable the rates of evolution of individual components, in what may be a complex mixture, to be followed.

However, the complexity of the material being analysed, or of the gas-phase components, often results in mass spectra which are difficult to interpret. In such cases a GLC is used to effect a preliminary separation before the single components are presented to the MS as they are eluted from the column. The product gases are continuously swept through a loop which is connected by an automatic sampling valve to the GLC. At suitable points in the TA experiment, the plug of gas contained in the loop is injected into the GLC and, in addition to the resulting chromatogram, the individual components are analysed by the MS as they emerge from the column. For this to be successful, short retention times are required so that a number of GLC determinations can be made during the course of a TA experiment. For this reason the GLC work is compromised to some extent and if sufficient resolution cannot be obtained, other methods are used.

A technique, which is particularly effective in analysing trace components, is to use the loop as a trap (by cooling it in liquid nitrogen or other suitable refrigerant) to collect all the products formed during the TA run. The entire range of products can then be "injected" into the GLC by flash-heating the previously cooled loop. Conventional GLC-MS can then be used to analyse these materials. Now there is no requirement for short retention times and the analysis can be carried out under optimum conditions.The equipment is linked to a microcomputer via a 12-bit, 8-channel analogue to digital converter for on-line data acquisition and subsequent processing.

APPLICATIONS OF TA-MS

Kettrup et al. (8) have used TA-MS in a study of coals. They analysed the volatile components in a gasflame coal and demonstrated the variation of the gas-phase components with temperature. This information, combined with the detailed TG and DTG results presents a unique finger print of a very a complex material and therefore contributes to a greater understanding of its nature.

In a continuing study of the applications of thermoanalytical techniques to archaeology, Wiedemann (9) has applied the full power of TA-MS to the investigation of the bust of Queen Nefertiti. The binding media used for the pigments was found to be a type of wax, the exact nature of which was established by means of TA-MS.

A more traditional application of TA-EGA to the thermal degradation of metal complexes is described by Kettrup et al. (10) who were able to deduce the reaction mechanism involved in the thermal decomposition of metal (II) acetylacetonates. The thermal analysis data permitted the relative stabilities of a series of metal chelates to be established and interpreted in terms of the electronic structure and properties of the cations involved.

The unique capability of the combination of TA-MS to solve difficult problems is illustrated by the work of Dyszel (7). Guar gum is a series of closely related polysaccharides, the structures of which differ only slightly. TG has been used in an attempt to distinguish the many forms of this family of materials, but with limited success. However, the addition of MS provided the necessary supplementary information to clearly distinguish between groups of samples exhibiting similar TG curves. Further more, analysis of the MS results led to a greater understanding of the thermal decomposition processes involved.

Catalysts play a vital role in the majority of chemical processes and without their aid much of modern chemical industry simply would not function. One traditional method of preparing catalysts is to thermally degrade a compound containing the elements of the catalyst, in such a way as to create the chemical structure, and particle shape, size and dispersion necessary for optimum performance. Short and his co-workers (11), in their studies of noble metal catalysts supported on pyrographite-coated carbon-fibre paper, used MS to study the products of decomposition of platinum-ammonia complexes, in conjunction with both DTA and TG, to investigate the structural and chemical properties and their dependence on preparative technique. Ciembroniewicz et al. (12) used a quadrupole mass spectrometer to analyse the gases evolved in the decomposition in vacuo, in air and in an atmosphere of inert gas, of ammonium paramolybdate, in their study of the mechanisms of formation of molybdenum oxide catalysts.

A versatile and flexible system for quantitative TA-GLC-MS has been developed by the author (13,14) and used to investigate the mechanisms of a variety of thermal decomposition processes and as a valuable tool in analysis of a wide range of materials, including high performance insulators, minerals, nuclear fuels, catalysts, and solid-state lubricants.

An important area of application is the study of the kinetics of reactions which produce gaseous products. Of particular interest are thermal decomposition reactions where the evolved materials are complex and the reaction therefore cannot be studied successfully by conventional weight-loss or pressure-increase methods (13).

The thermal decomposition of calcium propanoate (14) is such a reaction. Fig. 2 shows the apparently single step decomposition described by the TG and DTG curves. However, GC-MS of the total evolved volatiles revealed the presence of at least five components (fig.2). Having identified the products, a separate, isothermal, experiment was conducted to follow the rate of evolution of the major constituent, 3-pentanone. The data was stored by an on-line computer, via an 8-channel, 12 bit analogue to digital converter. Fig. 3 shows how a conventional alpha-time plot is constructed from the raw data, the calculations being carried out automatically by the computer. This isothermal work showed further detail, and kinetic analysis of the major process gave good Avrami-Erofeev plots, from which the activation energy and pre-exponential factor were calculated (fig. 4).

