CZECHOSLOVAK FOOTPRINTS IN THE DEVELOPMENT OF METHODS OF THERMOMETRY, CALORIMETRY AND THERMAL ANALYSIS

A tribute to professor Vladimir Šatava, DrSc, a mastermind of theoretical basis of thermal analysis, who celebrates his 90th birthday dedicating also the 55th anniversary since he becomes the Editor of the journal Ceramics-Silikáty

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A short history on the development of thermometric methods are reviewed accentuating the role of Rudolf Bárta in underpinning special thermoanalytical conferences and new journal Silikáty in fifties as well as Vladimir Šatava mentioning his duty in the creation of the Czech school on thermoanalytical kinetics. This review surveys the innovative papers dealing with thermal analysis and the related fields (e.g. calorimetry, kinetics) which have been published by noteworthy postwar Czechoslovak scholars and scientists and by their disciples in 1950-1980. Itemized 227 references with titles show rich scientific productivity revealing that many of them were ahead of time even at international connotation.

Historical roots of thermal sciences
- from thermoscopy to thermal analysis

One of the first modern-times considerations of heat and cold can be found in the treatise published in 1563 by B. Telesio. At the end of the 16th century the first air thermoscope appeared (G. Galileo about 1597) and in 1626 the word „thermometer“ was for the first time used to describe thermoscope equipped with scale with eight degrees (Leurechon in book “La Recreation Mathematique”). Shortly after, the world-known Czech educator J. A. Comenius inserted reflections on the role of heat and cold in nature into his work „Physicae Synopsis“ (1633) and then, in 1659, published another worth noting book „Disquisitiones de Caloris Frigoris et Natura.“ The first quantitative thermal law expressing the dependence of temperature of a cooling body (expressed in the scale of 8 degrees) on the time was published by J. Newton in 1701.

Meanwhile, other scientists had invented various types of the dilatation thermometers and had proposed various temperature scales. Romer (1701) had filled glass tube of thermometer with red wine and proposed a 60-degree scale. Fahrenheit (1724) proposed a temperature scale of 100 degrees from 0°F at the temperature of mixture of ammonium chloride, water and ice and 100°F at the human body temperature. Reaumur (1731) introduced the temperature scale with 80 degrees between 0°Re at water melting point and 80°Re at boiling point of water. A year later Delisle introduced an exotic scale with 240 degrees, which was later (1738) modified and adjusted to 150°D corresponding to the melting point of water and to 0°D at boiling point of water (240°D = -60°C), and this scale was being used in Russia for the whole hundred years. Only then Celsius (1742) came with its 100-degree scale (between the melting 100 and boiling 0 points of water, later switched to nowadays 0-100 by Linné).

The crucial experimental studies, thanks to which temperature became a clearly measurable physical quantity, was executed by Regnault in the 1840th, that is long after the Black (1761) distinguished between the specific heat (heat capacity) and the latent heat, Laplace and Lavoisier (1786) performed their first calorimetric measurements. In 1822 Fourier published his laws of heat transfer. Yet after detailed results of Regnault’s dilatometric and heat capacity measurements (1842), together with Carnot’s theorem (1824) and its consequent interpretation by Clapeyron (1834) - the basis was formed for the introducing of absolute temperature scale by W. Thomson (Kelvin 1848) and for the inception of thermodynamics as a new science.
The first noted use of thermometry as a method of thermal analysis took place in Uppsala in 1829 where F. Rudberg (1800-1839) recorded inverse cooling-rate data for various alloys. [1,2]. In 1883, H. L. Le Chatelier (1850-1936) adopted a somehow more fruitful approach plotting the time vs. temperature curves easily convertible to the relation of sample temperature vs. environmental temperature.

Several years later Le Chatelier (1887) had used Pt/PtRh thermocouple and he termed it as “thermoelectric pyrometer”. Later with his assistant A. Stanfield published in 1899 heating curves for gold, which almost stumbled upon the idea of DTA (“Differential Thermal Analysis”). They improved the sensitivity by maintaining the thermocouple ‘cold’ junction at a constant temperature and by measuring the differences between two high temperatures [4]. Among other well-known inventors was Russian N. S. Kurnakov (1860-1941) improving registration of his pyrometer by the photographic continuously recording drum [5]. The term “thermal analysis” was coined by G. H. J. Tammann (1861-1938) [6] around the year 1904 demonstrating the significance of cooling curves in phase-equilibrium studies of binary systems.

The first Czech university textbook on the physics of heat was “Thermika” by Č. Strouhal (1850-1922) published in 1908 [7] maintaining its informative value until today’s. The historical development and practical use of DTA in the territory of former Czechoslovakia [1, 2, 8] was linked with the names J. Burian (1873-1942), O. Kallauner (1886-1972) and J. Matějka (1892-1960) who introduced thermal analysis as the novel technique during the period of the so called “rational analysis” of ceramic raw materials [9] in order to investigate behavior of kaolinite [10, 11] at heating.

