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THERMAL ANALYSIS STANDARDS. NEED AND REALIZATION*

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ABSTRACT

Several organizations, internationally and in North America, have a current interest in thermal analysis standards. Of these, the activities of the Committee on Standardization, International Confederation for Thermal Analysis (ICTA) are the most advanced, with a group of temperature standards for DTA scheduled for approval in 1970. A review will be given of the experimental program leading to issuance of these standards, as well as programs underway in the ICTA on other aspects of thermal analysis standards. The current activities of other interested groups will also be reviewed.

THE NEED

Thermal methods of analysis have become one of today's routine approaches to material characterization, allowing investigations in research, development and applications to scan the effects of temperature on reactions and processes without the labor of repetitive isothermal tests. It has become possible to bring virtually any condition of matter to a thermal analysis experiment and, by appropriate designs of equipment and choice of conditions, the desired information can be produced from what is still basically a DTA, TG or similar experiment. Thus, thermal analysis possesses much more flexibility with respect to the sample than many investigative procedures.

This very flexibility has led to a great diversity of instrumentation, both commercial and custom. Not all such designs are applicable to all types of materials, and no one combination of conditions is optimum for all studies. The techniques are dynamic in nature, their results are highly dependent upon procedure, and it is not feasible to limit their value by specifying any one "compromise" set of conditions. Therefore, it is necessary to have some means to prevent purely procedural effects from confusing — or even obscuring — the processes under study. Unless the worker using thermal analysis can place his data in proper relation to those obtained elsewhere,

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likely under quite different conditions, and to known phenomena characterized by independent means, the value of his results is isolated and the full potential of the thermoanalytical approach is not realized.

These are among the considerations which, in 1965, led to formation of the Committee on Standardization of the International Confederation for Thermal Analysis (ICTA). The objectives were readily defined:

(*i*) to provide a common basis for relating independently acquired data;
(*ii*) to provide the means for comparing and calibrating *all* available instrumentation;
(*iii*) to provide the means for relating thermoanalytical data to physical and chemical properties defined by conventional isothermal means.

In addition, and in conjunction with the corresponding ICTA Committee on Nomenclature, the Committee on Standardization has the objectives:

(*iv*) to define good practice, both in experimentation and in reporting, so that the information obtained and communicated is of maximum value;
(*v*) to promote ease of communication through uniform nomenclature and data presentation.

These are broad objectives, designed to increase the value of thermal analysis to all workers, to provide leadership for the whole subject of thermal analysis standards, and to form a basis from which more mission-oriented standards or practices can evolve.

OTHER INTERESTED GROUPS

Before describing the ICTA programs, their accomplishments and future plans, a brief review will be given of other organizations currently concerned with some or all of these aspects of thermal analysis standards (Table I).

Historically, the International Standards Organization (ISO) was among the first groups to give attention to this problem. Late in 1964, ISO Committee TC-61 on Plastics organized Task Group WG-4 on "Thermal Properties" to explore the possibility of arriving at useful international recommendations for the thermal analysis of high polymers. The initial activity involved a study of one sample of poly(vinyl chloride), results of which do not appear to have been published. Another task group, WG-1, subsequently prepared a number of drafts of nomenclature and definitions, which have been circulated to other working groups within ISO prior to drafting a formal proposal.

Also concerned with thermoanalytical test methods for plastics has been ASTM Committee D-20, Sub-Committee 3b, the early activity being to prepare suggested nomenclature and definitions. In 1967 the ASTM recognized that test methods involving thermal analysis apply more widely than to plastics and, in 1968, a provisional sub-committee was constituted under Committee E-1 (Methods of Testing) to devise a program in cooperation with other ASTM Committees with the objective of defining general test methods employing thermal analysis. The four areas of

