Thermal Physics and Thermal Analysis

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Thermal Physics and Thermal Analysis

From Macro to Micro, Highlighting Thermodynamics, Kinetics and Nanomaterials

Springer

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Dedication and Acknowledgements

This book fulfillment was greatly supported by Dr. Pavel Holba (1940–2016), one of the most talented world thermodynamists, who unfortunately passed away during this volume completion, so that we are contented to dedicate this work to his memory.

The present book completion as well as the accomplishment of individual chapters was supported by Institutional Research Plan of Institute of Physics ASCR, v.v.i., while developed at its Join Research Laboratory with the New Technologies Centre of the University of West Bohemia in Pilsen. The financial assistance was provided by the CENTEM project (NTC, ZČU), reg. no. CZ.1.05/2.1.00/03.0088 that is co-funded from the ERDF as a part of the MEYS—Ministry of Education, Youth and Sports OP RDI Program and, in the follow-up sustainability stage supported through the CENTEM PLUS LO 1402.

The multi-institutional cooperation during the drafting of this book is greatly acknowledged, and the contributions by distinguished experts from an international array of world renowned scientists are recognized.

The present book is a stretchy continuation of the previous Volume 8 (*Glassy, Amorphous and Nano-Crystalline Materials: Thermal Physics, Analysis, Structure and Properties*—ISBN 9789048128815) and Volume 9 (*Thermal Analysis of Micro-, Nano-, and Non-Crystalline Materials: Transformation, Crystallization, Kinetics and Thermodynamics*—ISBN 9789048131495), complementing thus a coherent triptych with authoritative overview of cutting-edge themes of material science focused on solid-state chemistry, thermal physics, and analysis of various states of matter. It provides a new farsightedness of various concepts, often avant-garde and mostly not published yet.

Distinctive chapters featured in the book include, among others, calorimetry on timescales, glass transition phenomena, nonstoichiometry, kinetics of non-isothermal processes, kinetic phase diagrams, thermal inertia and temperature gradients, thermodynamics of nanomaterials, selforganization and econophysics, significance of temperature and entropy, hyperfree energy and Ehrenfest equations of higher order, biomaterials and microtextiles, significance of scientific works, and infiniteness. Advanced undergraduates, postgraduates, researchers, and academicians working in the field of thermal analysis and calorimetry, thermophysical measurements, thermodynamics and material sciences will find this contributed volume invaluable.

This is the third volume of the triptych volumes on thermal behavior of materials; the previous two (volumes 8 and 9) received over twenty thousands of downloads guaranteeing their worldwide impact ranking them between the twenty best books by Springer.

Initial Volume 8 was appreciatively instigated by thermoanalytical legends as US Professors A. Angel and B. Wunderlich, Bulgarian I. Avramov, Brazilian E. Zanotto or Japanese H. Suga and further based on the Czech and Slovak studies not so well internationally known yet but influential, among others mentioning N. Koga, M. Liška, J. Málek or P. Šimon.

The editors are pleased to present this forward-thinking compendium to public judgment convinced that the innovative ideas will serve duly the coming generation of thermal scientists.

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Foreword

The Eyewitness's Recollections on Thermal Analysis Maturity; the Half-Century Anniversary of Formation of the New Field, which is Now Due for Revision

The historic part of this preface is more than a recollection of the pertaining chronology. The present state of thermal analysis, as an inseparable part of thermal physics [1], is "resting on the shoulders" of its pioneers and their previous problems, controversies, and fallibilities. That gives us a relative perspective that our present achievements are neither absolute nor the last. A more detailed description than just a chronological enumeration of events was needed to link the previous ways of thinking with ours. This humbleness aside, we should be feeling lucky and happy that we are a part of this discipline, so uniquely diversified and bridging refined theory with technical applications, and the curious insight into materials with methodological inventiveness. The most exciting thermoanalytical discoveries, fundamental revisions of the theories, and enormous expansions of the research areas, are still ahead of us.

