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FOURTY YEARS OF THERMAL ANALYSIS IN HUNGARY

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Abstract

A brief survey is presented of the development of thermoanalytical methods, in Hungary and abroad between 1900 and 1990, and reveals a connection between the processes.

An overall picture is given of the activity of Hungarian thermoanalysts in basic research, the development of instruments and organizational work in science between 1950 and 1990.

Keywords: activity of Hungarian thermoanalysts, history, TA equipments

Introduction

In thermal analysis, as in any other natural science, the basis of knowledge is experimentation, a precondition of which, in turn, is the availability of a suitable instrument. Thus, the development of any particular branch of science and the industrial production of measuring instruments are very strictly correlated.

Thermoanalytical methods before 1960

A convincing example of the above-mentioned correlation is provided by the history of the development of differential thermal analysis (DTA), as studied in its international aspects [1–5]. This method was first elaborated by Roberts Austen in 1899. The signal-producing system of his instrument (an oppositely connected pair of thermocouples) is so simple that it has been used unchanged ever since. Although a DTA device could have been produced under laboratory conditions as well, half a century passed before the method came into general use. The general spreading of the method coincided with the appearance of the first industrial instrument (Eberbach Corp., USA, 1945). Soon, competing firms also showed up on the market. The result was an unbelievable increase in the number of publications, as curve 1 in Fig. 1 shows. This coincidence suggests a relationship between the spreading of a method and the appearance of an industrially produced instrument suitable for performance of the necessary experiments.

However, the question arises of why the increase in the number of publications dealing with thermogravimetry (TG) did not occur until 1960, as evi-

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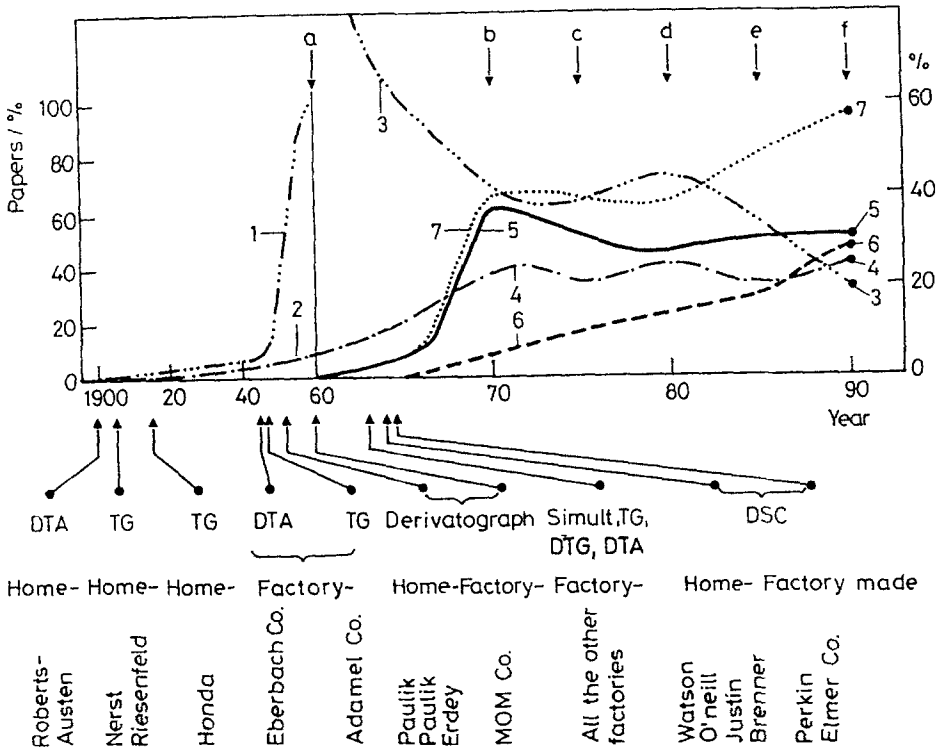

Fig. 1 The curves are destined to show, how the number of publications changed with time, in which researchers used traditional DTA method (curve 1), DTA or DSC techniques (curve 3), thermobalances (curves 2 and 4), derivatograph (a simultaneous TG, DTG, DTA instrument produced in Hungary by MOM, Hungarian Optical Works) (curve 5) or any other simultaneous TG, DTG, DTA instrument working on the principle of the derivatograph traded by different foreign firms (curve 6). Curve 7 is the sum of curves 5 and 6.

