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RECOMMENDATIONS FOR REPORTING THERMAL ANALYSIS DATA

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Recommendations for reporting of thermal analysis data relating to differential thermal analysis, differential scanning calorimetry, thermogravimetry and thermomechanical analysis were developed some two decades ago. Since that time there have been significant changes in the techniques, as well as a greater understanding of the effect of experimental variables on the results obtained from thermoanalytical experiments. This paper reports on a preliminary review of the Recommendations by the Task Group established by the ICTAC Committee on Standardization to undertake their revision. Particular attention has been paid to the properties of the sample; control of the instrument variables; and the data acquisition and manipulation by computers.

Keywords: data, recommendations, reporting, thermal analysis

Introduction

It has long been recognized that thermal methods of analysis are dynamic techniques, and that the results obtained are dependent on the chosen experimental conditions. In 1965 the First International Conference on Thermal Analysis established a Committee on Standardisation, and one of the outcomes of the committee was the production of a set of recommendations for Reporting Thermal Analysis Data [1–3]. In 1991, it was decided by the current Standardisation Committee to review the existing Recommendations, and a Task Group was established with the following major objectives:

– To review the existing 'Recommendations for reporting thermal analysis data' applied to the techniques of thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and evolved gas analysis (EGA), and to make changes where necessary.

– To consider the impact of data acquisition and manipulation technology and methods on thermal analysis techniques and to construct suitable recommendations for reporting these aspects.

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– To consider any new methods for which recommendations may need to be produced.

The following is a result of deliberations of the Task Group, and is the first draft of a document that will eventually replace the existing Recommendations. It is meant to stimulate discussion amongst practitioners of thermal analysis. The Task Group would appreciate comment or suggestions for inclusions or amendments.

Sample variables

90% of the samples investigated in thermal analysis are solids, at least at the start of the experiment. Solids have bulk and surface properties, a prehistory which is frozen into the structure, may contain impurities which affect the reactivity, and are not homogeneous. It is possible to prepare solids which have the same composition, but which exhibit very different thermodynamic and kinetic properties.

The procedures and properties of a solid that should be considered for specification include:

- sample size
- particle size
- methods of sizing, i.e. the use of crushing and grinding apparatus, size fractionation methods ...
- thermal and mechanical history
- method of preparation of the solid including industrial process conditions
- surface texture, e.g. the porosity of the surface, and the surface area
- any form of surface modification, which may be physical (e.g. compaction) or chemical
- compositional and phase analysis, and this should be considered for the intermediate products as well as the initial material
- isotropic and anisotropic nature of the solid, e.g. direction of fibre in composite materials

It may be possible to remove the thermal history by a pre-heat stage prior to the thermal analysis experiment. However, the pre-treatment may cause sintering with loss of surface area and increase in particle size, loss of rigidity, and in general alter the solid in undesirable ways. In many cases industrial laboratories are interested in rising temperature experiments that give information about the pre-history of the sample. On the other hand, measurement of thermodynamic properties will require removal of pre-history by, for example, melting, followed by measurement on a cooling curve. Hence the question of elimination of pre-history is dependent on what data are required and what can be done to the sample without loss of important structural features.

Although many samples can be stored without alteration over time without special precaution, others cannot. Storage conditions need to be stated. In particular, reactive solids, whether minerals freshly removed from an anerobic environment or those prepared with very high surface areas, need special consideration, as they are difficult to maintain in a pure state as their surfaces are likely to be undergoing rapid alteration.

The question of what constitutes a representative sample needs to be considered. The tendency in recent times is for equipment to be designed to require small samples in the mg range. It would be useful for the criteria used to judge the representativeness of a sample to be stated. Performing multiple experiments on the sample to assess reproducibility should also be encouraged.

Samples are sometimes diluted, and the degree of dilution and the diluent need to be specified.

Instrumental variables

In general terms quoting a specific manufacturer's model is a sufficient description of the apparatus used, since the apparatus is usually well described in the manufacturer's publicity brochures as well as in the scientific literature. However, modifications to the standard model need to be described. Relatively new techniques and the less common techniques need to be described in more detail so that the reader is able to determine the apparatus and processes being carried out.

The instrument variables can be discussed in two sections, those which are common to all techniques and those that are instrument specific.

