THERMAL METHODS OF ANALYSIS

PRINCIPLES, APPLICATIONS AND PROBLEMS

Peter J. Haines

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Thermal Methods of Analysis
Principles, Applications and Problems

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Preface

The wide range of applications of thermal methods of analysis in measuring physical properties, studying chemical reactions and determining the thermal behaviour of samples is of interest to academics and to industry. These applications prompted the writing of this book, in the hope that the descriptions, explanations and examples given would be of help to the analyst and would stimulate the investigation of other thermal techniques.

Thermal studies are a fascinating means of examining the samples and the problems brought to us by colleagues, students and clients. If time allows, watching crystals change on a hot-stage microscope, or measuring the properties and changes on a DSC or TG or any thermal instrument can be a rewarding activity, besides providing valuable analytical information.

This book started from a series of lectures delivered at Kingston University and at meetings of the Thermal Methods Group of the United Kingdom. The collaboration and information supplied to all the contributors by colleagues and instrument manufacturers is most gratefully acknowledged, as are the valuable contributions made at meetings of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) and at the European Symposia on Thermal Analysis and Calorimetry (ESTAC).

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Peter J. Haines

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Introduction to thermal methods

1

P.J. Haines

1.1 Introduction

The effects of heat on materials have fascinated and benefited humanity since the very earliest times. Even the observation of fires and the burning process was both a pleasurable, and if uncontrolled, painful experience. The use of fire to cook foods, and of ice to preserve foods, probably contributed greatly to the settlement and welfare of early peoples and cooking was perhaps the very first 'chemical experiment'. The production of both organic and inorganic pigments by heating natural materials allowed the decorative arts to develop [1].

The skills which people first acquired in the controlled use of heat allowed the manufacture of ceramics, mortars, glass and metals. Primitive apparatus dating from around 2500 BC [2] is known and the problems that arose with burning materials and the damage caused by fire are frequently seen in early settlements.

These skills, and the products they gave, were largely empirical 'arts' and their spread was jealously guarded by those who first discovered the most satisfactory technique. However, with the spread of information through travel, the methods were transmitted to people in other countries, who added their expert knowledge to improve the methods still further. The alchemists were responsible for many discoveries and their experiments in the synthesis and decomposition of natural and artificial substances laid the basis for modern chemistry [3,4]. Jabir ibn Hayyan wrote a *Book of Furnaces* and a *Book of Balances* around AD 800, but we have no evidence that he combined both [5]! In studying the history of materials, we also come to realise the effects that ageing has on their properties.

As the study of chemistry became more disciplined, the range of substances studied increased and it became necessary for scientists to be able to distinguish between different substances and materials. By studying their properties and reactions, it became possible to identify not only the constituents of a substance, but often the particular source from which it came. This is the beginning of the discipline known as *analytical chemistry*.

The modern student of chemistry or materials science may well start his or her experimental study of the subject by observing the nature of a range of materials, their appearance, mechanical properties and density and may then choose to heat the materials as a first attempt at classification [6].

A small sample, heated in a test tube, may undergo both physical and chemical changes and may alter in a large number of ways, or it may be completely stable. Table 1.1 gives some examples of behaviour that may be observed when solid substances are heated in air [6,7].

It must be noted that a single observation is often not complete in itself, but requires additional chemical or physical measurements. For example, we cannot know what gas is evolved without a simple chemical test or physical measurement, such as a spectrum. The need to use complementary analytical techniques must be recognised throughout any investigation.

The addition of some simple apparatus to determine accurately the temperature of the event, and to control the heating, or to measure colour,