Worth a special attention is an original development of weight measurements that is connected with the name S. Škramovský (1901-1983), who, at the Charles University, investigated thermal decomposition of complex oxalates which led him in 1932 to his own construction of an apparatus named “stathmograph” (from Greek “stathmos” = mass, weight) [12] that made it possible to measure mass changes. Independently (twenty years later), C. Duval used for his way of weight measurements the Latin-based term “thermogravimetry” that later became generally accepted in thermal analysis [13]. As the principle scheme of the stathmograph instrument is not generally known, it is perhaps worth mentioning to describe this early arrangement. Škramovský placed a weighted sample into the drying oven on a dish suspended on a long filament passing through a hole in its upper wall (forming the balance case) and hooked to an arm of an analytical balance. A mirror attached to the beam was reflecting the image of sligt slit into a slowly rotating drum lined with photosensitive paper. The unwanted vibration was reduced by an attached glass rod immersed into paraffin oil and temperature was registered automatically by means of a mercury thermometer provided by platinum contacts distributed along the whole length of capillary.

In the first years after World War II the other monographs appeared in the world literature (besides that by Duval [13]), which were devoted to microcalorimetry [14] and thermal analysis [15, 16] and an initial paper dealing with theory of DTA [17] was also published. At the end of 1950th a commercial device combining DTA and TG appeared under the name “Derivatograph” [18] for long providing a useful service to the Eastern scientists.

Much credit for the further development of modern thermal analysis was attributed with Rudolf Bárt a (1897-1985) who stimulated thermal analysis activity at his fellow workers (V. Šatava, S. Procházka, J. Vašíček, M. Čáp or I. Proks) at the Institute of Chemical Technology Prague (abbreviated as VŠChT) [19, 20, 21, 22]. Bárt a organized premature thermoanalytical meetings, the earliest was “the 1st Conference on DTA” (Prague 1956), the 2nd (Prague 1958) and the 3rd Conference on Thermography (Prague 1961) followed by the 4th Conference on DTA (Bratislava 1966). His friend R. C. Mackenzie (1920-2000) [23, 24] from Scotland was an invited guest at the 1961 meeting who was also one of the pioneers of applied DTA [23, 24]. Upon the previous communication with Russian L.G. Berg, Americans P. D. Garn and C. B. Murphy as well as Hungarian L. Erdey an idea for the creation an international society ICTA was cultivated and realized during the first international thermoanalytical conference in London 1965 [24] (where one of the authors also participated as invited speaker). It aimed to enabling easier contacts between national sciences, particularly across the separating “iron curtain”, which in that intricate time politically divided the East and West Europe.

Besides significance of the early Czech-written books on thermal science [7, 26], which appeared before and/or simultaneously with the credited international literature [8, 22] the indispensable figure in the Czechoslovak development of thermal analysis was undoubtedly Vladimír Šatava (*1922) [27-31]. He brought to the Czech scientific circles necessary theoretical basis on solid-state chemistry and physics [29, 30], pioneered methods of thermal analysis [18, 19, 27, 26], educating his students who thus followed his professional guidance and published esteemed books [27-33] completing thus the rich spectrum of Czech thermoanalytical literature [31-38], cf. Fig. 1. The individual contributions and innovative approaches have been affluent and focal which is worth of a more detailed portrayal, as exposed in the next paragraph, especially accentuating Czechoslovak source journals. Unfortunately, most of these rather cru-
cial papers disappeared in the shadows of time due to the Czech written texts. Only consequently a supply role started playing the novel thermoanalytical journals, Thermochimica Acta, which was cofounded by one of the authors back in the year 1970 as well as Journal of Thermal Analysis instigated by R. Bárt in 1969.

Less known book by J. A. Komenský “Investigation of the nature of heat and cold.” (Amsterodam 1659) in which the predicament of heat and cold is well discussed; “Thermics” by Č. Strouhal (1908) was an unique book describing the early but elementary treaties on heat, the almost unknown book on DTA (1957) was published ahead of time, basic book of solid-state chemistry and material thermal behavior was also published (1965) beforehand of international literature (unfortunately never translated). Far right is the Russian translation of Czech original book on theoretical basis of thermal analysis (1988), which became curiously a scientific bestseller as whole 2000 issues were sold in the former USSR within one week.

Methodical footpath identifiable on the territory of former Czechoslovakia

The greatest promotion of thermoanalytical methods came after fifties when the methodical bases were formed [39] and new techniques specified. In this period various Czechoslovak scientists played an important role as it is documented in the achievement book [40] and citation records [41]. Below listed papers relating the field of TA promoted in the former Czechoslovakia are assorted into several (but not very strict) categories. The referenced papers are supplied by original titles (given in English) and they are chronologically ordered within individual categories. All references were checked and corrected according to database WoS (Web of Science).