Items common to all techniques		
Physical	Geometry	Spatial relationship- arrangement between holder/furnace/sample/reference
	Simultaneous	What methods?
	Sample holder	Material, unusual properties/dimensions
Temperature programme	Heating/cooling rates	*T vs. t*
	Isothermal holds	
	Rate-controlled TA	How achieved?
Temperature	Calibration	How? Enthalpy as well?
	Display	Actual or programme temperature
	Baffles/shields	Any special arrangements
Atmosphere	What gases	Partial pressure of reactants
	Flow rate	Space velocity
		Combined purge gas

		Delay to other modules
	Thermal conductivity	
	Total pressure	If other than atmospheric
Items specific to a technique		
TG	Buoyancy and aerodynamics	Blank, Double furnace, baffles
	Geometry	Above, below, side
TM	Magnetic field gradient	Magnitude, direction
	Holder or sample	Freedom of movement (generally to be avoided)
	Transition temperature	End point, TG or DTG
EGA	Method	MS, GC, specific detector
	Interface	Time delay, trapping
	Sensitivity	
DTA/DSC	Method	Heat-flux, power-compensation
	Sensors	Type, sensitivity, placement
	Holder	Open, closed, flow through
TMA	Method	Single, Differential
	Sensor	LVDT, optical
	Material of construction	Correction required
	Thermocouple placement	
	Calibration	How?

Plots of T *vs.* t give some indication of the effect of heats of reaction on deviation from the set temperature programme. They can also be used to calculate an accurate heating rate as opposed to the stated value.

The gas composition, and any treatment of the gas in terms of purification procedures, need to be stated. Users should be aware that variation in composition can occur over time for what is nominally the same gas. There is a significant variation, for example, in the water content of compressed gas with change in the local humidity. When the gas passes over the solid, it may be at a temperature that is significantly lower than that of the solid unless special pre-heat methods are used. This temperature difference will obviously increase with increase of flow rate. This is a particularly important point when kinetic measurements are being

made. The usual way of presenting gas flow is to measure the inlet gas flow with a rotameter. However, this will not necessarily be the flow rate past the sample. This is more correctly presented as the space velocity. It should also be remembered that the rotameter is calibrated for one gas, and switching to another gas requires a correction factor to be applied.

Data acquisition and manipulation by computers

Attachment of the computer to thermal analysis equipment for the purpose of data acquisition and manipulation is a major innovation. There are two aspects to consider, hardware and software.

Hardware
- Are the thermocouples linearised, and cold junctions properly compensated?
- Are measurements really simultaneous?
- How many bit A/D conversion?
- How reproducible are the signals?
- How many significant figures are there in the data?
- How much filtering, averaging and signal conditioning take place?

Software
- The software version should be specified
- It should be possible to view the raw data prior to any smoothing
- Equations used in the derivation of properties need to be either given in the handbook or references to the literature given. An example is the form of the equation used in kinetic analysis. Even knowing the equation used does not indicate how the data are manipulated.
- What assumptions have been made about the system under study? In purity determination, for example, has ideal solubility of the impurity in the host been assumed?
- How often is the signal sampled? How many points are averaged?
- What is the best base line treatment to use? The straight line is the easiest method, but the method is likely to vary from instrument to instrument. What base line treatment is actually used?

It was generally thought that the scientist ought to be more in control of the situation. For instance, it would be most useful for the raw data to be viewed and then a personal decision made about the degree of any smoothing routine applied. The problem of the dual role of thermal analysis, as a set of research methods as well as for routine industrial monitoring, is apparent. In the latter case the operator does not in general want to have to make choices, and a fixed system is more appropriate.

Some companies will write user-specific software, which is a help as producing in-house material is very time consuming. It is also possible in some instruments to pull files and manipulate them.

The following information was suggested as needing specification in a scientific article.

- Instrument model
- Software Version
- Equations used to process data, or references to suitable literature
- The frequency of sampling, filtering and averaging of the signal
- In-house developed programmes
- Some indication of the smoothing and signal conditioning done by the author on conversion from analogue sensor to digital form. This information is not essential in any publication, but reference to where the information can be found in the manufacturer's documentation should be included.

New methods

Several methods have appeared since the production of the first set of Recommendations. These include such methods as dynamic mechanical analysis (DMA), thermally stimulated current analysis (TSCA) and dielectric thermal analysis (DETA). It was agreed that these newer techniques should have associated recommendations for reporting data. As a general comment, the use of SI units should be encouraged.

Members of the Task Group

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References

1 H. G. McAdie *et al.*, Anal. Chem., 39 (1967) 543.
2 ibid, 44 (1971) 640.
3 ibid, 46 (1974) 1146.

Zusammenfassung — Die Empfehlungen für die Darlegung von TA-Angaben bezüglich DTA, DSC, TA und TMA wurden vor einigen Jahrzehnten entwickelt. Seit dem gab es entscheidende Veränderungen der Techniken und auch der Einfluß von experimentellen Faktoren auf die aus thermoanalytischen Experimenten gewonnenen Resultate ist besser erforscht. Vorliegende Arbeit enthält zwecks Revision einen vorläufigen Überblick über die Empfehlungen der Arbeitsgruppe des ICTAC Committee on Standardisation. Dabei galt besondere Aufmerksamkeit den Probeneigenschaften, der Kontrolle der Instrumentenvariablen sowie der Datenerfassung und -verarbeitung durch Computer.