The statistics, resulting in curves 1–7 were prepared as follows: The number of papers, in which the instrument in question was applied and published in the given year (point a.: in book [1], points b–f.: in journals of TCA and JTA, further on in proceedings of different conferences, e.g.: 4th, 6th, 8th ICTA Conference) was taken as 100%

denced by curve 2 in Fig. 1. The literature data [6] reveals that, between the time of the evolution of the theoretical principles of the TG method (Nernst and Riesenfeld (1905), Honda (1915)) and the appearance of the first industrially produced thermobalance (Adamel Soc., (1945)), i.e. a span of 40 years, the users of this measuring technique constructed and built 'home-made' thermobalances operating on about 50 different principles (spring, torsion, chain, wedge, zero-type, etc.) [4–8], while 10 different industrial balances were marketed between 1945 and 1960, but in the meantime, the number of publications

showed hardly any increase (curve 2 in Fig. 1). We may ask what helps a measuring technique to spread. It seems that the start of industrial production is only a necessary, but not sufficient condition.

Figure 1 needs some further explanation. The curves show how the changes in time of the numbers of publications in which researchers used the traditional DTA method (curve 1), DTA or DSC techniques (curve 3), thermobalances (curves 2 and 4), the derivatograph (a simultaneous TG, DTG, DTA instrument produced in Hungary by MOM, Hungarian Optical Works) (curve 5) or any other simultaneous TG, DTG, DTA instrument working on the principle of the derivatograph, but marketed by different foreign firms (curve 6). Curve 7 is the sum of curves 5 and 6. For didactic purposes, the curves were recorded on different time-scales before (curves 1 and 2) and after (curves 3 and 4) 1960.

A reliable source [1] reports that a total of 3365 publications dealing with thermal analysis appeared up to 1960. In 1960 alone (Fig. 1, point *a*), the number of publications was 345. The number of previous publications is given as a percentage of this maximum value (curves 1 and 2).

Though the results of thermoanalytical work performed after 1960 can be readily followed at the international level in Thermal Analytical Abstracts (TAA) [9] and from statistics prepared on its basis [10], Analytical Chemistry, Thermochimica Acta (TCA), the Journal of Thermal Analysis (JTA) and various monographs [1–7] and reviews [8, 10–12, 31], as concerns the present paper they do not provide any support. The statistics resulting in curves 3–7 were prepared so that the number of papers published in the proceedings of conferences and in TCA and JTA in the given year (points *b–f* in Fig. 1) in which the instrument in question was applied for the experimentation was taken as 100%. This method of data collection, of course, is only of limited accuracy, and its reliability is based on the assumption that the numerical distribution of the papers not taken into account is similar to that of those chosen as model.

Thermal analytical methods after 1960

From an international aspect, an era of the history of thermal analysis came to an end in 1960. Until then, thermal analysts had used virtually either only DTA, or only TG in their researches; and parallel to use of the two techniques was very rare, and occurred only at the end of this period.

Around 1960, at the same time as the introduction of the simultaneous measuring principle, a revolutionary change took place in thermal analysis [11]. Some thermal analysts became followers of the simultaneous measuring techniques, while others, seeing the advantages of this new trend, started to apply DTA (or DSC) and TG instruments in parallel. They did not guess, or tacitly ignored the fact that curves recorded under different experimental conditions on

different instruments could show a phase shift, which could make their interpretation and explanation extremely difficult. This fault was also unwillingly accepted by those who wanted to supplement the picture obtained by DTA or TG investigations with the results of other studies (X-ray diffraction, infrared spectroscopy, thermal dilatation, microscopy, etc.). At present, it is exceptional for far-reaching conclusions to be drawn from DTA (or DSC) or TG curves alone. In this respect, curves 1, 2 and 3, 4 in Fig. 1 differ from each other.

The course of curve 5 in Fig. 1 proves that the number of publications describing results achieved through use of the derivatograph increased significantly not after the elaboration of the method (1954), but after the introduction of the industrial instrument (1960), and this, as refletced by curve 1, in a jumpwise manner.