Thermal analysis is a research method which studies, in dynamic, time-related ways, the relationships between temperature and some selected properties. This method dates back well into the nineteenth century, and it was initially called thermography. The term "thermal analysis" (TA) was introduced at the turn of twentieth century by Tammann [2] who was recording cooling curves in phase-equilibrium studies of binary systems. He was followed by others [3], performing more exhaustive study of the effect of experimental variables on the shape of heating curves, as well as the influence of temperature gradients and heat fluxes taking place within both the furnace and the sample. The associated differential thermal analysis (DTA) was initially an empirical technique, and its early quantitative studies were semi-empirical and based on intuitive reasoning. Though some theoretical understanding was build [3], it was Berg, using the Newton's cooling law, who gave the initial theoretical bases for DTA [4], later improved within the renowned Russian thermoanalytical school [5]. DTA became gradually the center of attention [6], thermogravimetry being the second, thanks to its quantitative benefits.

Fig. 1 Those who instigated the underpinning new fields of thermal physics and its indispensable branch of thermal analysis: Strouhal Čeněk (Vincenc) (1858–1922, Bohemia [15]), Berg [4] (1896–1974, USSR), Mackenzie [9, 16] (1920–2000, Scotland), who also helped for the formation of ICTA (International Confederation of Thermal Analysis); William Wesley Wendlandt [11, 17] (1927–2000, USA, the architect of Thermochimica Acta [18]), Keattch and Dollimore [19] (1920–2000, UK–USA, the initiator of the sister organization ESTAC—European Symposium of thermal Analysis and Calorimetry) and Cornelius Bernard Murphy [20] (1918–1994, USA, the first elected ICTA President)

It is high time now to recognize heat as an "instrumental reagent." Vold [7] was the first to take account of sample's thermal inertia, an essential factor of kinetic evaluation. That improvement, however, was repudiated by Borchard and Daniels [8] and that had a deleterious effect [10] on the subsequent DTA kinetic studies, persisting even now. Those improvements [6–7] remained largely ignored in the ensuing key books [9–11] and in many related papers. Therefore, the progress in this area (equation manipulation, thermal effects) can be best seen in the sphere of kinetic papers. The six most important founders of thermal analysis are shown in Fig. 1. There are certainly other noteworthy "architects" who could not be listed here, but most of them have been mentioned elsewhere [12–14].

As the result of WW2, Europe was divided into the free West, and the East occupied by USSR, with a profoundly deep split between them—political, military, economic, and cultural. Information coming from the free world had a disruptive potential for the communist doctrine, so the East-European science became a victim of the all-encompassing censorship and restrictions. Because of that, the East-European science, including thermal analysis, was developing to a great extent independently from that in the West. For this reason, the history of thermal analysis in the second half of the twentieth century needs to be told in two parts: in the West, and in the East, separately.

The Western Course of Thermal Analysis Advancement, and Foundation of Thermochimica Acta

The development of the Western stream of thermal analysis matured at the first International Symposium on Thermal Analysis [12] which was held at the Northern Polytechnic in London (organized by B.R. Currel and D.A. Smith, April 1965), consisting of about 400 mostly international participants. The choice of the invited lectures offered the first account of thermal analysts who founded the field's progress, such as B.R. Currell, D.A. Smith, R.C. Mackenzie, P.D. Garn, M. Harmelin, W.W. Wendlandt, J.P. Redfern, D. Dollimore, C.B. Murphy, H.G. McAdie, L.G. Berg, M.J. Frazer, W. Gerard, G. Lombardi, C.J. Keattch, and G. Berggren. The remarkable key lectures were read by P.D. Garn, G. Guiochon, and J.P Redfern, on kinetic studies, also by W.W. Wendlandt and M. Hermelin on the methods of thermoanalytical investigations. The organizers invited scientist from the informationally isolated countries of the Soviet Block, then represented by F. Paulik and J. Šesták giving the key lectures on the standardization of experimental condition and errors of kinetic data. This event was followed by the Aberdeen conference (September 1965) organized by J.P. Redfern and R.C. Mackenzie (Scotland), with the help of US C.B. Murphy, Czech R. Barta, Russian L.G. Berg, and Hungarian L. Erdey, with almost identical personal attendance.