Table 1.1 The effects of heat on solid materials

Effect	Possible conclusion	Example
Colour change		
Charring, burning with little residue	Organics, polymer	Paper, burning
Blackening with large residue	Metal oxide formed	$CuCO_3=CuO+CO_2$
Metal changes to powder	Oxidation	$2Mg+O_2=MgO$
Colour change	Transition metal salt or phase transition	HgI_2, red → yellow
Substance melts		
Melts at low temperature	Covalent?	Organics
Melts at high temperature	Ionic salts	NaCl
Substance sublimes		
White sublimate	Volatile solid Ammonium salts	NH_4Cl
Violet sublimate	Iodine	I_2
Vapours evolved (and characterised by additional tests)		
Water vapour (droplets)	Hydrates	$CuSO_4 \cdot 5H_2O$
Oxygen	Nitrates, chlorates	$2KNO_3=2KNO_2+O_2$
Oxides of nitrogen (brown fumes)	Nitrates	$2AgNO_3=2Ag+2NO_2+O_2$
Carbon dioxide	Carbonates	$ZnCO_3=ZnO+CO_2$
Physical changes		
Becomes more pliable	Plastics above T_g	
Expansion: (a) gradual	General expansion	
(b) abrupt	Phase change	
Swelling	Some intumescent materials	Polyphosphates
Shrinkage	Some strained polymers	Fibres
No effect	Stable oxides or temperature too low	MgO, Al_2O_3

plus any change in weight, or perhaps the extent of expansion or the nature of the volatiles evolved, gives a great deal more information to the analyst.

1.2 Historical development

The history of the development of thermal methods from earliest times is considered in papers by Mackenzie [2] which include an account of thermometry from the sixteenth century.

The definition of thermometric scales and the start of practical calorimetry in the eighteenth century, particularly by Lavoisier and Laplace [8] really brought about a revolution in our thinking and in the practical approach to studying the effects of heat. It led directly to the work of Fourier on heat conduction [9] and to the elegant experiments of Joule on electrical heating and calorimetry [10]. The chief drawbacks of their equipment were that it often required large samples and a long time to complete the experiment. Chemical reactions and physical measurements on gases were forerunners of today's analytical techniques

The development of scientific instruments during the earlier part of the twentieth century allowed the principles of thermal measurements to be established – for example, the measurement of the coefficients of expansion of silica by Henning [11] using an optical method led to the development of modern interferometric dilatometers [12] and the design of the thermobalance, especially by Honda [13], has led to the modern TG systems.

In the second half of the twentieth century, vast improvements in instrumentation, sensors, data acquisition, storage and processing have been made, especially with the advent of microprocessors. The precision, sensitivity and reproducibility of modern instruments are high, and their range of temperature of operation has extended, together with the quality of temperature control.

Thermal methods of analysis are now used in a very large range of scientific investigations. Besides the more 'chemical' areas, such as polymers, fine organic chemicals and pharmaceuticals, they have applications to electronics, in construction, geology and engineering, in materials science and in quality control. They often give information impossible to obtain by other analytical methods. Very often, a complex material, such as a polymer composite, will show definite and characteristic effects on heating which relate to its nature, composition and history. These observations are informative about its properties and working life.

1.3 Definitions

Because thermal methods have been developed by many workers, it was necessary to agree on a common terminology, and the International Confederation for Thermal Analysis and Calorimetry (ICTAC) has produced definitive publications and articles, both on the nomenclature and on the calibration methods to be used [14–17]. There are still some differences in usage, but in this text we shall use the ICTAC definitions and symbols throughout.

1.3.1 *Thermal analysis*

Thermal analysis (TA) is defined [17] as:

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.

The word *sample* is interpreted to mean the substance placed into the apparatus at the beginning of the experiment, and its reaction products.

The adjective is '*thermoanalytical*'.

The graphical results obtained are called the '*thermal analysis curve*', or by the specific name of the method.

The property used for study may be chosen from an extensive list, shown in part in Table 1.2.

In Table 1.2 careful distinction should be made between the terms *derivative* and *differential*. Differential techniques involve the measurement of a *difference* in the property between the sample and a reference – for example, in *differential thermal analysis (DTA)* where the difference in temperature between the sample and a reference is measured. Derivative techniques imply the measurement or calculation of the mathematical first derivative, usually with respect to time. For example *derivative thermogravimetry (DTG)* is the measurement of the *rate* of mass loss (dm/dt) plotted against temperature T.

In discussing the theories and results of thermoanalytical studies, we shall always use the 'SI' system of units and symbols [18] and, where necessary, conversion from older units will be made with the occasional exception of temperature which may be quoted in the (more familiar) degree Celsius (°C). The principal symbols and units to be used are given in Table 1.3. The usual prefixes are used, e.g. 10^{-3} m = 1 mm, 10^{6} Pa= 1 MPa, 10^{3} g = 1 kg, etc.