Subsequently, with a slight lag, instruments produced by different foreign firms which involved the use of simultaneous TG, DTA and DTG techniques, but basically adapting the measuring principles of the derivatograph, also started to spread (curve 6). However, in strange way, this latter curve never rose above curve 5 [12].

A comparison of the course of the sum of curves 5 and 6 (curve 7) with those of curves 3 and 4 demonstrates that the simultaneous measuring techniques mainly gained ground at the expense of the DTA method. This seems unfounded, since the first DSC instrument appeared in 1965. The introduction of this measuring technique undoubtedly meant the renaissance of the related DTA method. This is proven by the distribution of the number of papers. Between 1975 and 1986 this ratio changed from 2:1 to 1:2 (DTA:DSC), and the later shift continued in the same direction.

Thus, the years after 1960 were characterized by a competition between different thermal analytical methods.

The Hungarian simultaneous TG, DTA, DTG instrument: the derivatograph

At the Department of General and Analytical Chemistry at the Technical University in Budapest, thermal analytical research was started in 1951. At that time, Professor László Erdey of the Department began writing a text-book on the methods of gravimetric analysis [13], in which he intended to publish the thermoanalytical curves of analytical precipitates. The purchase of an instrument from abroad was out of the question, due to financial difficulties. Therefore, in 1954, Jenő Paulik, together with the author, constructed the first 'home-made' simultaneous TG, DTA, DTG instrument, the derivatograph, based on a common analytical balance [14]. This 'home-made' instrument is

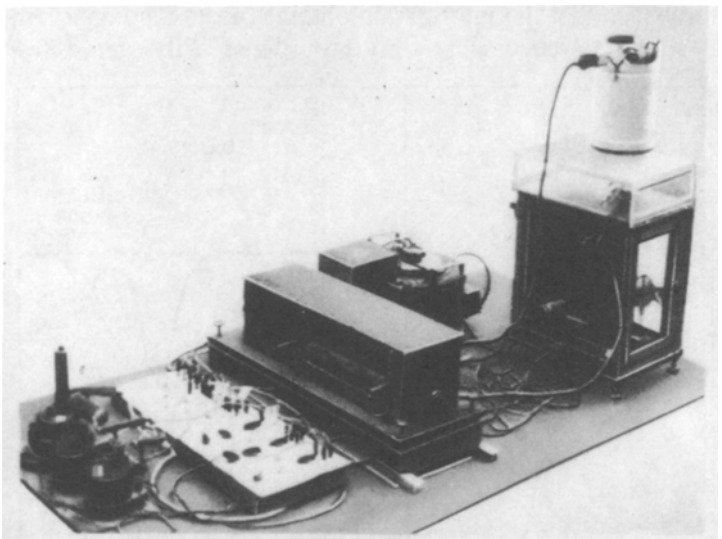

Photo 1 Home made derivatograph [14]. Museum in Várpalota, Hungary

now exhibited in the Museum for Chemistry in Várpalota. It is depicted in Photo 1.*

It had earlier been observed that the TG curve of a complex sample, such as that of bauxite, cannot provide much information concerning the qualitative composition of the sample (Fig. 2.1). From theoretical considerations [11, 14, 15, 18, 19] the authors were convinced that the derivative of the TG curve (the DTG curve) would exhibit increased resolution (Fig. 2.2). An additional advantage is that it created a basis for the comparison of TG and DTA curves (Fig. 2.3).

Thus, a deriving instrument was constructed which consisted of a permanent magnet and coils moving together with the arm of the balance [5, 11, 14, 15, 18, 19], and this became a very important element of the derivatograph.

It also turned out during the research work that the information originating from several simultaneous measurements was much more than the simple sum of the individual data. This is convincingly illustrated in Fig. 2, which relates to the possibility of assaying ad determining the composition of a bauxite sample. From the TG curve alone, not even the qualitative composition of the sample can be determined (Fig. 2.1), whereas a simultaneous TG, DTA, DTG, EGA study (Fig. 2.4) allows quantification of the individual mineral components [11, 12].

* Author is indebted to Dr. I. Kováts, director of the Várpalota Museum, for Photo 1.