During those conferences, culminating at the first ICTA conference in Worcester (USA 1968) [21], the Elsevier publishing house, advocated by Prof. W.W. Wendlandt (USA), realized the need to create an international journal covering thermal analysis. And so in early 1970s, the journal Thermochimica Acta (TCA) started the publishing

Fig. 2 Editorial Board meeting of Thermochimica Acta in Grado (6th ESTAC, September 1994). *Upper from left* T. Ozawa (Kyoto), J. Šesták (Prague), J. Hay (one time TCA Editor, Birmingham), W. Hemminger (one-time TCA Editor, Brunswick), E.L. Charsley (Leeds), J. Dunn (Pearth), part-hidden M. Richardson (Teddington), V.B. Lazarev (Moscow), part-hidden P.K. Gallagher (Columbus), J. Rouquerol (Marseilles). *Sitting from left*: L. Whiting, (one time TCA Editor, Midland), G. Arena (Catalania), G. DelaGatta (Torino), H. Suga (Osaka). In 1990s, several more renowned thermal analysts participated at the TCA EB such as J.R. Allan (Edinburgh, V. Balek (Řež), E.H.P. Cordfunke (Petten), G. D'Ascenzo (Rome), D. Dollimore (Toledo, USA), C.M. Earnest (Rome), W. Eysel (Aachen), J.H. Flynn (Washington), A.K. Galwey (Belfast), F. Grønvold (Oslo), J.-P.E. Grolier [Aubiere), L.D. Hansen (Provo), K. Heide (Jena), L.G. Hepler (Edmonton), R.-H. Hu (Beijing), R.B. Kemp (Aherystwyth), A. Kettrup (Paderborn), I. Lamprecht (Berlin), F. Paulik (Budapest), O.T. Sorensen (Roskilde), or S.St.J. Warne (Newcastle)

process, which continued for twenty-five years by its founder [18] and legendary editor Wesley W. Wendlandt (1920–1997), with the help of the group of already renowned scientists, making the first international TCA Editorial Board: B.R. Currell, T. Ozawa, L. Reich, J. Šesták, A.P. Gray, R.M. Izatt, G. Beech, M. Harmelin, H.G. McAdie, H.G. Wiedemann, E.M. Barrall, T.R. Ingraham, R.N. Rogers, J. Chiu, H. Dichtl, P.O. Lumme, R.C. Wilhoit, G. Pannetier, G.M. Lukaszewski, E. Sturm, G.A. Vaughan, with support of D.A. Smith, S. Seki, M.J. Frazer, C.J. Keattch, and/or G. Berggren (Fig. 2). The journal had its seat in Huston (Texas, USA) gradually joining the best established and recognized international periodicals. Only one of those authors of the earliest TCA board is remaining now as a yet active member.

TCA grew fast, and during the first ten years of its existence it increased the number of pages tenfold. The credit largely belongs to the editor [18], whose scientific reputation and guidance, as well as his own articles substantially contributed to the success. The TCA publications focused on the hot topics identified during the former conferences, especially those dealing with the theoretical basis of general thermoanalytical kinetics [22–26]. Unfortunately, less attention was paid to DTA theory [27] which later became more abundant [28, 29], but its treatment mostly overlooked the factor of sample's thermal inertia [7, 30] ignoring the first kinetic software which did address sample's heat inertia [33]—the readers were probably apprehensive to be overwhelmed by the complexity of the problem which would require a revision of the commonly practiced procedures. Five papers [22–26] from the first two years of TCA's existence are worth highlighting. They analyzed the consequences of the Garn's book [10], which provided the early core of non-isothermal kinetic studies. Those papers have received an abundant citation response, namely (Scopus) 29, 282, 70, 802, and 8, respectively. They altogether provided a starting point to the subsequent kinetic studies, resulting in books [31–33], the latest of which just preserved mathematical exploitation of kinetic equations, but paying not enough attention to other critical assessments [34–36]. The ICTAC's Kinetics Committee issued "Recommendations" [37], which received a high citation response ($\sim$800), but that may be seen rather relative since they advise how to precisely evaluate and correctly publish not fully truthful kinetic numbers [36]. Hundreds of valuable kinetic publications and some more recent TCA papers received equally high citation response such as [38] with 180 or [39] with 230 citations.

