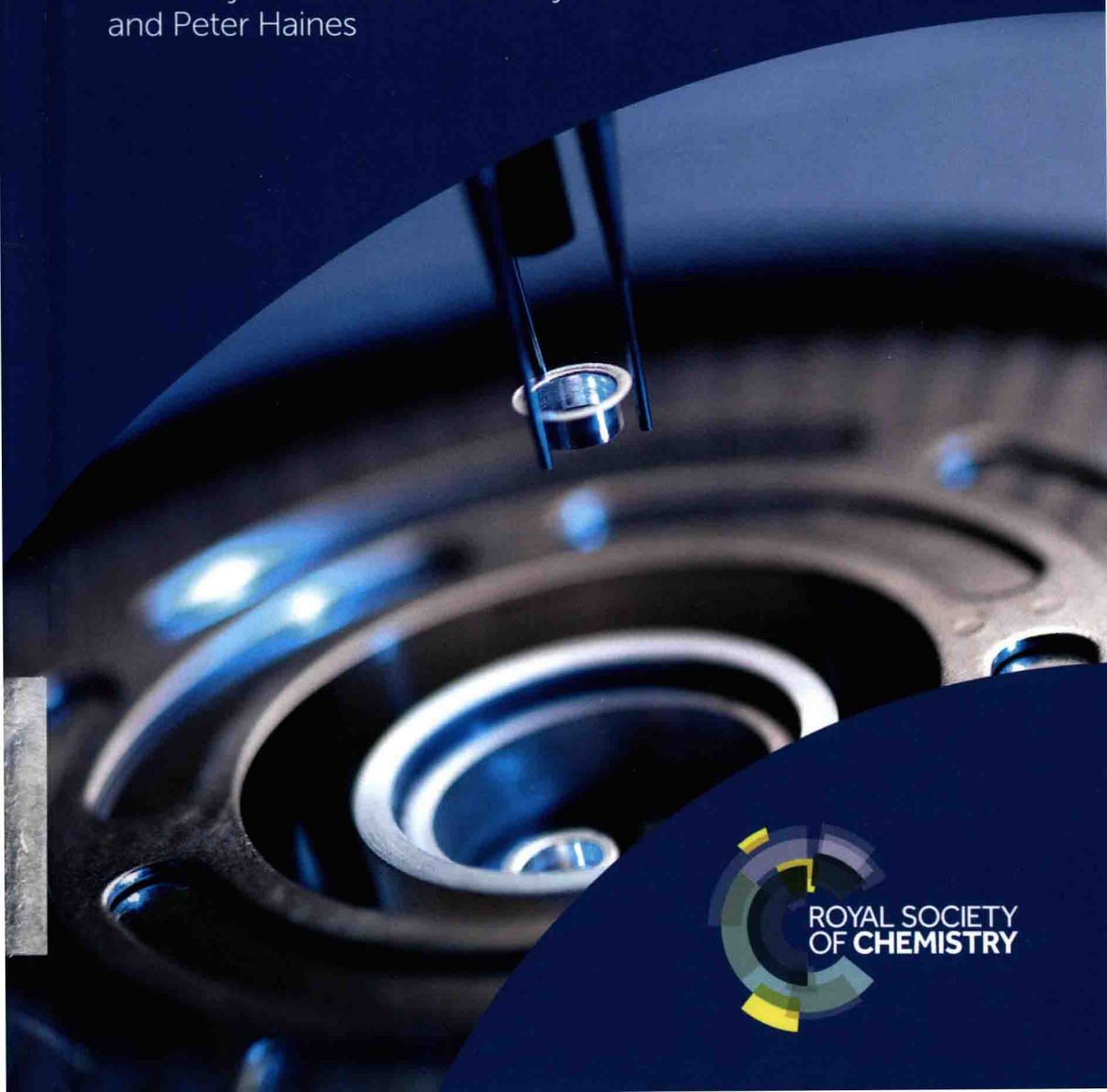
2nd Edition

Principles of Thermal Analysis and Calorimetry

Edited by Simon Gaisford, Vicky Kett and Peter Haines



ROYAL SOCIETY OF CHEMISTRY

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Preface

The Thermal Methods Group (TMG), part of the Royal Society of Chemistry (RSC), exists to promote the education, awareness and application of thermal and calorimetric methods in the UK. Over the years, many illustrious names in the thermal analysis field have served on the TMG committee and 2015 is a special year as it marks the 50th anniversary of its founding. As part of the anniversary celebrations, the current TMG Committee decided to produce a revised and updated version of its textbook, *Principles of Thermal Analysis and Calorimetry*. The first version, published in 2001, provided an excellent introduction to thermal analysis and calorimetric techniques, but the past decade has seen the development of better technology and new techniques. This revised text therefore seeks to address these new developments, in addition to providing the background to the core techniques as in the first edition.

