

Recommendations for Names and Definitions in Thermal Analysis and Calorimetry

ICTAC Nomenclature Committee

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Introduction

This is a new document on nomenclature in thermal analysis and calorimetry. In part it is based on the reports of the Nomenclature Committee of ICTA, published e.g. by R.C. Mackenzie in "Treatise on Analytical Chemistry" Part 1, Vol. 12, Section J, 2nd Ed., (P.J. Elving, Ed.) Wiley, New York, 1983, pp. 1-16, in Pure & Appl. Chem., **57** (1985) 1737-1740, and in "For Better Thermal Analysis and Calorimetry", Ed. III (J.O. Hill, Ed.), 1991, pp. 6-14.

The former definition of thermal analysis was:

Thermal Analysis (TA)

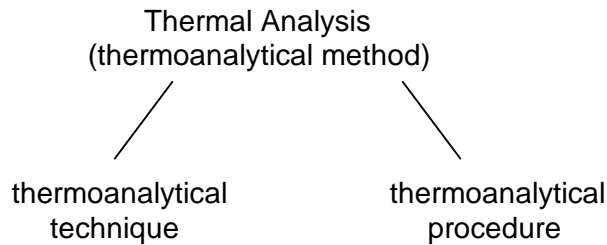
A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.

The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these.

Revisions seemed to be necessary to

- overcome improprieties of the former definition of thermal analysis:
 - In most cases not a sample property is monitored but the change in a sample property.
 - Analysis means much more than monitoring (see below).
 - Monitoring against time includes measurement at ambient temperature alone, that means, almost every measurement is "thermal analysis".
 - In most cases not the temperature of the sample is programmed but the temperature of the environment of the sample.
 - A specified atmosphere is not essential for the general definition. Atmosphere is an operational parameter like others.
 - Temperature programme means a predetermined sequence, this excludes sample controlled temperature regimes.
- include calorimetry (because ICTA - International Confederation for Thermal Analysis - has been changed in 1992 to ICTAC - International Confederation for Thermal Analysis and Calorimetry). As regards calorimetry, only some basic ideas about classification are presented. The systematic development of a structured nomenclature cannot be the task of an ICTAC committee alone but should be done in close collaboration with IUPAC.
- provide a hierarchical structure in the classifications using the sample property under study as a classification criterion.
- separate clearly primary techniques from purely operational modifications (e. g. from Photo-DSC, Controlled-Rate Thermal Analysis, High-Pressure DSC).

- distinguish thermoanalytical techniques from thermoanalytical procedures:



Thermal Analysis means the totality of a thermoanalytical method, it covers both the thermoanalytical technique (measurement of a change in a sample property) and the thermoanalytical investigation procedure (evaluation and interpretation of the measured values).

Not to separate techniques from methods leads to confusion with regard to naming (e. g. Differential Thermal Analysis but Thermodilatometry).

Therefore, thermoanalytical techniques are characterized by the suffix "metry" whereas the more comprehensive thermoanalytical methods are indicated by adding "analysis".

- provide a classification structure that leaves room for new techniques.

Definition of Thermal Analysis and of Calorimetry

Thermal Analysis (TA) means the analysis of a change in a sample property, which is related to an imposed temperature regime.

Calorimetry means the measurement of heat.

Names and Definitions of Thermoanalytical Techniques and Methods

Heating or Cooling Curve Determination (Thermometry)

Measurement of the change of the temperature of the sample while it is subjected to a temperature regime (heated or cooled).

(Thermoanalytical method: **Heating or cooling curve analysis**)

Differential Thermometry (DT)

Measurement of the change of the difference in temperature between the sample and the reference sample while they are subjected to a temperature regime.

(Thermoanalytical method: **Differential Thermal Analysis, DTA**)

Differential Scanning Calorimetry (DSC)

Measurement of the change of the difference in the heat flow rate to the sample and to a reference sample while they are subjected to a temperature regime.

Thermogravimetry (TG)

Measurement of the change of the mass of the sample while it is subjected to a temperature regime. (Thermoanalytical method: **Thermogravimetric Analysis, TGA**)

Thermomechanometry (TM)

Measurement of the change of a dimension or a mechanical property of the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermomechanical Analysis, TMA**)

Special technique:

Thermodilatometry (TD)

Measurement of the change of a dimension of the sample with a negligible force acting on the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermodilatometric Analysis, TDA**)

Thermomanometry

Measurement of the change of the pressure exerted by the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermomanometric Analysis**)

Thermoelectrometry (TE)

Measurement of the change of an electrical property of the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermoelectrical Analysis, TEA**)

Thermomagnetometry

Measurement of the change of a magnetic property of the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermomagnetic Analysis**)

Thermoptometry (TO)

Measurement of the change of an optical property of the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermoptometric Analysis, TOA**)

Special technique:

Thermomicroscopy

The sample is observed by means of a microscope while it is subjected to a temperature regime.