We should appreciate the pioneering role of TCA having published the first concise paper coining the term "heat inertia" and showing its effect on kinetics [30]. It is not a fault of the journal that paper [30] was overlooked and was not incorporated in further kinetic software. Moreover, the historical data clearly show the key influence of kinetic studies on the TCA publication scope [36, 37], recently touching advanced treatises providing detailed characterization of samples by averaging the temperature values at different locations within the sample [40], incorporation of a cooling constant [41], merging the impact of gradient [42] necessary to better direct future research of modern kinetics [33].

In 1969, Paul D. Garn, a pioneer of thermoanalytical kinetics (then of the Akron University, Ohio), founded the North American Thermal Analysis Society (NATAS), becoming its first president. Presently, NATAS is a large organization, with many sections, and remaining very active for the last 47 years. It organizes conferences annually, publishing their proceedings as NATAS Notes. Information about NATAS, and links to the other national thermoanalytical organizations, can be found at [43]. Garn's scientific life was not happy. He disagreed with the mainstream of the thermoanalytical kinetics, criticized it relentlessly [34], and he was logically deconstructing its fundamental faults, so his arguments were systematically ignored. The other researchers were unwilling to revise their most basic assumptions and "start from scratch." Only now, long after his death, his line of thinking seems to be getting some traction.

Several Japanese researchers (Ihmory, Takagi, Honda) developed their original designs much earlier than the first European (Nernst, Škramovský, Guichard, Duval) and American (anonymous, later Cahn) thermobalance instruments became commercially available in 1950s [13, 14]. Those Japanese designs pioneered the technique in several ways: Saito's TG was top loading, Shibata and Fukushima used electromagnetic force. It was followed by other masterminds as Ozawa (non-isothermal kinetics) and Suga (calorimetry and non-crystallinity) which was detailed in our previous historical chapter [14].

The Eastern Stream of Thermoanalytical Progress and Foundation of Journal of Thermal Analysis

The other Eastern branch became active in the difficult times when persecution and discrimination of politically active scientist was common in those countries. The science in the so-called Eastern Block had to work in almost full isolation from the thermal analysis of the rest of the world. From late 1940s to late 1980s, most of the scientists in the Soviet Block were neither allowed to communicate with the West, nor permitted to travel there. The Western literature was only scarcely available; purchasing Western instrumentation was generally out of question. That resulted in a "schism," into the "Western" thermal analysis and "Eastern" one [12–14, 44]. Paradoxically, that isolation from the West created some benefits by forcing the Eastern thermal analysts to build their own instruments, e.g., the famous Hungarian Derivatograph (T+DTA+TG+DTG) [45], the only relatively easily available thermoanalytical instrument in Eastern Europe, or "Pyrometr Kurnakova" (DTA), thousands of which were manufactured in USSR, primarily for geological exploration.

The contributions to the thermoanalytical theory by scientists from USSR should not be overlooked [4, 5, 46] to mention just these of the hundreds who combined broad scientific background with practical attitude. The mainstream thermoanalytical theory could benefit from both, but their books and articles, published mostly in the Cyrllic font, remain almost completely unknown in the West.

Cut-off from the West by the communist "Iron Courtain," the East-European thermal analysts were actively working toward acquiring scientific, cultural, social and political information from the free world. Contacts with Western thermal analysts were performed by letters, joint publications, and participation in international meetings. The very difficult access to publish internationally dictated the need to find local forum for thermoanalytical publications. One of them turned out to be the Czechoslovak scientific journal "Silikáty" founded by R. Barta as early as 1956 and long edited by Šatava [47]. It became famous for promoting publications in the sphere of thermal analysis [44]. Since those papers, naturally for the circumstances, were published in the Czech language, they did not get the international attention they deserved. However, some of them did contribute to acquiring initial insight into the role of temperature gradients in kinetic evaluations [48].

