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GENERAL PAPER

Analytical Methods Committee

Evaluation of analytical instrumentation. Part XVIII. Differential scanning calorimetry

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The Analytical Methods Committee has received and approved this report from the Instrument Criteria Sub-Committee.

The Royal Society of Chemistry,
Burlington House, Piccadilly, London, W1V 0BN, UK

Introduction

This report was compiled by the above Sub-Committee of the AMC, which consisted of Professor S. Greenfield (Chairman), Dr M. Barnard, Dr C. Burgess, Professor S. J. Hill, Dr K.E. Jarvis, Dr M. Sargent, Dr P. Potts, and Dr J. Price with Mr C.A. Watson as Honorary Secretary. Initial input of the features for consideration, with the reasons for their consideration, was undertaken by Mr D.J.H. Edwards, to whom members of the committee express their thanks.

The purchase of analytical instrumentation is an important function of many laboratory managers, who may be called upon to choose between a wide variety of competing systems, which are not always easily comparable. The objectives of the Instrumental Criteria Sub-Committee are to tabulate a number of features of analytical instruments, which should be considered when making a comparison between various systems. As is explained below, it is then possible to score these features in a rational manner; this enables a scientific comparison to be made between instruments as an aid to equipment qualification.

The over-all object is to assist purchasers in obtaining the best instrument for their analytical requirements. It is hoped that this evaluation will, to some extent, also help manufacturers to supply the instrument best suited to their customer's needs. It is perhaps pertinent to note that a number of teachers have found the reports of use as teaching aids.

No attempt has been made to lay down a specification. In fact, the Committee considers that it would be invidious to do so, rather it has tried to encourage the purchasers to make up their own minds as to the importance of the various features of the equipment that is on offer by the manufacturers. This report of the Sub-Committee deals with the application of differential scanning calorimetry (DSC).

Notes on the use of this document

Column 1	The features of interest.
Column 2	What the feature is and how it can be evaluated.
Column 3	The Sub-Committee has indicated the relative importance of each feature and expects the users to decide on a weighting factor according to their own application.
Column 4	Here the Sub-Committee has given reasons for its opinion of the importance of each feature.
Column 5	It is suggested that scores are given for each feature of each instrument and that these scores are modified by the weighting factor and sub-totals obtained. Addition of the sub-totals will give the final score for each instrument.

Notes on scoring

1. Proportional scoring (PS). It will be assumed, unless otherwise stated, that the scoring of features will be by proportion, e.g. Worst/0 to Best/100.
2. Weighting factor (WF). This will depend on individual requirements. All features mentioned in the tables have some importance. If, in the Sub-Committee's opinion, some features are considered to be of great importance they are marked I. Those features of greatest importance are marked as VI (very important). A scale should be chosen for the weighting factor, which enables the user to discriminate according to needs, e.g. ×1 to ×3 or ×1 to ×10. The factor could amount to the total exclusion of the instrument.
3. Sub-total (ST). This is obtained by multiplying PS by WF.

With these requirements in mind, the user should then evaluate the instruments available on the market while bearing in mind the guidelines and any financial limitations. In many instances it will quickly become clear that several different instruments could be satisfactory and non-instrumental criteria might then be important. However, in some specialised cases only one or two instruments will have the ability or necessary features to carry out the analysis.

The guidelines are intended to be used as a checklist of features to be considered, mostly of the instrument itself, but some also of its service requirements and of the relationship of the user with the manufacturer. Their relative importance will depend on the installation requirements of the instrument and the tasks for which it will be used. Therefore, to some extent, the selection process will inevitably be subjective, but if all the points have been considered it should be an informed choice.

It must be noted that instrument design and test conditions greatly affect the resulting thermograms, so that when comparing instruments, results from similar experimental conditions must be compared.

The Committee consider that, in general, DSC are safe in normal use, but care should be taken when handling coolants and sample pans from the instrument which might be at extreme temperatures.

Finally, as many laboratories are now working to established quality standards, consideration should be given to third-party certification of the manufacturer to quality standards such as the ISO 9000 series. The service/calibration organisation should be certified to ISO17025 by the United Kingdom Accreditation Service.

Other reports

The Analytical Methods Committee has published the following reports in the series:

Part I	Atomic absorption spectrophotometers, primarily for use with flames, Anal. Proc., 1984, 21, 45. Revised in Analyst. 1998, 123. 1407.
Part II	Atomic absorption spectrophotometers, primarily for use with electrothermal atomizers, Anal. Proc. 1985, 22, 128. Revised in Analyst, 1998. 123, 1415.
Part III	Polychromators for use in emission spectrometers with ICP sources, Anal. Proc., 1986, 23, 109.
Part IV	Monochromators for use in emission spectrometers with ICP sources, Anal. Proc., 1987, 24, 3.
Part V	Inductively coupled plasma sources for emission spectrometry, Anal. Proc., 1987, 24, 266.
Part VI	Wavelength dispersive X-ray spectrometers, Anal. Proc., 1990, 27, 324.
Part VII	Simultaneous wavelength dispersive X-ray spectrometers, Anal. Proc., 1991, 28, 312.
Part VIII	Instrumentation for gas–liquid chromatography, Anal. Proc. 1993, 30, 296.
Part IX	Instrumentation for high-performance liquid chromatography. Analyst, 1997, 122, 387.
Part X	Instrumentation for inductively coupled plasma mass spectrometry, Analyst, 1997, 122, 393.
Part XI	Instrumentation for molecular fluorescence spectrometry, Analyst, 1998, 123, 1649.
Part XII	Instrumentation for capillary electrophoresis, Analyst, 2000, 125, 361.
Part XIII	Instrumentation for UV–VIS–NIR spectrometry, Analyst, 2000, 125, 367.
Part XIV	Instrumentation for Fourier transform infra red spectrometry, Analyst, 2000, 125, 375.
Part XV	Instrumentation for gas chromatography–ion-trap mass spectrometry, Analyst, 2001, 126, 953.
Part XVI	Evaluation of general user NMR spectrometers. To be published.
Part XVII	Instrumentation for inductively coupled emission spectrometers. To be published.
Part XVIII	Differential scanning calorimetry. To be published.
Part XIX	CHNS analysers. To be published.
Part XX	Instrumentation for energy dispersive X-ray fluorescence spectrometry. To be published.

