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THERMAL ANALYSIS AS PART OF THE QUALITY SYSTEM WITHIN INDUSTRIAL LABORATORIES

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Abstract

The use of thermal analysis as part of a quality system in industry can be effective only if the techniques are made to conform to high standards of quality assurance. Achieving these high standards is not problem free and there remain many issues which require the attention of thermal analysts in industry and academe. Fundamental aspects which have been considered include limitations due to instrument design, problems in computerised control and analysis. A key aim is towards validation of data at international level.

Keywords: quality assurance, standardisation, validation

Introduction

Virtually all industrial processes leading to well specified final products depend on knowledge and control of temperature, time and atmosphere effects during manufacture. Thermal analysis techniques, therefore, can have a significant role in predicting and monitoring the quality of production by assessing changes in the physical or chemical nature of the raw materials, intermediate and final products.

In order to achieve, or to become part of, an effective quality assurance system there must be strict control of the thermal analysis techniques employed, particularly where the measurements are made using more than one instrument and are performed in a variety of locations. The key aspects to be considered are those required to obtain 'equivalent data' and these will encompass all factors necessary to validate the precision and accuracy associated with the measurement. Quality systems do not necessarily guarantee an 'absolute' measure, i.e. a result which could never be challenged. However, a quality system is required to supply fully traceable, reproducible sets of output data determined using prescribed methods and procedures which incorporate, whenever possible, the use of Standard Reference Materials (SRM's).

In common with a wide range of analytical techniques, there are many difficulties associated with obtaining 'equivalent data' using thermal analysis. The limitations identified can be minimised by tight control of, for example, specimen size,

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preparation and evaluation methods employed within laboratories. The design of hardware, software and firmware are generally outside of the control of the analytical staff, yet these are equally important parameters which must be taken into consideration. Where differences, or errors, are detected in systems used within a QA role there can be serious implications – technical, financial, legal, ...

Increasing involvement with quality makes it necessary to raise the awareness of users to the relevant issues and to examine the options which could be employed to minimise potential problems. Any solution will inevitably mean that a lot of background effort is required, but this could be shared amongst the industrialists, academics and instrument manufacturers concerned with the issues. Businesses which use thermal techniques as an integral part of ISO9000 [1], GLP [2], UKAS [3] (NAMAS) or other accreditation systems will have significant requirements in this sector. Programmes to evaluate variability in analytical techniques and promote data validation are currently being commissioned throughout Europe.

Thermal analysis as part of the quality system

Industry has always needed a 'quality system' to ensure that the product meets a specification. In the past this has often taken the form of statistical quality control, or random checking of the products, and was used to detect inferior grade or failed materials. It did not always seek to identify, or to eliminate, the causes of poor production quality. Systems have evolved which attempt to include the latter. All methods and procedures are designed to be fully traceable to pre-determined standards, including those set by any external auditing authorities [1–3]. The systems will not generate an absolute guarantee of continuous, successful production since there remains a dependence on analytical instrumentation and human inputs, but the requirements are geared towards as high a success rate as possible. Thermal analysis is a group of techniques which can make an important contribution in this area, perhaps for two principal reasons. The most obvious of these is the dependence of the majority of industrial processes and product properties on the effects of temperature. Secondly, the information derived from thermal analysis measurements is often very significant when used in support of structure related data produced by other, more fundamental, analytical techniques (e.g. NMR, FTIR). Thermal analysis is a powerful secondary technique.

Performing these actions effectively requires that the thermal analysis techniques must be closely integrated within the quality system, i.e. be subjected to the same basic control procedures, to ensure validity and reproducibility of the relevant output data. Today, the vast majority of industries have ISO9000 [1] type accreditations which control methods and procedures and include systems which make all actions fully traceable and auditable. Where these include analytical methods, the applied methods and procedures are also closely controlled, wherever possible to a national or international standard. This is taken one stage further by accreditation bodies such as UKAS [3] in the UK. Their key aim is to ensure that any analytical equipment, measurement procedures, output data, etc., are specified and controlled to a very

high degree. The requirements would be to, or beyond, the national standard as specified in the primary accreditation documentation for that body. The analytical data is essentially being validated to an agreed and often well established standard.

