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Thermochimica Acta 256 (1995) 1–8

thermochimica acta

# Aspects of quality assurance within the industrial thermal analysis laboratory ☆

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**Abstract**

The use of thermal analysis as part of the quality systems in industry can be effective only if the techniques are made to conform to high standards of quality assurance. Achieving the high standards required is not always straightforward and there are a large number of potential and unresolved problems.

Fundamental aspects which have to be considered include limitations due to instrument design, computerised control and analysis, validation of data and the overall requirements of, or conformance to, international quality programmes.

*Keywords*: Calibration; Quality assurance; Quality control; Standardization; TA; TMA

## 1. Introduction

Thermal analysis (TA) techniques are increasingly used in industry in support of research, development and quality assurance (QA) functions. Many industries have realised that, in order to remain competitive, to comply fully with customers' and legislative requirements, there is a need to apply stringent control to the quality of raw materials, processes and products.

To be effective, the analysis techniques used for this purpose must also conform to high QA standards. Achieving these high standards is not always straightfor-

☆ Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.


*SSDI* 0040-6031 (94) 02164-3

ward. The thermal analysts in industry are totally dependent on commercially available instrumentation, yet have had little influence over the design of the hardware or the software associated with its use.

Consequently, instrumental variability and inadequate correction procedures are problems which have a significant effect on the validity of QA assessments. Fundamental aspects which need to be considered include instrument design, computerised control and analysis, standardisation and accreditation systems. These factors are important in all industrial applications of TA, but have a special relevance within larger industries where production and analysis take place on an international scale.

## 2. Quality assurance within thermal analysis

The increasing use of thermal analysis techniques within industry has been driven by the need to provide "first quality" products which comply fully with customer requirements.

Virtually all large companies, and a growing percentage of smaller companies, have their own thermal analysis laboratories incorporated into the overall quality assurance process, or have access to external thermal analysis consultancies; many of the latter are located in universities. One of the key functions of these laboratories is to develop and use methods which can be applied in both QA and quality control (QC) roles. The thermal analysis technique, or the way in which a specific technique is applied, is obviously very dependent on the industry for which the work is being carried out. However, the following criteria are common to all industries and are often used to justify expenditure on thermal instrumentation.

Firstly, there are technical reasons why it is necessary to monitor the product which is being made, the raw materials from which it is made and the processes associated with manufacture; this is simply to ensure that a process or a product will meet a specification. Commercially it is important to be able to check that a finished product is as specified; this is to guarantee that the buyer gets what is paid for. An integral part of all this is legal considerations; these can include specification guarantees and assurances that the product complies with the requirements of national or international regulatory authorities. Regulatory compliance has particular relevance in the pharmaceutical industry. Increasingly important is input to accreditation systems such as BS5750 [1], ISO9000 [2], NAMAS [3], GLP [4] or directives within the European Community. The most significant criteria for industry, which impinge on all the issues discussed, are the financial implications. There is a constant requirement to maintain or improve quality standards within companies, principally to minimise the likelihood of significant financial losses, or reduction in commercial credibility, as a direct result of the production and supply of inferior or poor quality products.

It is therefore clear that to have an ongoing role in industry the analytical techniques used must produce reliable, consistent data, i.e. conform to a high level of quality assurance within the techniques themselves. There is a diverse range of

commercial equipment for any given technique and it is essential that the degree of "standardisation" necessary is well established. Use of quality systems such as NAMAS, GLP, and BS/ISO do remove many of the intrinsic problems, in production or analysis, but experience has shown that these cannot provide an absolute guarantee of success. Some of the analysis aspects have already been considered by the Community Bureau of Reference (BCR) in Brussels [5], which has co-ordinated programmes to study results from a range of analytical laboratories within the European Community. A fundamental requirement for industrial laboratories is the ability to produce "equivalent data", i.e. the same information, from the same samples using the same basic procedures. This has relevance in smaller companies, but can be far more critical within the larger companies which operate interdependent production and analysis facilities throughout the world.

Thermal analysis must be included in any general review of analytical techniques or procedures; some of the issues which affect a review, and are currently the subject of discussion at international committee level, will be considered below. The most important factors are associated with computerisation; very few, if any, thermal analysis systems used by industry today are independent of microprocessor/computer control or data processing.