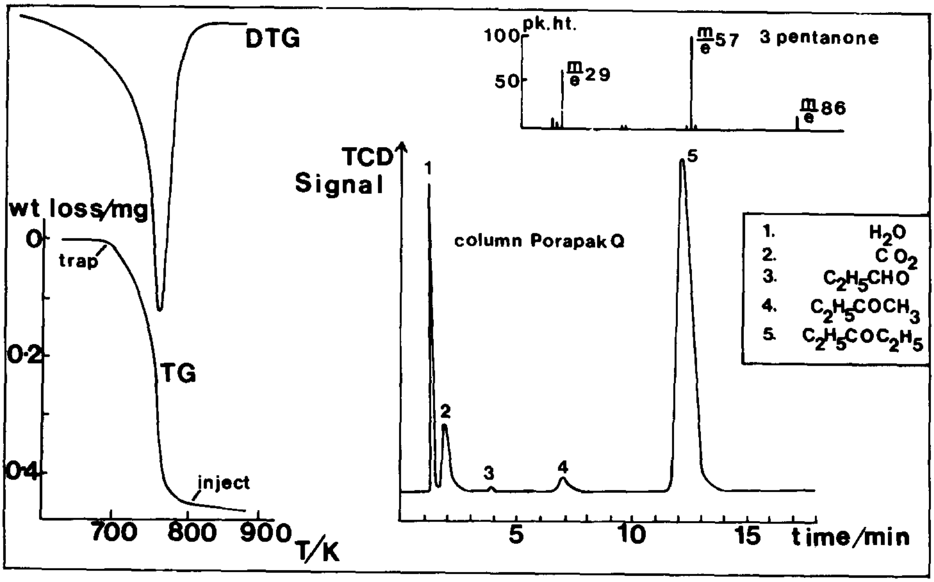

fig.2. TG, DTG and TG-GLC-MS of calcium propanoate. The chromatogram of the total evolved products is shown, together with the mass spectrum of one of the 5 components, 3-pentanone. Sample mass : 1mg, heating rate : 30K per minute, atmosphere : helium flowing at 70 ml per minute.

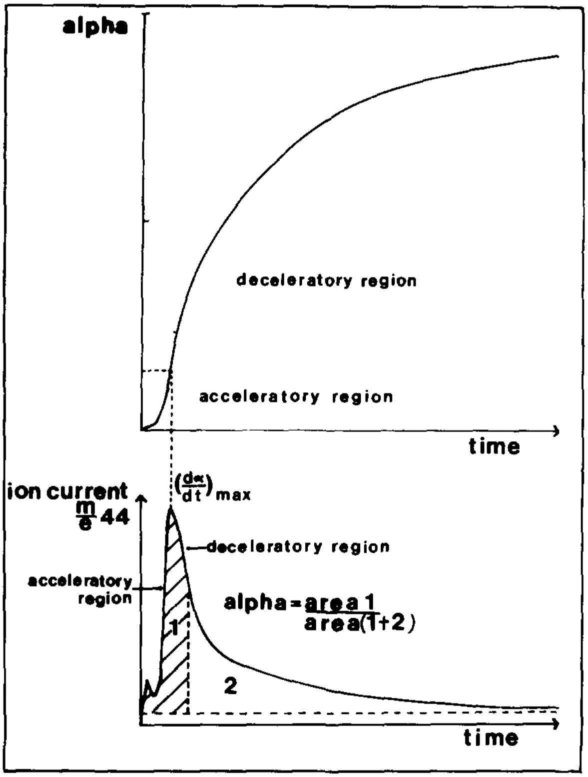

fig. 3. An EGA profile for the thermal decomposition of calcium propanoate

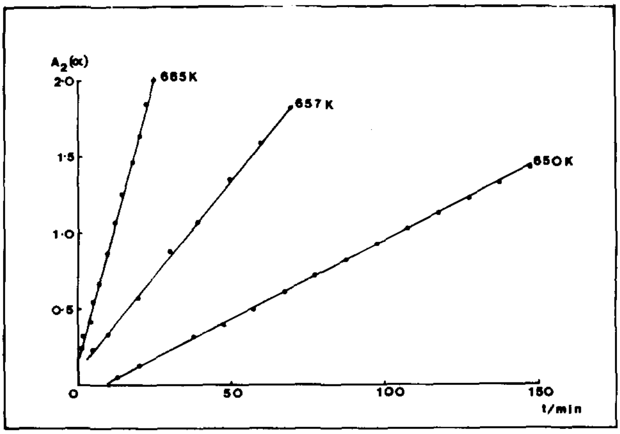

fig. 4. Avrami-Erofeev (n=2) plots for the isothermal decomposition of calcium propanoate, calculated from the SIM (m/e = 86) data

The ability of the more sophisticated TA-EGA methods to cope with complicated systems is illustrated by the work of Yuen and Mappes (15) who employed a combination of TA-MS and GLC-MS to unravel the thermal degradation of a range of materials from petroleum coke to a variety of polymers, an example of which is a copolymer of ethyl acrylate/ethyl hexyl acrylate.

A more down to earth application is described by Mandarino (16) who was able to identify and characterise a sample of the rare mineral Weddellite by TG-MS. Weddellite is found in a variety of unlikely places. Originally discovered in the Weddell sea, it has since been found in ancient Chinese wall paintings and the urinary calculi of the hippopotamus.

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