Thermoacoustimetry

Measurement of the change of imposed acoustic waves after passage through the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermoacoustic Analysis, TAA**)

Thermosonimetry (TS)

Measurement of the sound emitted by the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermosonimetric Analysis, TSA**)

Thermally Stimulated Exchanged Gas Measurement (EGM)

Investigation of the gas exchanged with the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermally Stimulated Exchanged Gas Analysis, EGA**)

Special techniques:

Thermally Stimulated Exchanged Gas Detection

Monitoring of the amount of gas exchanged with the sample while it is subjected to a temperature regime.

Thermally Stimulated Exchanged Gas Determination

Determination of the composition (and amount) of gas exchanged with the sample while it is subjected to a temperature regime.

Thermally Stimulated Emanation Measurement

Measurement of the amount of radioactive gas (emanation) released by the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Emanation Thermal Analysis, ETA**)

Thermodiffractometry

Measurement of the change of a structural property of the sample while it is subjected to a temperature regime.

(Thermoanalytical method: **Thermodiffractometric Analysis**)

Statement**Classification, Names and Definitions of Calorimetric Techniques**

No generally accepted classification system is so far available for calorimeters. A relatively clear and useful system as established in thermal analysis, i.e. which even includes the individual techniques, seems - at first glance - hardly possible in calorimetry.

What are calorimeters?

Calorimeters are used to measure heat and heat flow rates. Depending on which kind of heat-generating or heat-consuming process is concerned (combustion, solid-state transition or the like), which kind of sample is concerned (solid, liquid, gaseous, living being, of great volume, etc.) and

under which conditions the calorimeter is to be used (temperature, pressure, atmosphere, etc.), a great variety of different calorimeters has been developed.

Classification system

The arrangement of the calorimeters in a classification system should be based on a simple and logical structural order according to the calorimetric technique and suitable for practical application. Several classification criteria have been suggested (cf. Literature). The attempt to classify every calorimeter in every detail leads to a lack of clarity and is insignificant in practice. A particular difficulty in the classification of calorimeters arises from the fact that many calorimeters can be operated in various modes so that a specific instrument must often be classified in different ways, depending on the mode of operation. The same is often true of the measuring principle which can be changed in certain calorimeters. The problem of calorimeter classification is that, first, a simple primary classification criterion orientated to the instruments available must be found and that, secondly, clear and flexible classification must be guaranteed without too many additional criteria being applied.

Literature:

W. Hemminger and G. Höhne: "Calorimetry" pp. 131-133, Verlag Chemie, Weinheim (1984)

J. Rouquerol and W. Zielenkiewicz, *Thermochim. Acta* **109** (1986) 121-137

G. Höhne, W. Hemminger and H.-J. Flammersheim: "Differential Scanning Calorimetry" pp. 193-194, Springer Verlag, Berlin (1996)

Explanatory Comments, General Definitions and Classification Schemes

1. Definition of Thermal Analysis and of Calorimetry

A separate definition of calorimetry is added. No uniform definition of thermal analysis and calorimetry has so far been accepted (see statement "Classification, Names and Definitions of Calorimetric Techniques").

The gist of thermal analysis is the measurement of the **change of a property** which is related to an **alteration of the sample temperature**. Only this combination/sequence gives the basis, reason and justification to define a special field of measuring methods and to combine many different techniques into "thermoanalytical" techniques.

Analysis means that the whole experimental process including the evaluation and interpretation procedures of the measured values is covered (see "Introduction").

Property means any thermodynamic or material property, chemical composition or structure.

Temperature regime means any sequence of temperatures with respect to time which may either be predetermined (temperature-programmed) or sample-controlled. Sample-controlled temperature alteration means that a feedback signal from the sample controls the temperature to which the sample is subjected.

Temperature regime includes:

- stepwise change from one constant temperature to another (this includes the isothermal mode of operation, see below)
- linear rate of change of the temperature (constant heating or cooling rate)
- modulation of a constant or a linearly changing temperature with constant frequency and amplitude
- free (uncontrolled) heating or cooling

Any combination of these modes of operation is possible.

Isothermal techniques belong to thermal analysis if at least one alteration from a specific temperature (even ambient temperature) to another takes place; i.e. only measurements at ambient temperature do not belong to thermal analysis.