Thermal analysis

Initially the brief from the Committee was to consider "thermal analysis".

Thermal analysis includes four major techniques:

– DSC, for measuring changes in entropy with temperature. Split into two groups—heat flux DSC-quantified

differential thermal analysis (DTA), normally also referred to as DSC, and power-compensated DSC. A newer technique is modulated DSC.
– Thermal mechanical analysis (TMA), for measuring changes in dimensions with temperature.
– Thermal gravimetric analysis (TGA), for measuring changes in mass with temperature.
– Dynamic mechanical thermal analysis (DMTA), measuring changes in modulus with temperature.

There are also several combined techniques:

– DSC/TGA, DSC or TGA and FT-IR, DSC or TGA and GC, DSC or TGA and MS and atomic force microscopy/DSC.

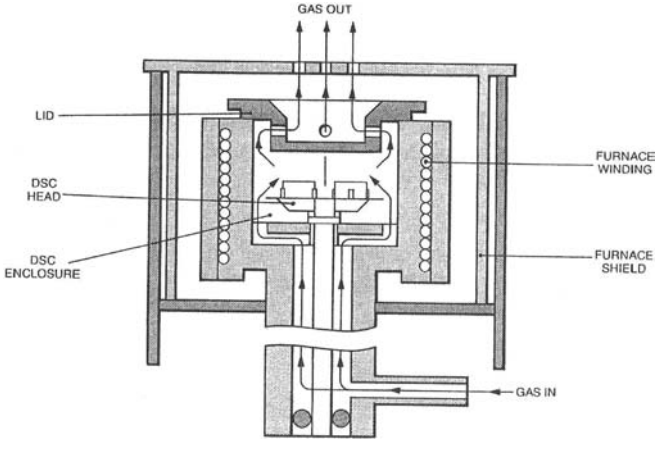
The committee decided that the above list of techniques was too large for one paper. After much discussion it was agreed that this paper should be about classical heat-flux DSC, to encompass the widest range of manufactured instruments and the most common techniques and applications of thermal analysis.

Basis of instrumentation

DSC measures the temperature difference between a sample and an inert reference material whilst being subjected to a defined temperature regime. This might be during heating, cooling, or isothermal, or a programmed combination of these. The sample and reference material are usually held in aluminium, platinum, or glass pans. Aluminium pans are generally used and may be open, crimped with a lid or hermetically sealed.

Heat-flux DSC is a derivative of DTA in which the former, by linking the instrument to a computer with associated software, quantifies heat flow.

There are many nuances on the general scheme of the measuring "head" of a heat flux DSC but all follow a similar basic design:



Samples and reference materials in pans sit on plates, which are in thermal contact with thermocouples. These are enclosed by a furnace, which enables heating/cooling of both. The heating/cooling can be controlled via a third thermocouple or the thermocouple of the reference material.

In general the temperature difference between the sample and reference is recorded against the sample temperature. The temperature difference for a known mass of substance is calibrated against an inert substance of known specific heat such as sapphire so that rather than temperature difference, heat flow is plotted against sample temperature.

In power-compensated DSC the individual sample and reference have their own heaters and thermocouples/resistance thermometers. While undergoing a programmed temperature regime, the temperatures of the sample and reference are kept constant by varying the energy to the heaters. The energy difference equals the heat flux and it is this which is plotted against temperature to produce the thermogram.

In essence, both heat-flux DSC and power-compensated DSC give the similar results.

Competitive techniques

DSC is a quick and simple technique to use. A drawback is that results can depend on instrument design, test conditions, and sample thermal history. Although DSC gives valuable information about the physical structure of materials it should not be used in isolation, rather as a complementary technique. For example, purity measurements are better performed by chromatography, and simple melting points by hot-stage microscopy.

Typical measurements performed by DSC

– Melting points
– Heat flow
– Molecular transitions, e.g. glass transitions and crystallinity changes
– Thermal degradation/oxidation
– Purity
– Reaction kinetics, curing reactions
– Phase diagrams
– Interactions

The first task in the selection of an instrument is to examine the range of measurements that it will be expected to perform. Care should be taken not to specify these requirements too closely as uses change with time. The analytical scientist should also not try to envisage every potential application or the selection criteria might become too detailed.

References

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4. ASTM E928 Determination of purity by differential scanning calorimetry, International Confederation for thermal analysis
5. USP XXV <891> Thermal analysis, International Confederation for thermal analysis
6. USP XXV <661> Containers, polyethylene containers, International Confederation for thermal analysis