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TABLE I

OTHER GROUPS INTERESTED IN THERMAL ANALYSIS STANDARDS

Starting year	*Group*	*Program*	*Current status*
1964	ISO TC-61 (WG-4)	Examination of one sample PVC by DTA and TG according to "national practice"	Not published
	ISO TC-61 (WG-1)	Nomenclature and Definitions	Draft stage
1965	ASTM D-20 Sub 3b	Nomenclature and Definitions	Under study
1968	ASTM E-1	Nomenclature and Definitions	ICTA and D-20 Recommendations under study
		Meetings	First program April, 1970
		Reference materials	3 Materials under evaluation, for temperature range 50–100 °C
		Test methods	Task Groups to cooperate with E-27 (Hazardous Materials)
1968	SAMA	Uniform terminology	Under study
		Specifications for Instrument Performance	Under study
		Reference Materials	Under study

activity include (*i*) nomenclature and definitions, which is now reviewing published ICTA and suggested ASTM D-20 terminology; (*ii*) meetings; (*iii*) reference materials, which has considered three materials for potential calibration of DTA in the region of 75 °C and which has obtained encouraging results with hexachloroethane; and (*iv*) test methods, which is reviewing with other ASTM Committees specific areas where existing or new test procedures can better be accomplished by thermoanalytical methods.

The most recent group to show interest in thermal analysis standards is the Scientific Apparatus Makers Association (SAMA). Their objectives are to provide uniform terminology for use by member companies in their trade literature as well as uniform methods for specifying instrument performance involving, possibly, use of certain common reference materials.

Thus, with the possible exception of overlapping approaches to nomenclature, these various groups are concerned with relatively specific concepts related to standardization, while the ICTA deals with the broad problems shared by all areas of the techniques. A good level of communication exists between the ICTA and these groups so that each may take advantage of the other's work.

ICTA PROGRAM AND RESULTS

DTA temperature standards

To accomplish the objectives stated above, the ICTA has brought together a committee having high technical caliber, a broad international base, and wide-ranging liaison with other interested groups (Table II). The top priority was given to standardization relative to DTA, since this is currently the most widely used of the thermoanalytical methods.

The ICTA program is designed to provide a common basis on which all DTA results can be assessed, instrument performance evaluated, and essential calibration made. To do this requires standard materials suitable for use in any design of equipment and under whatever conditions a particular study may involve. Thus, by including one or two curves of standard materials obtained under the conditions of any particular study, it is possible for the reader to relate the subject matter to the performance of his own instrumentation and to evaluate the quality of the published data.

The ICTA program is further designed to cover the temperature range 0–1000 °C, this being the range which is of greatest present application, while also investigating possible standard materials for the sub-ambient and >1000 °C temperature ranges.

While melting or freezing points have traditionally been used as temperature standards, the ICTA Committee decided in favor of Solid I $\rightleftharpoons$ Solid II first-order phase transitions for use in dynamic DTA. There are a number of significant reasons for this decision:

(*i*) Not all instrumentation can be used with samples which melt. Two of the most common designs of sample holders are not liquid tight: the cylindrical flow-through cavity in a block, and the sleeve enclosing a vertically exposed thermo-

TABLE II

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS, COMMITTEE ON STANDARDIZATION

				Liaison with
Chairman		(Canada)	H. G. McAdie	(2), (5), (6), (8), (10)
Vice-Chairman		(U.S.A.)	P. D. Garn	(2), (10)
Secretary		(U.K.)	R. C. Mackenzie	(7), (8)
National Delegates		(France)	C. Mazières	(1)
		(German D.R.)	K. Heide	(11)
		(Hungary)	F. Paulik	
		(Japan)	H. Kambe	(9)
		(Sweden)	R. S. Forsyth	
		(Switzerland)	H. G. Wiedemann	(4)
		(U.S.S.R.)	I. S. Rassonskaya	(12)
		(U.K.)	D. A. Smith	(8)
		(U.S.A.)	R. W. Pfeil	
Representative Delegates	ASTM	(U.S.A.)	Vacant	
	ISO	(—)	Vacant	
	NBS	(U.S.A.)	O. Menis	
	Soc. Anal. Chem.	(U.K.)	C. J. Keattch	(3)
	SAMA	(U.S.A.)	Vacant	
Ex-Officio Delegates	ICTA	(U.S.S.R.)	L. G. Berg	(12)
		(U.S.A.)	C. B. Murphy	
		(U.K.)	R. C. Mackenzie	(7), (8)
		(U.K.)	J. P. Redfern	(8)