2. Names and Definitions of Thermoanalytical Techniques and Methods

Thermomechanometry: For the sake of the new systematic approach, the former terms for Thermomechanical Analysis (TMA) and its various methods had to be redefined:

- Thermomechanical Analysis → static force TMA
- Dynamic Load TMA → dynamic force TMA
- Thermodilatometry → Thermodilatometry
- Dynamic Mechanical Analysis (also named Dynamic Mechanical Spectrometry) → modulated force TMA

Thermoelectrical Analysis includes measurements with and without any kind of electric field. That means, Dielectric Thermal Analysis is a special case of Alternating Current Thermoelectrical Analysis. Analogous statements are valid with respect to Thermomagnetic Analysis.

Thermally stimulated Exchanged Gas Measurement means the determination of the composition and/or amount of gas exchanged with the sample. Here the composition/amount of the gas is measured, which means that a corresponding change of the sample composition and/or mass occurs.

The term **exchanged** is used (instead of evolved) to include both directions of gas flow, from and to the sample.

Various kinds of analytical techniques are used for Thermally Stimulated Exchanged Gas Detection and for Thermally Stimulated Exchanged Gas Determination.

3. General Definitions

A **physical quantity** is e. g. temperature, force, pressure, chemical composition.

Static mode of operation means any physical quantity acting on the sample is constant with time.

Dynamic mode of operation means any alteration with time of any physical quantity acting on the sample. The alteration may be predetermined (programmed) or controlled by the sample itself.

Modulated mode of operation is a special variant of the dynamic mode of operation in which the alteration of a physical quantity acting on the sample is characterized by frequency and amplitude. The modulated quantity should be specified.

Thermally stimulated means that particles, photons or phonons are released from the sample through a thermal stimulation, i. e. activation.

Differential methods of measurement compare the property to be measured simultaneously with a property of the same kind under identical experimental conditions.

Simultaneous methods of measurement apply two or more techniques to a single sample at the same time. (Abbreviations of the techniques should be connected by a hyphen.)

Derivative means determining the rate of change of a sample property (the first derivative with respect to time).

Notes

- **Representation of thermal events in DT and DSC.** The DT output signal corresponds to the temperature difference between sample and reference sample, $\Delta T_{SR} = T_S - T_R$. In the case of endothermic events in the sample, the DT measuring signal tends towards negative ΔT values. The DSC output signal should (after calorimetric calibration) always be recorded as heat flow rate ΔF_{SR} (unit: W). Positive heat flow rates must then be assigned to endothermic effects (the same is true if $C_S > C_R$). In the DSC curve, peaks caused by endothermic events thus point to the positive ΔF direction.
- The designations **micro** or **macro** are not recommended for usage unless it is clear whether the terms relate to the sample size (mass, volume), the size of the instrument, the value of the measured signal (which could be amplified) or the quantity.
- The term **photo** which may be used in connection with any instrument where there is an irradiation of the sample should be avoided.

Abbreviations of Modes of Operation and Special Methods

Use lower case letters for the abbreviation of modes of operation and special methods connected by a hyphen to the thermoanalytical technique or method.

Examples:

hf-DSC	heat flux Differential Scanning Calorimetry
pc-DSC	power compensating Differential Scanning Calorimetry
mt-DSC	modulated temperature Differential Scanning Calorimetry
sf-TM	static force Thermomechanometry
df-TM	dynamic force Thermomechanometry
ac-TE	alternating current Thermoelectrometry

4. Classification Schemes

The following tables are not part of the Definitions. The basis of the tables are classification principles which are suitable to establish a classification system which provides a methodic scheme in which both established and new techniques and methods can be incorporated. The sample property, the change of which is under investigation, will be the primary classification criterion, see Table "*Primary Classification Scheme of Thermal Analysis and Calorimetry*". Additional classification criteria will be required for some of the TA methods listed in this table. This sub-classification will be made according to the stress to which the sample is subjected or according to the special kind of monitoring used to make the respective quantity accessible to the measurement, see Table "*Secondary Classification Scheme of Thermal Analysis*". Both, the thermoanalytical techniques and the thermoanalytical methods are listed.

Primary Classification Scheme of Thermal Analysis and Calorimetry			
Property under study	Thermoanalytical/Calorimetric Technique (Abbreviation)	Thermoanalytical/Calorimetric Method (Abbreviation)	Remarks
Temperature	Thermometry	Heating/Cooling Curve Analysis	
Temperature difference	Differential Thermometry (DT)	Differential Thermal Analysis (DTA)	
Heat	Calorimetry		(Needs an extensive sub-classification system because of the variety and variability of calorimetric techniques.)
	Differential Scanning Calorimetry (DSC)		
Mass	Thermogravimetry (TG)	Thermogravimetric Analysis (TGA)	(see sub-classification)
Dimensions/mechanical properties	Thermomechanometry (TM)	Thermomechanical Analysis (TMA)	
Pressure	Thermomanometry	Thermomanometric Analysis	
Electrical properties	Thermoelectrometry (TE)	Thermoelectrical Analysis (TEA)	(See sub-classification)
Magnetic properties	Thermomagnetometry	Thermomagnetic Analysis	
Optical Properties	Thermoptometry	Thermoptometric Analysis (TOA)	(See sub-classification)
Acoustic properties	Thermoacoustimetry	Thermoacoustic Analysis (TAA)	(See sub-classification)
Chemical composition/ crystalline structure/ microstructure			(See sub-classification)