The thermal analysts in industrial laboratories responsible for developing methods of analysis, i.e. procedures which will accommodate a diverse range of instrumentation, a wide range of operator experience and many unknowns with respect to the conditions of operation, have had to consider in depth which factors might affect the final results. This is one stage of the method optimisation process, to remove or account for any experimental or procedural effects which might adversely influence the data. The same considerations have to be used when assessing the suitability of a thermal technique for inclusion in a quality system such as BS5750 or ISO9000 or, perhaps on a more intensive scale, for incorporation into a NAMAS Accreditation Schedule. For the latter it is necessary to demonstrate the validity of the measurement itself, in addition to the way in which the measurement was achieved.

Within thermal techniques, a typical list of parameters which have a significant effect on certain aspects of output data, and therefore have to be considered, might include the following:

(1) temperature: calibration, standards, precision, rate effects etc.;
(2) specimen environment: gas type, flow rate, furnace size etc.;
(3) specimen size/type: thermal history, preparation, stability etc.;
(4) enthalpy: calibration, standards etc.;
(5) modulus: calibration, clamping etc.;
(6) Software validation: input vs. output, processing algorithms, version etc.

The list is not exhaustive, merely a few starting points from which the thermal analyst can begin an appraisal. Because thermal analysis is the study of a given process or processes as a function of temperature, it is a fundamental requirement that temperature must be accurately controlled or assessed to produce a reliable measurement. These criteria appear relatively straightforward and the vast majority of thermal analysts, using commercial equipment, do obtain results which seem to

demonstrate that their own equipment and the methods which they use are reliable and reproducible. However, it is often the case that, when subjected to wider comparisons, e.g. inter-laboratory testing, or measurements from different manufacturers' equipment, larger discrepancies then become more obvious. This has important implications. For temperature measurement it would be necessary to return to the list above and to reconsider this one aspect in greater detail.

Consequently, a second list is generated which examines several factors concerned directly with temperature in a system.

Factors associated with assessment of temperature

(1) Calibration: standards, procedures, frequency, records etc.;

(2) standard reference materials (SRMs): source, traceability, accuracy/precision, storage etc.;

(3) furnace design: — size, sensor position, purge quality, deposits etc.;

(4) software/firmware: input vs. output, linearisation, corrections, ageing etc.;

(5) rate effects: thermal lag (zero rate correction), software, SRMs etc.;

(6) independent assessments: accredited thermocouples or PRTs;

(7) collaborative testing: precision, test procedures, standardisation etc.;

(8) cooling: calibration, SRMs, sensor position etc.

Again, although there are many items identified, the list is incomplete. However, it serves to illustrate that in order to achieve satisfactory accuracy and precision for temperature measurement in a thermal analysis system it may be necessary to consider these criteria at length. Returning to the original list, the remaining headings can be treated in a similar manner. This will produce at least fifteen different, but largely interrelated, aspects to consider with respect to each original topic. The detailed lists are not reproduced here, but some of the main parameters will be expanded on below. Previous papers have dealt with various issues which have arisen from the inability to achieve satisfactory agreement in data between thermal analysis instruments [6,7], and many have discussed means of improving the measurements [8–10].

The most commonly used thermal analysis techniques in industry are DSC, DTA, TGA/TG, TMA and DMA. Individual and collective problems associated with these techniques remain and still have to be overcome. A selection of these is now discussed in the context of quality assurance.

One of the principal issues which has not been fully resolved is the correction required when cooling using DSC. The use of a liquid crystalline material to calibrate the temperature axis is seen as a way forward, but to date there are no such standard reference materials issued by the standards centres NIST [11], LGC [12] and BCR [5] for use in industrial QA applications. A liquid crystal standard must therefore be developed, one which is traceable, is readily obtainable by all industrial users, and has proven purity, stability and shelf-life. It is reasonable to assume that, despite a wide variation in DSC furnace design, equivalent data should be readily obtained during heating experiments and that the precision and accuracy of most testing procedures in heating mode can be more reliably determined.