Journal "Silikaty" originated from the first Czechoslovak (more or less first international) conference on thermal analysis, mostly dealing with DA. It was organized by R. Barta in Prague as early as 1955 (titled "Thermography Discussions") [47]. That was followed by a series of thermoanalytical conferences, such as the first Thermography Day (1958 in Bratislava) and the 2nd Conference on Thermography (1961 in Prague, already with an international participation including Dr. R.C. Mackenzie. The most important of those events was the first international thermoanalytical conference behind the iron curtain: the 4th ICTA in Budapest 1974, where the thermoanalytical West and the East had a chance to work together, underpinning the bases of various advanced methods (cf. Fig. 3.).

Worth noting are the Soviet conferences on thermal analysis [55] (formerly named "thermography") starting in Kazan 1953 and 1957, followed by the All-Union conferences in Riga 1962 and continued in Moscow 1969, etc. In early 1970s, other major TA conferences took place in Germany, Hungary, and Poland. In 1972, jointly with J.P. Redfern and G. Liptay, R.C. Mackenzie started publishing a periodical Thermal Analysis Abstracts (TAA), prepared by a team of reviewers covering the East- and West-European countries. After 20 years, that service was stopped in 1991 due to the proliferation of computers. Several books and articles [31, 32, 46, 51, 54–58] largely contributed to the growth of thermal analysis.

Despite severe political difficulties, Judit Simon and Eva Buzagh followed the example of the "Silikáty" and fashioned a team consisting of renowned L. Erdey, the F. and J. Paulik brothers, J.P. Redfern, R. Bárta, L.G. Berg, G. Lombardi, R.C. Mackenzie, C. Duval, P.D. Garn, S.K. Bhattacharyya, A.V. Nikolaev, C.B. Murphy, T. Sudo, D.J. Swaine, W.W. Wedndlandt, J.F. Johanson, and consulting editors F. Szabadvary and G. Liptay (of this group, only three remain now), publishing thus the first thermoanalytical-focused journal, in a record-short time [59]. It helped to facilitate the communication between the East and West.

Kinetics became an important subject [60–63] of the two first JTA volumes, but again little attention was paid to DTA's theory [64]. Thermal inertia was practically absent in JTA, and only passingly mentioned elsewhere [48]. The early JTA issues contained articles on modern kinetics [65–68], including its critique [69, 70].

Fig. 3 Young scientists participating at 1974 ICTA in Budapest who represented a new groundswell for the rising field of thermal analysis; *from left* Jean Rouquerol (*1937) [49] France, Hemminger (*1937) [50], Germany, Schultze (*1937), [51] Germany, Jaroslav Šesták (*1938), [17, 52] Czechoslovakia, Simon (*1937) [53] and Ferenc Paulik (1922–2005), [45, 54] both from Hungary

The 1985 ICTA in Bratislava, cf. Fig. 4, became the topmost achievement of the Czech–Slovak thermal analysts, who bravely prepared and carried out an open international conference in then communistic Czechoslovakia; such initiatives were "strongly discouraged" by authorities. The geopolitical split of thermal analysis into "East" and "West" lasted forty years, the length of a typical active period in the life of a scientist. That schism ceased to exist in 1989, the Soviet Army withdrew from stationing in the Eastern Europe, so communism in Europe was allowed to collapse and most countries of these two "blocks" merged.

Fig. 4 Celebrating the 20th anniversary of ICTA foundation: The ICTA Council meeting in the castle Liblice (near Prague) taking place at the occasion of the 8th ICTA Conference in Bratislava 1985 (former Czechoslovakia). *From left* Giuseppe Della Gatta (Persuading additional term Calorimetry in ICTAC, Italy), Erwin Marti (Switzerland), Jaroslav Šesták (8 ICTA program chair, Czechia), *behind* Klaus Heide (Germany), Slade St.J. Warne (ICTA Vice-president, Australia), Hans-Joachim Seifert (ICTA President, Germany), Patric K. Gallagher (ICTA Past-president, USA), Joseph H. Flynn (USA), Tommy Wadsen (Sweden), John Crighton (England), John O. Hill (Australia), Paul D. Garn (USA), Vladislav V. Lazarev (Russia), Walter Eysel (Germany), Bordas S. Alsinas (Spain), Edward L. Charsley (England, former president), *behind* Shmuel Yariv (Izrael, secretary)