Secondary Classification Scheme of Thermal Analysis				
Property under study	Secondary classification criteria/distinguishing features	Thermoanalytical Technique	Thermoanalytical Method	Remarks
Dimension/mechanical properties	With or without any kind of force acting on sample	Thermomechanometry (TM) (Generic term)	Thermomechanical Analysis (TMA) (Generic term)	
	Static force	Static Force Thermomechanometry (sf-TM)	Static Force Thermomechanical Analysis (sf-TMA)	
	Special case: Negligible force	Thermodilatometry (TD)	Thermodilatometric Analysis (TDA)	
	Dynamic force	Dynamic Force Thermomechanometry (df-TM)	Dynamic Force Thermomechanical Analysis (df-TMA)	
	Special case: Modulated force	Modulated Force Thermomechanometry (mf-TM)	Modulated Force Thermomechanical Analysis (mf-TMA)	
Electrical properties	With or without any kind of electric field	Thermoelectrometry (TE) (Generic term)	Thermoelectrical Analysis (TEA) (Generic term)	

Continuation

Property under study	Secondary classification criteria/distinguishing features	Thermoanalytical Technique	Thermoanalytical Method	Remarks
Magnetic properties Optical properties	Without superimposed electric field Alternating electric field (dynamic mode)	Thermally Stimulated Current Measurement (TSCM)	Thermally Stimulated Current Analysis (TSCA) Alternating Current Thermoelectrical Analysis (ac-TEA) (Generic term) Special case: Dielectric Thermal Analysis (DETA)	(Various techniques to measure susceptibility, permeability etc.)
	With or without any kind of magnetic field	Thermomagnetometry (Generic term)	Thermomagnetic Analysis (Generic term)	
		Thermooptometry (TO) (Generic term)	Thermooptometric Analysis (TOA) (Generic term)	
	Intensity of radiation emitted Intensity of total radiation reflected or transmitted	Thermoluminescence Measurement (TLM) Thermophotometry	Thermoluminescence Analysis (TLMA) Thermophotometric Analysis	

Continuation

Property under study	Secondary classification criteria/distinguishing features	Thermoanalytical Technique	Thermoanalytical Method	Remarks
Acoustic properties	Intensity of radiation of specific wavelength(s)	Thermospectrometry	Thermospectrometric Analysis	
	The refractive index is measured	Thermorefractometry	Thermorefractometric Analysis	
	The sample is observed by means of a microscope	Thermomicroscopy	Thermomicroscopic Analysis	
	Acoustic waves are monitored after having passed through the sample	Thermoacoustimetry (Generic term)	Thermoacoustic Analysis (TAA) (Generic term)	
	Acoustic waves emitted by the sample are monitored	Thermosonimetry (TS)	Thermosonimetric Analysis (TSA)	
Chemical composition/ crystalline structure/ microstructure	Analysing the change in chemical composition and/or in the crystalline structure and/or in the micro-structure of the sample	Thermodiffractometry	Thermodiffractometric Analysis	Various techniques are used: (optical, nuclear, X-ray, electrical, etc.)
	special case: Diffraction techniques			

Continuation

Property under study	Secondary classification criteria/distinguishing features	Thermoanalytical Technique	Thermoanalytical Method	Remarks
	<p>special cases: Investigation of gas exchanged with the sample</p> <p>Determination of the composition and/or amount of gas</p> <p>Monitoring of the amount only</p> <p>Determination of the composition (and the amount)</p> <p>Release of trapped radioactive gas from the sample is monitored</p>	<p>Thermally Stimulated Exchanged Gas Measurement (EGM) (Generic term)</p> <p>Thermally Stimulated Exchanged Gas Detection</p> <p>Thermally Stimulated Exchanged Gas Determination</p> <p>Thermally Stimulated Emanation Measurement</p>	<p>Thermally Stimulated Exchanged Gas Analysis (EGA) (Generic term)</p> <p>Emanation Thermal Analysis (ETA)</p>	<p>(Various techniques)</p> <p>(e. g. by gas chromatography, mass spectrometry)</p>