EXAMPLES OF SYMBOLS USED IN THERMAL METHODS

(a) If the symbol refers to an *object* (*the sample, the furnace*) then it should have a CAPITAL LETTER subscript:

Temperature of reference	T_R	K
Sample mass	m_S	kg
Temperature difference	ΔT	K

(b) If the symbol refers to a *phenomenon* (melting, bending) or to a *point*, then it should have a *small* letter subscript:

Table 1.2 Thermal methods

Technique	Abbreviation	Property	Uses
1. Thermogravimetry (Thermogravimetric analysis)	TG TGA	Mass	Decompositions Dehydrations Oxidation
2. Differential thermal analysis	DTA	Temperature difference	Phase changes Reactions
3. Differential scanning calorimetry	DSC	Power difference	Heat capacity Phase changes Reactions Calorimetry
4. Thermomechanical analysis	TMA	Deformations	Mechanical changes Expansions
5. Dynamic mechanical analysis	DMA	Moduli	Phase changes Polymer cure
6. Dielectric thermal analysis	DETA	Permittivity	Phase changes Polymer changes
7. Evolved gas analysis	EGA	Gases	Decompositions Catalyst and surface reactions
8. Thermoptometry		Optical	Phase changes Surface reactions Colour changes
Less frequently used techniques			
9. Thermosonimetry	TS	Sound	Mechanical and chemical changes
10. Thermomagnetometry	TM	Magnetic	Magnetic changes Curie points
11. Thermoluminescence	TL	Light emitted	Trap depths
12. Emanation thermal analysis	ETA	Gas released	Structural changes
Also used			
13. Simultaneous thermal analysis	STA	Two or more techniques used on the same sample at the same time.	
14. Controlled-rate thermal analysis	CRTA	The rate of change of the property is held constant	

Glass transition temperature	T_g	K
Melting temperature	T_m	K
Initial temperature	T_i	K
Final mass	m_f	kg

A THERMODYNAMIC DIVERSION

When a substance is heated, its physical properties and sometimes its chemical nature change, and these may be represented by chemical

Table 1.3 SI units and symbols for therrmal methods [14, 18]

Quantity	Symbol	Unit(s) and abbreviation(s)	
Basic units			
length	l	metre	m
mass	m	kilogram	kg
time	t	second	s
electric current	I	ampere	A
temperature	T	kelvin	K
amount of substance	n	mole	mol
Derived units			
energy	E	joule	J = kg m^2/s^2
power	P	watt	J/s
force	F	newton	N(= kg m/s^2)
pressure	p	pascal	Pa (= N/m^2)
concentration	c	molarity	mol/dm^3
frequency	ν	hertz	s^{-1}
Combined units			
heat	q	J	
heat capacity	C	J/K	
internal energy	U	J	
enthalpy	H	J	
free energy	G	J	
entropy	S	J/K	
thermal conductivity	k	J/(s m K)	
density	ρ	kg/m^3	
rate of reaction	v	$mol/(m^3 s)$	
order of reaction	n		
fractional extent of reaction	α		
rate constant of nth-order reaction	k	s^{-1} $(mol/m^3)^{n-1}$	
activation energy	E	J/mol	
molar gas constant	R	J/(K mol)	
stress	σ	Pa	
strain	ϵ	–	
bulk modulus	K	Pa	
tensile modulus	E	Pa	
shear modulus	G	Pa	

equations and by thermodynamic functions showing the properties of the system. For a fuller treatment of the discipline of thermodynamics, the reader is advised to study a good textbook on physical chemistry, such as those listed in [19].

The *First Law of Thermodynamics* expresses the principle of conservation of energy. When heat is absorbed by a system under specified conditions – for example, at constant pressure – the heat energy of that system changes. At constant pressure this is represented by a change in the *enthalpy H*.

$$\Delta H = q_p \tag{1.1}$$

Under *standard* conditions – which are, for gases, 1 atmosphere pressure, and for liquids and solids, pure material at 1 atmosphere – we may write the

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