The focus of this text is on the underlying theory and operating principles of each technique. Each chapter has been written by an expert in the field and has been reviewed by the Committee. A review of thermal analysis nomenclature, as approved by the International Union of Pure and Applied Chemistry, is provided before discussion of the individual techniques. In addition to the well-established techniques of differential scanning calorimetry (DSC), isothermal calorimetry, thermogravimetric analysis and mechanical analysis, this text discusses a wider range of techniques such as dynamic vapour sorption, dielectric thermal analysis, modulated-temperature DSC, sample-controlled thermal analysis and hazard calorimetry. Some recent, and very exciting, new approaches are also introduced, such as modifications to localised thermal analysis and hyphenated techniques.

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We hope, therefore, that you find the book interesting, informative and stimulating, and it helps you in starting to use thermal methods or in improving your current analyses. We also hope that you will join us in promoting thermal methods, through word-of-mouth or by contributing to the work of the TMG, either by attending our annual meetings and training courses, becoming a member or joining the Committee. Further details can be found at our web-site.

Simon, Vicky and Peter
www.thermalmethodsgroup.org.uk

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1 TMG History

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1.1 Introduction

In 2015, the Thermal Methods Group (TMG), an interest group of the Royal Society of Chemistry (RSC), entered its 50th year. It seems appropriate therefore to not only look back to its origins but also to review briefly its activities since its formation and its current role in the field of thermal analysis and calorimetry. For readers interested in a more detailed account of the formation of the Group, there is an excellent paper covering the first twenty one years of the TMG's history.[1]

1.2 The Early Years

The 1960s were an exciting time for thermal analysis. The field was growing rapidly and the range of commercially available equipment was expanding, including the introduction of both power-compensated and heat flux differential scanning calorimeters. In addition, a significant number of thermal analysts were engaged in building their own equipment, particularly in the field of simultaneous thermogravimetry–differential thermal analysis.

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At that time, there was no forum in the UK where thermal analysts could meet so, in 1964, John Redfern and Cyril Keattch decided to investigate the possibility of forming a group by holding a thermal analysis symposium at the Battersea College of Technology (now the University of Surrey). The response exceeded the organisers' expectations and some 100 delegates attended the meeting. The discussions that took place during the technical sessions, and at the buffet supper afterwards, enthusiastically endorsed the idea of formally establishing a thermal analysis group.

This aim was realised on the 24th February 1965 when the UK Thermal Analysis Group was formed as part of the Society for Analytical Chemistry. The inaugural meeting took place on the evening of May 28th 1965 at the Chemical Society, Burlington House, Piccadilly, where the new Committee was confirmed. The Group's first Chairman was Robert Mackenzie with John Redfern as Vice-Chairman, Cyril Keattch as Secretary and Alan Hodgson as Treasurer. The 1st AGM was held in December 1965 and the Group was well and truly launched with its first two-day meeting in April 1966. This consisted of a visit to the laboratories of Pilkington Bros. Ltd on the first day and a meeting at the Royal College of Advanced Technology, Salford (now the University of Salford), on the second day on the "Characterisation of Residues after Thermal Treatment".

In 1972, the name of the Group was changed to the Thermal Methods Group to reflect the wide range of techniques falling within its scope. Following the merger of the Society of Analytical Chemistry and the Chemical Society in 1975, the Group became part of the Analytical Division of the Chemical Society. In 1980, following the merger of the Chemical Society, the Royal Institute of Chemistry and the Faraday Society, the Group became part of the Analytical Division of the newly formed Royal Society of Chemistry. The objective of the TMG is to promote awareness of all thermoanalytical, calorimetric and related techniques by a range of activities, including a regular programme of scientific meetings, training workshops and publications.