(1) AFNOR (France). (2) ASTM (U.S.A.). (3) BSI (U.K.). (4) DIN (West Germany). (5) ISO TC-61 (Plastics). (6) IUPAC Commission on Physical Chemical Data and Standards. (7) OECD Materials Research Advisory Group. (8) Soc. Anal. Chem. (U.K.). (9) Soc. Anal. Chem. (Japan). (10) SAMA (U.S.A.). (11) TAN (German D.R.). (12) U.S.S.R. Commission on Thermography.

couple bead where the thermocouple leads are not sintered into the ceramic support. Dilution of the sample, when used for calibration purposes, is an expedient of limited value, requiring increased ΔT sensitivity and introducing possible problems of diluent–sample interaction especially with diluents porous enough to retain all the liquid phase produced.

(*ii*) A number of feasible melting point standards will contaminate the sample holder by forming alloys *e.g.* platinum with Pb, Zn, Sb, *etc.* Unless the holder can be isolated from the sample, or a disposable holder used, this contamination cannot be tolerated. Similar contamination of thermocouples will result if these are exposed.

(*iii*) Many DTA systems do not have *true* atmosphere control. Use of metal melting points requires the ability to impose an inert atmosphere particularly when the melting point is above a few hundred degrees. Traditional use of metal melting points has also usually employed relatively large masses of metal under conditions where skin effects are not critical, whereas in DTA small samples have a high surface: volume ratio and skin effects are more pronounced.

(*iv*) The melting of standard reference organic compounds also requires good atmosphere control. In addition such materials may introduce problems of decomposition and/or relatively high vapor pressure which eliminate their use as standards.

(*v*) On melting, changes in other physical properties such as heat capacity, thermal conductivity, specific volume, are often much larger than corresponding changes accompanying $S_I \rightleftharpoons S_{II}$ processes. Further, in the case of melting metals, high surface tension may form these into beads rather than a uniform film conforming to the sample holder shape. This, together with the presence of any oxide layer, would cause considerable change in thermal contact and distortion of the record.

(*vi*) The effect of impurities on melting points is more pronounced than on $S_I \rightleftharpoons S_{II}$ transitions.

For these reasons the ICTA Committee initially reviewed over 200 reported $S_I \rightleftharpoons S_{II}$ transitions[1], from which twelve systems were selected for international evaluation. The results of this evaluation, and the procedures employed have been reported in detail[2]. From this evaluation eight materials were provisionally accepted as DTA temperature standards (Table III) and experimental evidence indicated these should be considered for use in the heating mode only, due to problems of supercooling in a number of cases.

Because several of the specimens used in the first evaluation did not produce the well-defined thermal effects desirable in a DTA temperature standard, a variety of further specimens were examined to select materials having satisfactory "thermal purity". At the same time a number of other transitions, suggested following publication of the earlier work[2], were examined. To provide assistance to other groups, while

TABLE III

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS, COMMITTEE ON STANDARDIZATION PROVISIONAL DTA TEMPERATURE STANDARDS

ICTA standard	*Transition temperature*	*Ref.*
KNO_3	127.7	2
$KClO_4$	299.5	2
Ag_2SO_4	412.[a]	2
SiO_2	573.	2
K_2SO_4	583.	2
K_2CrO_4	665.	2
$BaCO_3$	810.	2
$SrCO_3$	925.	2
In	157.	2
Sn	231.9	2

[a]This value is in doubt; a considerable weight of evidence suggests 430±2°.

recognizing the above-mentioned limitations, the melting points of high-purity indium and tin samples were included as potential DTA temperature standards. Bulk quantities of these materials were purchased and aliquot samples circulated to 41 laboratories in 15 countries. Detailed test instructions were prepared by the Committee, based on the principle that *the operating conditions of each instrument should be those normally employed.*

Each investigator will supply a minimum of duplicate runs on each material, with the materials examined in a random order. From each curve (Fig. 1) the extrapolated onset and peak temperatures will be measured, together with the arbitrary peak area defined by the triangle ABC in units of $°C^2mg^{-1}$ to be independent of chart speed, amplification, and thermocouple calibration factors. Approximately 20 instrumental and design parameters will be supplied by each investigator and the entire data programed for computer analysis including tests for systematic bias.