The first category „TA generally” consists of articles [42-57] deals mostly with thermal analysis in a general way including papers published mainly in Czech journals Silikáty and Chemické listy, and in Slovak journal Chemické Zvesti.

The second category “Special methods of TA” is devoted to original principles and unique techniques developed and put into operation by Czechoslovak scientists. The articles described e.g. dielectric TA [58], thermogravimetry [59, 60, 63], accelerated TA [62], permeability TA [65], photometric TA [66], period TA [68] (becoming a forerunner of today’s temperature modulated methods of TA), differential hydrothermal analysis [70] and [71, 74], quick TA [78], thermoelectrometry [79, 80], decrepitating TA [82] and themomagnetometry [83]. A distinctive consideration should be allocated to the characterization of radioactive measurement called emanation thermal analysis (ETA) which is connected mainly with authors V. Jesenák [64], V. Balek [67, 75, 76] and J. Tölgyessy [81].

An explicit part of the papers was devoted to the description of own constructions of apparatuses for TA measurement as a consequence of at that time existing inaccessibility of commercial TA instruments. This type of articles is included into category Apparatuses of TA [84-101]. Early instruments as were opportunely produced by laboratory groundwork, such as DTA belong into this category. The production way of latterly produced TG apparatuses was paved by the development of a Czech thermogravimetric instrument named “TEGRA” and constructed by A. Blažek [37, 87]. Early instruments were opportunely produced by laboratory groundwork, such as DTA [84, 86, 91, 97].

A rich sphere of Czechoslovak research was also formed by calorimetric contributions [103-127] registered in category Calorimetry. Worth accentuating is an initial classification of calorimeters according to the temperature difference between the sample-block $T_B$ and surrounding jacket $T_J$ as early suggested by J. Velíšek [117].

Consequent category Theory of DTA/DCS is associated with a gradual development of theoretical basis of thermal measurements mostly focused on the DTA [128-140] curiously noting early the associated effect of gradients [129, 130]. It involved problems of

Figure 1. Some favored book related to the topic of thermal science
calibration and standardization of temperature and heat measurements by employing solid solution [135, 140], application of heat pulses [134], conductivity issues [138] as well as a detailed analysis of the complex composition of a DTA peak including the effect of heat inertia [135, 137]. One of the frequently cited and widely applied treaties was the Hrubý glassforming coefficient [133] based on the DTA determination of characteristic temperatures during glass crystallization (inquisitively becoming the best cited paper in the history of Journal Czechoslovak Physicists with 372 citations). Such achievements were only possible by the impact of prosperous Czechoslovak school on thermodynamics [27-34]. The other corresponding papers [141-162] are included into category *Thermodynamics and phase equilibria*.

Another special attention is paid to the studies on reaction dynamics which topic is included into the category *Kinetics* [163-199]. Early kinetic studies were explicitly offered by studies of V. Šatava whose kinetic evaluation method [175] have been broadly exploited and quoted by international resources (several hundreds of citations) and frequently named as the “Šatava kinetic method” [31, 34, 35, 174, 183]. Such a popularity of theoretical works aimed to elucidate predicaments of reaction kinetics [34, 35, 183] became the heart of the so-called Czech school of nonisothermal kinetics recently continued both in Czech [195-198] and Slovak republic [190, 191, 199]. Worth noting is the first ever published algorithm for the computer calculation of kinetic data [171] and the review paper [170] which despite the Czech language became the best cited article in the journal history. In feedback stance the papers [177, 179] undertook abundant citation responses becoming thus the best cited papers in relevant journals (562 and 132 respectively) and bringing into literature the notations named in the international literature after the authors (i.e., the Šesták-Berggren [178] as well as the Holba-Šesták [180] kinetic equations). Not less important have been the contributions by recently deceased *Ivo Proks* (1926-2011), who factually paved the way to the development of methods using the modulated temperature modes [68], early accounting on temperature gradients and measurement accuracy [129, 132], improved solution calorimetry [104, 113, 118] thus significantly contributing the elementary attributes of thermochemistry and thermodynamics. Worth mentioning are also his imperative studies on historical root of thermodynamics [8, 220, 222, 224, 225] as well as the work by *J. Brandštejn* [93, 100, 108, 115, 120, 125] in the field of titrimetry.

Not less important were also the related articles about mechanic properties (which was one of favored of the Šatava’s research topics [208, 217]), diffusion studies [203-212] and early measurements of electrical and heat conductivity [202, 214-217] inserted into category *Mechanical and transport properties* [200-216]. The last category of Czechoslovak papers dealing with TA is labeled as *History and nomenclature*. It contains reviews of historical aspects of thermometry and thermodynamics [221-227] and associated nomenclature issues [219, 220].