1.3 TMG Committee Structure

The management of the operation of the Group is the responsibility of the TMG Committee, which is elected at the Annual General Meeting, normally held during the April scientific conference. The Chairman, Vice-Chairman and Immediate Past Chairman of the TMG serve for a

period of two years and Committee members for the three years, with the possibility of a further three-year extension. The posts of Secretary and Treasurer are renewable. The Committee hold "face to face" meetings at least twice a year and these are supplemented by telephone conferences where necessary. In addition, sub-committees are formed to deal with specific activities such as training courses and the planning of meetings. The TMG Committee actively welcomes new members, particularly those that can widen its range of thermal analysis and calorimetric expertise.

A complete list of the TMG Chairmen, Secretaries and Treasurers is given in Tables 1.1–1.3, respectively. The Group has been

Table 1.1 A list of TMG Chairs

1965	Robert Mackenzie	Macaulay Institute for Soil Research, Aberdeen
1967	John Redfern	Battersea College of Technology, London
1969	David Dollimore	University of Salford
1971	John Sharp	University of Sheffield
1973	Keith Barrett	ICI Dyestuffs/Patent Office
1975	Fred Wilburn	Pilkington Bros. Ltd.
1977	Dick Still	University of Manchester Institute of Science and Technology
1979	Ted Charsley	Stanton Redcroft Ltd
1981	Graham Clarke	North East Surrey College of Technology
1983	Peter Laye	University of Leeds
1985	Derek Nowell	Hatfield Polytechnic
1987	Peter Haines	Kingston Polytechnic
1989	Jenny Hider	Consultant
1991	Bob Whitehouse	Cabot Plastics
1993	David Morgan	British Geological Survey
1995	Jezz Leckenby	TopoMetrix Corporation
1997	Steve Warrington	Loughborough University
1999	Trevor Lever	TA Instruments
2001	Jim Ford	Liverpool John Moores University
2003	Keyna O'Reilly	University of Oxford
2004	Mark Phipps	TA Instruments
2006	Mike Reading	University of East Anglia
2008	Simon Gaisford	School of Pharmacy, University of London
2010	Ian Priestley	Syngenta Ltd, Huddersfield
2012	Paul Gabbott	PETA Solutions
2014	Vicky Kett	Queen's University Belfast

Table 1.2 A list of TMG Secretaries

Cyril Keattch	1965–1999	Industrial and Laboratory Services
Richard Wilson	1999–2006	SmithKline Beecham
Catherine Barnes	2006–present	GlaxoSmithKline

Table 1.3 A list of TMG Treasurers

Alan Hodgson	1965–1979	Cape Asbestos Company Ltd
Dick Still	1979–1996	University of Manchester Institute of Science and Technology
Mike Richardson	1996–2004	National Physical Laboratory
Simon Gaisford	2004–2006	School of Pharmacy, University of London
Mike O'Neill	2006–2010	University of Bath/Aston University
Simon Gaisford	2010–present	UCL School of Pharmacy

exceptionally fortunate in having long-serving Secretaries and Treasurers who have provided valuable continuity during the 50 years of the Group's history and who have worked tirelessly on the Group's behalf. In particular, mention should be made of the Group's first Secretary, Cyril Keattch, who held the post from 1965 until his untimely death in 1999.

1.4 TMG Meetings

The TMG initially held two or three meetings a year, frequently in conjunction with other groups of the Society of Analytical Chemistry or Royal Institute of Chemistry. The meetings covered a wide range of topics ranging from "Protection of the Environment" to "Controlling Explosives" and were sometimes held in the afternoon or evening. A particular effort was made to meet in different parts of the UK in order to reach as many of the membership as possible. By the 1980's, the Group had developed a pattern of holding a two-day meeting in April and a one-day meeting in November.

In general, the meetings were on specific subject areas and, as a result, TMG members might not attend a meeting for several years if their own field was not featured. In 1995, it was decided that a National Thermal Analysis Conference (TAC) would be held in place of the normal two-day April meeting. This would be open to all areas of thermal analysis and calorimetry and would help promote a regular attendance by Group members. The first TAC was held in Leeds in