Fig. 5 Budapest, Hungary, March 2015. Honorary celebration and farewell to the long-running JTAC editor-in-chief, Professor Judit Simon. *From left* Petru Budrugeac (Romania), Peter Šimon (Slovakia), Alfred Kállay-Menyhárd (Deputy JTAC editor-in-chief since 2014), Judit Simon (Honorary JTAC Editor), György Liptay (Honorary consulting Editor), Jaroslav Šesták (Czechia), and Imre Miklós Szilágyi (JTAC co-editor since 2014)

As the field of thermal analysis broadened its scope, the journal changed its name to Journal of Thermal Analysis and Calorimetry (JTAC) with Judit Simon managing it as the editor-in-chief until, unbelievably, 2013, see Fig. 5, almost twenty years longer than the legendary TCA editor W.W. Wendlandt. Four international publishing companies (Heyden, Wiley, Kluver, and now Springer) and the Hungarian Academic Publisher have been engaged in printing the journal, and the original impact factor of 0.2 has grown to the present 2.2, reaching that of TCA. JTAC became also famous in presenting on its pages the proceedings of the most important conferences (ICTAC, ESTAC, and recent CEEC TA).

Thermal Analysis has Reached Adult Status; Time for Revisions

On wrapping up the history, it seems clear that the process of developing the theory of thermal analysis [3–11, 47–58] has not been completed yet, and it needs a revision and upgrading, which may not be welcomed by some orthodox users. For instance, the phenomenological theory of kinetics [8, 10, 17, 22–26, 31–39] demonstrates inclination to mathematical sophistication and disregard to physical meaning or usefulness. One such neglected aspects are the thermal inhomogeneities inside samples, unavoidable even in the smallest ones, since in thermal analysis temperature is constantly changing.

The logistic approach [66] provides an alternative insight into the reacting interfaces, based on the propagation of defects, which, interestingly, resembles progression of infectious diseases. New strategies such as [66], and others [65, 68–70], are welcome, but we lack in more fundamental things, in first place we are in need of understanding the processes related to heat and temperature, taking place inside thermoanalytical samples [71–74]. The fact that transferring heat takes time has been known since Newton's cooling law [75] and from the fundamental Tian's calorimetric equation [76]. That knowledge has not been incorporated into thermoanalytical theoretical treatises as much as it deserves [30, 37, 78]. On top of that knowledge, experiments have shown that gradients of temperature [40, 72] and of gaseous decomposition products (if any) are inescapable even in submilligram samples [77], so ignoring them is not justifiable. Those gradients, interwoven with the thermal inertia, with the chemical equilibria, phase transitions and reaction fronts [10, 78], reflect the complex and dynamically changing situation inside thermoanalytical samples. Such difficulties are especially severe at the high cooling rates of novel chip microcalorimetry [79, 80], important in the new field of kinetic phase diagrams [81]. This vast range of problems has been glossed over by the thermoanalytical mainstream [33, 37, 50]. A new proposition for thermal analysis theory, addressing this complexity [30, 40, 71–74], as well as the new meaning of temperature while changing at ultrafast rates [80, 81], is expected to get underway.

In the area of theory, a two-pronged effort is needed: abandoning some unjustifiable practices and improving the legitimate ones. Of the unjustifiable practices, calculating activation energy [34–36, 69] and temperature [79] in situations where it is not sure whether such calculations are legitimate at all, should be stopped by researchers and rejected by reviewers and publishers. Calculating activation energy for transport-controlled processes (which we often do, while no undergraduate student of chemical engineering would) or reporting temperature values with several decimal places when the error margin may be one hundred degrees or more (in ultrarapid quenching) is a futile "academic" exercise. The common practice of adding qualifiers "formal," "apparent," or "of no real meaning" to activation energy is a lame excuse for using inadequate models. Thermal analysis can help some technical disciplines such as geopolymers [82], semiconductors [83, 84], biocompatible inorganic [85], and building materials and catalysts [86] in solving their problems, but trust will not be possible without proving the reliability of the results and the legitimacy of the underlying theories.