It is readily seen that the information obtained from a comparison of different thermal analytical curves can only be utilized if the curves were in fact

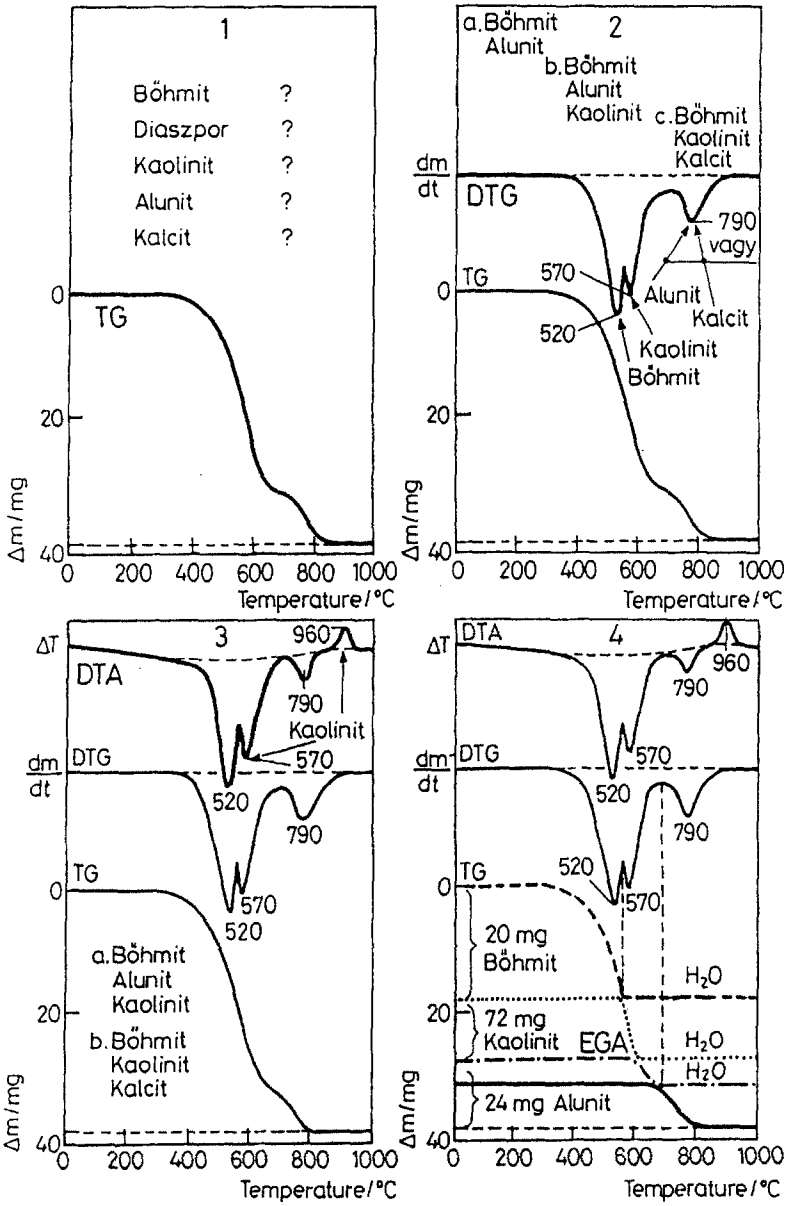

Fig. 2 Improvement in the reliability of the detection and accuracy of the determination with the increase of simultaneous methods (TG, DTG, DTA, EGA) applied in the case of the examination of mineral components in bauxite

recorded simultaneously, on one and the same sample. Curves recorded on different instruments are shifted in phase because of the different experimental conditions [11, 18, 19].

These three measuring technique principles co-exist in the first simultaneous TG, DTG, DTA instrument, the derivatograph [5, 11, 14–22], whose successful career (Fig. 1, curve 5) is based on the recognition and industrial realization of the above three principles.

For an accurate description of the mode of investigation, expressions such as 'parallel', 'simultaneous', 'differential' or 'derivative' were introduced at that time, together with the abbreviations DTG, DTD, etc.