Following data assembly, coding, analysis, and review by the Committee,

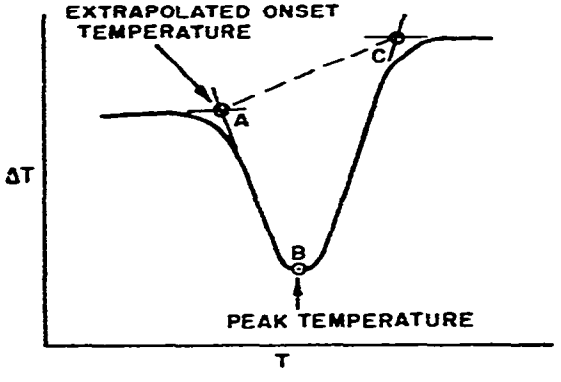

Fig. 1. Definition of temperatures and peak area used in ICTA International Test Program.

certification of this first group of DTA temperature standards is expected before the end of 1970. Realization of these standards one year in advance of original planning is a tribute to the enthusiasm and dedication of those who have contributed to the ICTA programs.

Further standards

The need for sub-ambient DTA temperature standards has been stated clearly[3], as well as for the standards usable above 1000 °C. Systems suitable for use in both these temperature ranges are being reviewed experimentally by task forces from the ICTA Committee. The Committee as a whole is continuing to seek suitable systems for the temperature intervals not adequately covered by the group DTA-1, and continues to invite suggestions from interested workers.

The problem of TG temperature standards has been approached in three ways. A series of decomposition processes were examined by the Committee which concluded that such processes were not acceptable as potential standards[2]. Current approaches involve evaluation of the Curie-point technique as well as use of the DTA temperature standards under conditions involving an arrested balance and an extra thermocouple inserted at the sample location.

Other accomplishments

The objectives of the ICTA Committees include methods of improving communication and understanding between thermal analysts. Two documents have been published: Recommendations for the Reporting of Thermal Analysis Data[4], which have been adopted as editorial policy by more than 50 scientific journals, as well as by at least one national standards body; while the ICTA Nomenclature Committee has published a detailed and consistent set of definitions, conventions and general recommendations[5].

FUTURE PROGRAMS

The Committee will continue to investigate further materials for use as DTA temperature standards concurrent with increased emphasis on TG temperature standardization. With the increasing application of newer thermoanalytical techniques such as evolved gas analysis, thermomechanical analysis, *etc.*, specialized reference materials will be required which the Committee plans to study.

Arrangements are well advanced to market ICTA standards so as to produce the broadest possible international distribution. Every effort will be made to facilitate the use of these materials by thermal analysts throughout the world, so that their efforts may be of increased value to their colleagues.

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REFERENCES

1 F. D. ROSSINI, D. D. WAGMAN, W. H. EVANS, S. LEVINE, AND I. JAFFE, *Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stand. (U.S.), Circ.*, 500 (1952).
2 H. G. MCADIE, in R. F. SCHWENKER, JR. AND P. D. GARN (Eds.), *Thermal Analysis*, Academic Press, New York, 1969, Vol. I, p. 693; Vol. II, p. 1499.
3 R. L. BOHON, *Proc. Toronto Symp. Therm. Anal., 3rd*, (1970) 33.
4 H. G. MCADIE, *Anal. Chem.*, 39 (1967) 543.
5 R. C. MACKENZIE, *Talanta*, 16 (1969) 1227.