A broader definition of thermogravimetry extends beyond materials characterization and includes such uses as modeling of thermo-chemical fabrication of advanced materials or optimization of thermochemical processing of materials and parts. At present, most researchers who are trying to optimize processes such as CVD or steel carburization, either do not use weight recording at all, or merely apply it in the "before-and-after" mode. Catalysis offers a rich opportunity for insightful thermogravimetry [86]. Reactive analytical thermogravimetry, by imposing chemical reactions with gases onto the sample, determines the percentage of the components. However, this vast R&D potential requires expansion of capabilities of the instrumentation. There are two classes of TG users: one is those who want problem-free, quick results; the other class is those who want to use TG instruments for advanced research. The first group are satisfied by the present "push button" design of TG's, and they do not mind that the instrument's software denies the user chances to review its algorithms—allegedly because of trade secrets. The elegant, compact styling hides the "guts" of the instrument and discourages the users from experimenting because they are afraid to damage that costly piece of equipment. The second class of users needs capabilities which are not offered now. It is highly desirable that TG instruments match the requirements of these two classes of users: one for routine analyses mostly required by industrial laboratories, and another that would be better suited for the scientific and industrial research. In addition to the present "push-button" class of TG instruments, manufacturers may consider adding an advanced, "transparent," and flexible class. On top of this, specialized versions of TG's could address several areas of specific applications; the desired features can be found in [86].

The present shape and structure of thermal analysis was neither obvious at its conception, nor are we sure that it is the best possible. We believe that progress means practice-verified improvements, which not just changes. Since what counts in science is "better" rather than "new," then returning to some older thermoanalytical concepts mentioned here, could result in additional progress.

Authors of this preface are happy to have been parts of thermal analysis for fifty years and contributing to it by their publications ranging from some old, groundwork articles [12, 13, 17, 30, 77, 86] of which the "SB equation" [25] became the best cited paper in thermoanalytical history, to the recent "hot topics" ones, related to heat inertia and thermal gradients [72–74], to reliability of experimentally observed temperature under its fast changes [80, 81], to equilibrium background conditions [78] and to the summarizing books and articles [10, 11, 17, 19, 33, 46, 49–52, 56–58].

Two books provide a broader view on thermal analysis: the underlying bibliographical book by Wunderlich [87] (1930–2012, citation response >17,000, H-index >70) thoroughly chronicles it, while Sestak's memoirs [88], present thermal analysis as an widespread themes connected to econophysics, environment, interdisciplinary science and even philosophy (see Fig. 6), showing also author´s accomplishment in art photography.

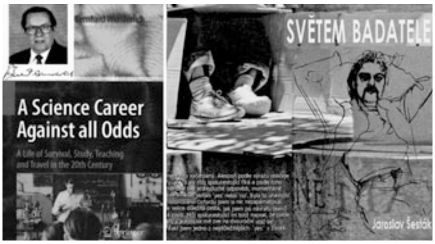
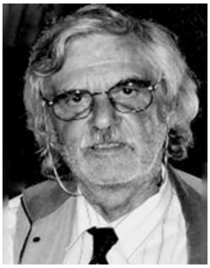


Fig. 6 Book covers of recent biographical publications related to thermal analysis

It is worth noting that the previous two books [89, 90] in this series “Hot topics of thermal analysis” [53] (Vols. 8 and 9) reached a high popularity; they were ranked by Springer among the 20 best downloaded and cited publications. We are convinced that this third continuation, Volume 11, will perform equally nicely.

Prague, Czech Republic/La Habra, USA
May 2016



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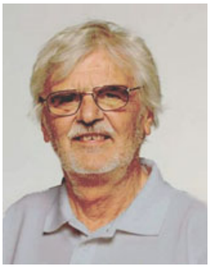

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