Techniques which use larger furnaces (TGA, DTA, TMA and DMA) can be calibrated satisfactorily for temperature if the design can accommodate measure-

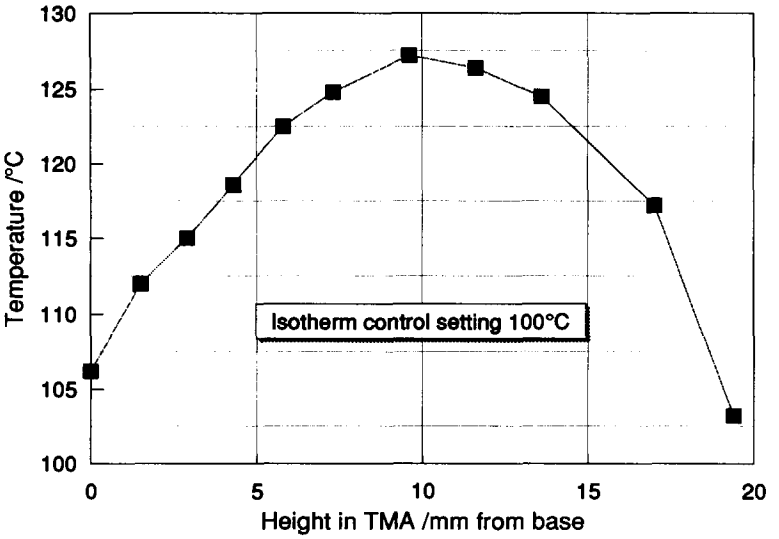


Fig. 1. Temperature distribution in the TMA furnace.

ment using a small amount of a standard reference material. However, problems still remain with respect to the positioning of single temperature sensors and the wide temperature distributions observed within the furnace and across the specimens during heating. The size of the specimen used in virtually all TA testing is a compromise between good temperature distribution through the specimen, the resolution of the test procedure and the statistical requirements of the original sampling. Specimens should be as small as the latter constraints will permit, and the temperature sensor should ideally be located as close as is practicable to the specimen.

TMA furnaces are not huge, yet all suffer from poor temperature distribution. This is illustrated in Fig. 1, which is a fairly typical observation. These data were obtained by maintaining the furnace temperature isothermally, nominally set to 100°C, and by remotely moving the thermocouple to controlled depths within the furnace. The first observation is that all recorded temperatures exceed the pre-set 100°C, but this could be readily corrected by the calibration software. However, the maximum temperature difference up and down the furnace is close to 25°C; these differentials are not so easily eliminated.

There is evidence too which indicates that horizontal temperature distributions are also significant. Other techniques have also been used to demonstrate that temperature differences of $\approx 10$°C along a 15 mm sample can exist during a 5°C $min^{-1}$ heating cycle. The measurement of expansion coefficient using any TMA would be marginally affected by these effects, but what has to be treated with caution, or assigned wider temperature precision limits, is a measure of transition

properties for such relatively large specimens. In DMA furnaces, particularly early designed models, these effects were even more marked. Furnaces were 50–150 mm I.D. (the I.D. in TMA is generally $< 20$ mm) and contained a lot of metal and ceramic, all of which influenced uniform, reproducible heat flow into and away from the specimen. Such furnaces are not easily calibrated, and in many cases it is impossible to use a traceable standard for this purpose, mainly because a suitable standard has not been developed. Other aspects which still require some standardisation are the measurement and validation of the applied forces in TMA and DMA and also how force might vary with probe displacement. It is often possible to develop local performance check routines involving "secondary" standards, which can help in defining and assessing the precision available. However, for the QA laboratory, especially when operating within a schedule set by a recognised control body, there is often a need to demonstrate "first order traceability".

Secondary standards, by definition, reduce both the accuracy and the precision limits which can be quoted for data; this has the effect of widening test specifications.

Accuracy and precision are affected by the hardware, but can also be significantly changed by the software or firmware versions which existed at the time of analysis or which are subsequently used to perform data analysis on archived raw data.