In 1961, the derivatograph was developed further by making it suitable for measuring the dilatation curve (TD) and its derivative (DTD), and also for the simultaneous measurement of weight and dilatation changes in the same sample [11, 15, 18, 19].

Five years later, an adapter was attached to the instrument [11, 15, 18, 19], enabling the user to couple the TG, DTG and DTA studies with simultaneous determination of the gaseous products liberated in thermal decomposition (SO_3, CO_2, CO, NH_3, Cl_2, etc.), by absorbing them quantitatively in an aqueous solution and titrating them selectively, automatically and continuously with a suitable standard solution. The method is called thermal gas titrimetry (TGT) (Fig. 2).

The elaboration of the technique for a quasi-isothermal, quasi-isobaric TG investigation (Q-TG) meant the introduction of an entirely new measuring principle. The essence of this method is a heating technique [20], which elevates the temperature of the oven not at a uniform rate, but, on the basis of a feed-back principle, regulated by the transformation itself. When a transformation starts, the regulation system automatically provides the temperature difference between the sample and the oven, ensuring that the studied transformation takes place at a strictly constant rate several orders of magnitudes smaller than under the usual conditions.

On the other hand, an essential part of the development was the 'labyrinth crucible', which ensures that equilibrium transformations always occur under a pure, self-generated atmosphere, i.e. at a partial pressure of 100 kPa of the evolving gaseous decomposition products [21].

Although these conditions do not fully satisfy the requirements of physical chemistry, they at least closely approach them. The fact that thermal analytical transformations can be described more satisfactorily by this method than by the traditional ones [16–22] can be judged on the basis of Fig. 3. This illustrates the TG and Q-TG curves of the decomposition of $Ni(NH_3)_6Cl_2$.

Under quasi-isothermal, quasi-isobaric conditions, thermal dilatation (Q-TD) [17–19], thermal gas titrimetric (Q-TGT) [17–19], DTA and DSC (Q-DTA, Q-DSC) [19] measurements can all be performed.

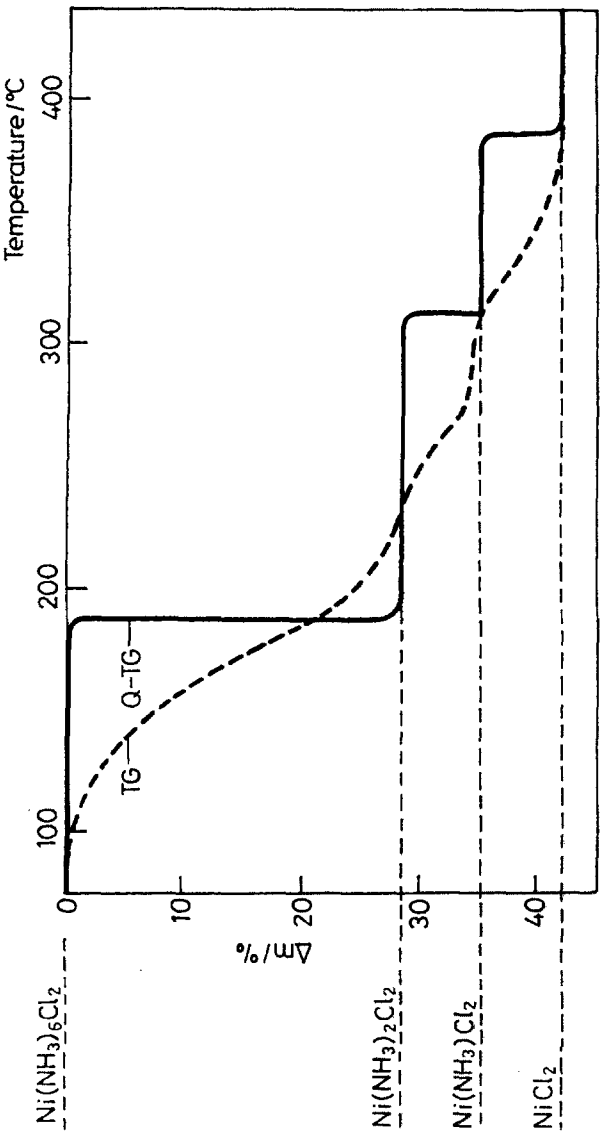

Fig. 3 Weight changes of $Ni(NH_3)_6Cl_2$ examined by using non-isothermal (TG) and quasi-isothermal (Q-TG) heating techniques