Compliance against the standards specified in the control document means that methods and procedures, equipment and equipment records, sample and specimen handling, records and archives are examples of the areas which can be audited. The training of the staff, their attitude to the quality process and any sub-contracted work are important too. Whilst all of this can impose a significant time and cost penalty within a group, there is huge commercial benefit to be derived from ensuring that the measurements are made to known levels of precision and accuracy against traceable standards. It should mean that it is possible to generate 'equivalent data' at any location using established criteria. This is a very important aspect within global industries, where source and supply of products can be situated anywhere in the world.

The actions required to ensure that valid and reliable analytical measurements have been made are not trivial. Even within the thermal techniques most commonly used in industry, i.e. DSC, TMA, TG, DMA, it can take many months to establish the basis of a test method and to validate all aspects of the measurement associated with a method. The aim here is to highlight a few of the problems encountered, to illustrate what has to be considered, with an overall purpose of raising awareness of the thermal analyst to some of the main issues.

Temperature is the key factor in all thermal measurements, yet despite the use of recommended calibration procedures the variation in temperature data derived from thermal analysis instrumentation can be remarkably outside an acceptable specification. The use of computer control and evaluation would appear to remove some of the uncertainty in the temperature measurement, but in reality this is one of the contributing factors to the differences which have been encountered. The user has to be aware of all aspects of the hardware, software and firmware interactions which might occur and is heavily dependent on reliable information from the equipment suppliers in this respect. In Table 1, the data shown is taken from DSC measurements for the recrystallisation exotherm derived from cooling Nylon 6 and Nylon 6:6 materials. The temperature derived from the test method is used as an indicator to process performance and material quality. The test specification for the peak temperature was set within ±2°C, but as can be seen from Table 1, differentials were as much

Table 1 Variation in DSC exotherm peak maxima for polymer recrystallisation – before and after correction for three DSC instruments of the same type

Sample type	Original temperature/°C		Corrected temperature/°C	
	range of crystallisation	difference	range of crystallisation	difference
Nylon 6 nucleated	230.5–236.4	5.9	236.6–236.9	0.3
Nylon 6	218.2–225.0	6.8	224.3–225.5	1.2
Nylon 6:6	183.5–190.3	6.8	189.6–190.8	1.2

as 7°C for measurements made on the same material when evaluated using three different instruments. The instruments were of the same make and type, but had different software and firmware versions in place which gave rise to the temperature differences. A secondary correction procedure had to be established to overcome this problem which avoided acceptance of 'out of specification' polymer or rejection of 'in specification' polymers based on the incorrect versions of the test data.

TMA furnaces are generally much larger than those employed in DSC systems and as a result the temperature distribution is much wider. The distribution of temperature has been determined on such furnaces and have been shown to be as much as 25°C top to bottom and the same side to side across the furnace; typical data are given in Table 2. Hence, placement of the specimen and the specimen dimensions are important in ensuring any reproducibility during testing procedures. Critical to all of this is the placement of the temperature measuring device (thermocouple, PRT); unless this is well controlled, even test reproducibility becomes difficult. Measurement in TMA is dependent on the probe loading, i.e. an effect of the force used in conjunction with the probe area. During performance check testing, to confirm reproducibility of the TMA force, it became clear that this too was a function of software/firmware version and a critical setting of the hardware options during the setting-up procedures. These were not referred to in any calibration procedures and the user would not be aware of any changes, without some means of independent checks; controlled Standard Reference Materials (SRM) do not exist for this purpose. The result of these errors were observed changes in probe force/displacement factors of at least 2×. Changes of this magnitude would be very relevant to 'softening temperature' measurements derived from TMA.