The magnitude of these problems has been considered previously [6,7] in work to promote improvements in the level of standardisation of data essential to the industrial TA/QA laboratory. Several issues associated with the computerisation of thermal analysis instrumentation have been raised by the current President of ICTAC, Takeo Ozawa. His article in the ICTAC News, June 1993, entitled "Too beautiful curves", was not a consideration of bodily form but a warning on the dangerous tendencies in the electronic and software manipulation of raw data. One difficulty lies in validating that a given input produces the same output in absolute terms. In previous papers it has been demonstrated that temperature corrections introduced via software have been inconsistent, that the control parameters are often firmware dependent and that, to ensure that an acceptable degree of reproducibility is established, it would be necessary to introduce standardisation measures. There is a general feeling within the central bodies responsible for policy matters in analytical measurement that all software must become open to scrutiny, that it must be made possible to validate centrally all the algorithms used to manipulate raw data and that a scheme for registration of any given software must be established to record version status and any changes as these occur. Obviously it is recognised that there is a need to protect the commercial aspects of supplier software, and this could be readily incorporated into any registration system. Important to the QA laboratory is the need to archive, store, retrieve and re-evaluate data for periods up to 10 years (6 years for NAMAS); few people would disagree that there are many potential software and hardware problems associated with data retrieval over long periods. Relevant guidance and recommendations are given in NAMAS publications [13,14].

## 3. Quality assurance of thermal analysis: the future

Increased levels of standardisation will become a key feature of most analytical functions in industry and within the academic institutions providing a consultative service. This will cover terminology, calibration procedures, precision assessment, etc. and would ideally be controlled by a central committee. This will inevitably require greater collaboration between thermal analysts, within and between companies, plus closer links with academics and suppliers. Integrated closely with this aspect would be moves toward more widespread and more frequent use of inter-laboratory testing. There will be a need to develop and extend the availability of standard reference materials; these are the basis of all calibration routines and performance check procedures. Software and associated computer equipment will be more tightly controlled than it has been to date, a factor which is likely to impinge to the greatest extent on the suppliers of commercial thermal analysis equipment. "In-house" software used for QA purposes would require registration and auditing. Finally, there is the need to educate users in the application of thermal techniques; to impart not only a solid academic capability but, equally as important, to develop the *attitude* required to be able to contribute fully within a "quality" culture.

## 4. Conclusions

The use of thermal analysis as part of quality systems in industry can only be fully effective if the techniques are made to conform to high standards of quality assurance. The significance to industry has been demonstrated, and hopefully a greater awareness of the problems which can and do exist in this field has been encouraged. One aim was to stimulate thought and discussion by those with a responsibility for the industrial application of thermal techniques. The subject remains somewhat open-ended, with important practical questions still to be resolved. However, assuming the right policy decisions, procedures and attitudes are established, thermal analysis will continue to be an essential component of the modern industrial world.

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[2] ISO9000: 1987: Quality management and quality assurance standards — guidelines for selection and use. Comprises ISO9001–ISO9004. Issued by the International Organization for Standardization, 1987.

[3] NAMAS: National Measurement Accreditation Service, operated by the UK National Physical Laboratory. The main documents are M10 and M11. Provides laboratory accreditation traceable to national and international standards.

[4] GLP: Good Laboratory Practice. Principles established by various national authorities (FDA, DOH), based on the OECD document Good Laboratory Practice in the Testing of Chemicals, published 1982. Mutual acceptance agreements exist between UK and USA and between UK and Japan.
[5] BCR: Community Bureau of Reference (DG XII), Rue de la Loi, 200, B-1049 Brussels. Established by the European Commission to help laboratories in member states provide accurate, reliable and equivalent methods, procedures and data. BCR is involved in inter-laboratory testing and supplies standard reference materials.
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[12] LGC: Laboratory of the Government Chemist, Teddington, Middlesex, TW11 0LY, UK. Centre for the production, analysis and certification of standard reference materials for purity, enthalpy of fusion and melting point.
[13] NAMAS document NIS 37, A Guide to Managing the Configuration of Computer Systems (Hardware, Software and Firmware) used in NAMAS Accredited Laboratories, 1st edn., October 1993.
[14] NAMAS document NIS 40, Storage, Transportation and Maintenance of Magnetic Media, 1st edn., October 1990.