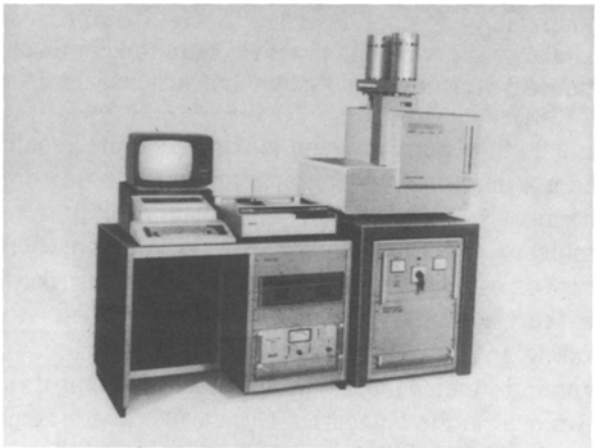

Photo 2 Derivatograph C [23]

The derivatograph was first produced industrially by the Gyengeáramú Műszeripari Szövetkezet (Electronic Instruments Cooperative, Budapest) in 1959, while its serial production was started by the Hungarian Optical Works (MOM) (Budapest) in 1962 (Fig. 1). The reason why the computer-assisted version of the derivatograph [22] appeared only in 1985 was the computer embargo against Hungary. This instrument is shown in Photo 2.

The Hungarian Optical Works is to be blamed for not producing follow-up options to the instrument, in spite of the existing market needs. Prototypes and experimental models were developed in several cases, and handed over to researchers for testing. They applied these models in their work with success for decades.

a – Device for the simultaneous measurement of mass change and dilatation [11, 15, 17–19].

b – Modification of the quasi-isothermal heating regulator for Q-DTA measurements [19].

c – Device for measuring changes in thermomagnetic properties [19].

d – Device for the continuous and selective measurement of water, carbon monoxide or carbon dioxide evolution (Kristóf and Inczédy [23, 24]).

e – Coupling of the derivatograph with a mass spectrometer produced in Hungary (Berecz, Bohátka, Langer and Szöőr [25]).

f – Detector for simultaneous determination of the flash-point (Simon and Androsits [26]).

Unfortunately, this unjustified hesitation was also characteristic of other firms. For example, Hungarian instrument-producing firms did not recognize

the advantages originating from the very early realization and production of the high-accuracy temperature control designed by Gál, Muráti and Sztatisz [27], which proved to be very successful in practice, or of the computer-assisted thermogravimetric–mass spectrometric system constructed in Hungary first by Székely and Till [28].

The development of the derivatograph took place at the Technical University in Budapest, where a small thermoanalytical group belonging organically to the Hungarian Academy of Sciences carried out research work. Its original task was to investigate problems of thermal analysis that were of theoretical and technical importance. However, when the researchers encountered tasks that were difficult to solve in the traditional way in the course of their work, they often succeeded in finding an appropriate instrumental solution. In such cases, they built a test specimen in their laboratory, controlled its appropriate functioning and then handed it over to the Hungarian Optical Works for adaption and fabrication. For example, the first 'home-made' computer-assisted version of the derivatograph shown in Photo 2 was constructed [22] under laboratory circumstances by the same research group. Its system project was designed by J. Paulik and the author, and the software was written by M. Arnold, L. Domokos, P. Somogyvári and G. Veress.

The fact that the derivatograph was developed in two different types of background proved a fortunate one, since the interests of science and industry generally differ. Our science was stimulated by a desire for a better knowledge of thermal processes, i.e. by the development of instruments with better resolution and selectivity, while industry is mainly interested in the reduction of costs and magnification of the profit. However, experience shows that these different interests are not always irreconcilable.

About 4000 derivatographs were produced and exported by the Hungarian Optical Works in the period 1962–1990. Some 200 instruments were sold in Hungary. It is characteristic of this large number of derivatographs that research results achieved with a derivatograph are reviewed in 3200 publications [19]. The number of papers to which access is difficult due to their publication in less common languages and journals may be roughly the same.