Table 2 Temperature distribution along a TMA furnace – isothermal control 100°C

Thermocouple height above base/mm	Measured temperature/°C
0	106
3	114
6	122
9	128
13	125
19	103

In DMA the relatively large specimen and furnace sizes also need to be considered when looking to generate 'equivalent data' from a range of instruments. The placement of the temperature probe is again very critical and the quality of this probe, along with its interaction with the temperature generating software, has also been shown to be critical too. In a measurement using an independent, fully accredited thermocouple mounted close to the temperature sensor in a DMA the 'true temperature' differed by –40°C at +300°C and by +20°C at –100°C, with agree-

ment only at 0°C. This could be traced to the inadequacy within the temperature measurement aspects of the software, compounded by the difficulty of using well established or commercial SRM's in some DMA systems. Use of the latter would have identified the problem, but use of independent thermocouple to assess temperature would still be necessary to guarantee full compliance. Large temperature differences were also seen in DMA when some systems were used with, or without, a cryogenic cooling accessory for a specific test. On the same material, the peaks in the loss data, E'' max or tanδ max, were shifted by approximately 10°C, as shown in Table 3. This effect was traced to localised cooling within the clamp region of the specimen, but remote from the temperature sensor. This best illustrates the need to ensure that any test method is specified fully in all aspects and that the effect of any change should be checked thoroughly and not assumed to be irrelevant to the procedure.

Table 3 Effect of localised cooling within clamp region of DMA – change in E'' max: cast PMMA control specimen

Temperature range of analytical method/°C	Heating rate/ °C min^{-1}	Frequency/ Hz	Loss peak, E'' max/°C
20 to190	2	1	115
0 to 190	2	1	119
–100 to 190	2	1	126
–100 to 190	2	1	124

Thermogravimetry is widely used by industrial quality control laboratories and although temperature differences are not always a prime requirement of a specification, it is important to be able to reproduce the test data on different instrumentation. Mass changes can be readily calibrated using fully accredited, traceable, standard masses supplied for the calibration of laboratory microbalances. However, in a recent 'round robin' survey of TG instruments within the company, using an analytical grade sodium bicarbonate performance check material, significant temperature effects were identified; Table 4. Mass changes were accurate, but it became clear that all instruments calibrated using the long accepted 'Curie point' magnetic standards differed in the output temperature scale by up to 15°C when data were compared for the instruments calibrated internally using the fusion of a metal SRM (e.g. indium, zinc) based procedure. The latter would have two advantages: proximity of the standard to the temperature sensor and precision of the temperature event. It should be emphasised that the method of calibration, rather than the type of instrument, is the main issue that has to be tackled here.

Hopefully the few examples referred to above will encourage those responsible for thermal analysis measurements, particularly where these are part of a wider quality assurance system, to examine or to re examine the factors which might influence the quality of the output data. Without any doubt, there are disadvantages in the bureaucracy and time costs that may result, possibly even reducing the ability to pro-

Table 4 Thermogravimetry: effect of calibration method on measured onset temperatures for the decomposition of analytical grade sodium bicarbonate

System	Heating rate/ °C	Calibration method	TG	DSC
			extrapolated onset temp./°C	
Perkin Elmer	10	magnetic	152	–
TA Instruments	10	magnetic	151	131
Mettler	10	magnetic	152	–
Netzsch	10	metal	140	132
Mettler	10	metal	140	130
Rheometrics	10	metal	137	125
TA Instruments	10	metal	145	–

vide the rapid responses often required in industrial problems. However, these aspects are balanced by the use of a fully documented, formal system which incorporates full traceability and can be expected to produce reliable and validated data. It is important that everyone has the option of producing 'equivalent data' and this is particularly relevant to the quality groups which have to monitor products globally on a range of instrumentation. In addition to the scientific considerations, there are often important commercial or legal implications closely linked to these issues. To ensure that this is achieved there is increased need for standardisation, possibly driven from a central body. Other essential requirements are for a wider range of SRM, much tighter control of software, firmware versions and the need to involve everyone who can contribute towards achieving the alignment of methods, procedures and output data.

References

1 ISO9000: 1987: Quality management and quality assurance standards - guidelines for selection and use. Comprises many standards issued by the International Organisation for Standardisation, 1987.
2 GLP: Good Laboratory Practice. Principles established by various national authorities (FDA, DOH), based on OECD document Good Laboratory Practice in the Testing of Chemicals, published 1982. Mutual acceptance agreements exists between UK and USA, UK and Japan.
3 UKAS: United Kingdom Accreditation Service. Provides laboratory accreditation traceable to national and international standards. Main documents M10 and M11.