**CONCLUSIONS**

The Czech researches have richly contributed to thermal science and it would be a misfortune to allow their input to slip into oblivion. Clearly, one of the most important moments in the development of modern thermal analysis was the establishment of the journal *Ceramics-Silikáty*, launching 1956 by Rudolf Bára. Vladimír Šatava was its chief editor within the years 1957-1967. This period was also credited with creating the foundations of thermal analysis and physical chemistry in general [29-31]. Šatava inspired his students and coworkers, cf. photo, by continuously broaden his own scientific interest in elucidating solid-state reactions which subsequently flourished into publication of various thermoanalytical books [34-39]. Equally important was the introduction of various novel thermoanalytical methods [58-83] which preceded the international know how, e.g. the emanation thermal analysis [50, 64, 67, 75, 76, 99] that has become the source of a commercially produced instrument. Specially the Czech contribution to the DTA technique [62, 71, 84-86, 91, 96, 97, 128, 131, 133, 136, 137] deserves a distinctive attention, the Czech written book published in 1957 [26] preceded international publications and was later followed by well cited Czechoslovak books [31-38]. Solid grounds of DTA were accomplished in 1976 by the consistent theory made up by Holba and Šesták and published in Ceramics-Silikáty [135, 136]. Fundamental contributions already appeared in the first issues of the journal *Silikáty*. Unfortunately, they did not get into a wider attention of international public due to the Czech language,. Nevertheless the Czech journal...
Ceramics-Silikáty as well as its sister’s Chemické Listy and Czechoslovak Journal of Physics has remained important domestic as well as international sources and platform of many original ideas and we should be thankful to the effort of their originators as well as their current editors.

References

4. Stanfield A.: On some improvements in the Roberts-Austen rendering pyrometer, with notes on thermo-electric pyrometry; Phil. Mag. 46, 59 (1898).
7. Strouhal Č.: Thermika; JCMF, Praha 1908.
10. Matějka J.: Chemical changes of kaolinite on firing; Chemické listy 13, 164 (1919); and 182 (1919).
12. Škramkovský S.: Apparatus for automatic registration of dehydration at rising temperature; Chemické listy 26, 521 (1932).
20. Šatava V.: Significance of DTA in the industry of cements; Stavivo 31, 15 (1953).
27. Šatava V.: Documentation on thermal analysis; Silikáty 1, 240 (1957).
29. Šatava V.: Úvod do fyzikální chemie silikátů; (Introduction to Physical Chemistry of Silicates), SNTL, Praha 1965.
41. Šesták J.: Citation records and some forgotten anniversaries in thermal analysis; J. Thermal Anal. Calor. in print 2012 (DOI:10.1007/s10973-011-1625-3).

TA generally

42. Šatava V.: Temperature regulators for thermography; Silikáty 1, 204 (1957).


Special methods of TA


59. Šatava V.: Simple registration thermobalance; Silikáty 1, 188 (1957).


61. Šatava V., Stránský K.: Gradient furnace with defined atmospheres; Silikáty 3, 343 (1959).


70. Vepřek O., Rykl D., Šatava V.: The study of hydrothermal processes by the DTA method; Thermochim Acta 12, 7 (1974).


72. Šatava V., Vepřek O.: Effect of the sample thermal conductivity on the calibration constant in DTA; Thermochim Acta 17, 252 (1976).


Apparatuses of TA

84. Sokol L.: Automatic apparatus for DTA; Silikáty 1, 177 (1957).

85. Šatava V., Troušil Z.: Simple construction of apparatuses for automatic DTA; Silikáty 4, 272 (1960).


90. Malinger M., Brandstett J.: Use of Czechoslovak ther-

Calorimetry
111. Pekárek V.: Possibilities and present state of calorimetric experiments; Chem. Listy 69, 785 (1975).

Theory of DTA/DCS
128. Štava V.: Differential thermal analysis; Silikáty 1, 207 (1957).
129. Proks I.: Influence of rate of temperature increase on the quantities important for the evaluation of DTA curves; Silikáty 5, 114 (1961).
130. Šesták J.: Temperature effects influencing kinetic data accuracy obtained by thermographic measurements under constant heating; Silikáty 7, 125 (1963).
Mechanical and transport properties


218. Šatava V.: Strength and microstructure of cast gypsum; Ceramics-Silikáty 40, 72 (1996).

History and nomenclature


221. Hlaváč J.: The present state and perspective view of the material research; Silikáty 29, 169 (1985).


227. Proks I.: Celok je jednodušší ako jeho časti; (Whole is simpler than its parts), Publ. House of Slovak Academy of Sciences, Bratislava 2012.