Activity of Hungarian thermoanalysts during the past 40 years

It is worth mentioning that many Hungarian researchers applied DTA (J. Erdélyi, G. Grasselly, J. Grofcsik, V. Koblencz, K. Nagy, E. Nemecz, K. Sasvári, I. Székely, T. Takács and Á. Zalai) and TG (T. Damokos, A. Hegedűs and M. Weltner) as early as around 1950 [3, 5]. The instrument-constructing and method-developing activities of Földváry-Vogel and Kliburszki deserve particular attention [29], as does the atlas compiled by Földváry-Vogel [3], which presents the DTA curves of about 250 minerals in a systematic way, together with their interpretation, based in part on work by Hungarian scientists.

Hungarian researchers utilized the advantages of the Hungarian instrument, and very lively scientific activity started when the derivatograph appeared on the market.

The Hungarian institutions (university departments, academic and technical research institutes and chemical industry research laboratories [30] that have carried out significant research activity in thermal analysis number about 80. Like the diagram in Fig. 1, this number is based on a statistical calculation from the number of papers published between 1960 and 1990.

A publication list (500 papers) prepared on the basis of a survey by the Analytical Committee of the Hungarian Academy of Sciences [31] characterizes the individual scientific activity of Hungarian thermoanalysts in the period 1980–1990.

As concerns the position of Hungarian thermoanalytical research in Hungarian research work in general, a survey by the Information Board of the Hungarian Academy of Sciences provides an answer [32]. This Board investigated which papers of Hungarian authors performing basic chemical research are cited most frequently in international scientific journals (from all the papers published from Hungarian universities, academic and industrial research institutes in the period 1980–1990). This survey was made on the database of the Science Citation Index of the Philadelphia Institute of Scientific Information. The Table published in this survey lists 18 papers, of which 3 are on thermoanalytical subjects, occupying the third [33], ninth [34], and twelfth [17] places.

Hungarian thermoanalysts also exerted useful activity in the field of science organization.

The Hungarian Chemical Society in 1967, and the Analytical Section of the Hungarian Academy of Sciences in 1973, felt the necessity to form their own specialized thermoanalytical groups. Both groups adequately fulfilled their assignment. They organized conferences and courses connected with laboratory practice (with international participation), and also regular national lecture sessions in cooperation with each other. They carefully cultivated links with related international organizations, and coordinated national research work by means of visits to and discussions at different institutions.

Numerous thermoanalysts have contributed to the work of The Council of the International Confederation of Thermal Analysis (ICTA) and the European Society of Thermal Analysis and Calorimetry (ESTAC) councillors. Others have participated in their special committees (standardization, nomenclature and publication committees) for decades [35, 36].

An important event occurred in the history of Hungarian thermal analysis when in 1974 the ICTA approved the organization of the 4th ICTA Conference in Budapest. This Conference was attended by 650 participants with 150 accompanying persons from 30 countries, and 277 lectures were presented, 53 of

them by Hungarian authors [37]. At that time of international political division, Hungary played the special role of a bridge between scientists from West and East. Scientists from Western and Eastern Europe wanted to become personally acquainted with each other, independently of politics, and it seemed appropriate to meet half-way, in order to overcome travel restrictions.

A number of Hungarian scientists have also taken part in the editorial work of the Journal of Thermal Analysis, Thermochimica Acta and Thermal Analytical Abstracts.

Orientation in a scientific field is greatly promoted by surveys of earlier results. The 'Atlas of Thermoanalytical Curves' published by Liptay fulfils this task [38]. This atlas contains the simultaneous TG, DTG, DTA curves of about 350 compounds, investigated by numerous Hungarian thermoanalysts.

The first international thermoanalytical journal, the Journal of Thermal Analysis, was founded by Hungarians, in 1969. The first Editors-in-Chief were É. Buzágh and J. Simon. For their pioneering work and exemplary editorial activity, they were awarded ICTA medals in 1988.

The activity of all Hungarian thermoanalysts was acknowledged by the North-American Thermoanalytical Society in 1974 through the award to J. Paulik and the author of the Mettler Award of the ICTA, and by the Russian Academy of Sciences when its Thermoanalytical Committee awarded them the Kurnakov Memorial Medal.

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