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THERMAL ANALYSIS FROM A NUMERICAL ASPECT

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This publication surveys the present state of thermal analysis from a numerical aspect. It deals with the applied methods and techniques, the substances studied, and the journals publishing papers on thermal analysis.

The question often arises of the present state of thermal analysis and the directions of development of thermoanalytical methods. Subjective opinions can not provide an exact answer, which must be based upon numerical data relating to a long period.

The results of a 3-year period have been surveyed in an earlier publication [1]. Wendlandt [2] reported data on the percentage distribution of the most frequently used methods, and analyzed the position of publishing in Thermochimica Acta [3].

In the present work a 6 year period is surveyed (1975–1980) as a function of the number of abstracts from Thermal Analysis Abstracts.

The number of publications reported in TAA for each year is shown in Fig. 1. (Unfortunately, the thermoanalytical publications appearing in the USSR are not included here.) The continuously growing number of abstracted papers speaks for itself. It can be supposed that more than these indicated papers on thermal analysis are published throughout the world, but that they are dispersed to such an extent in the various journals that they cannot be collected in an abstracting journal concentrating on methodology.

The numbers of publications given in the bibliographic columns of the Journal of Thermal Analysis in the years in question are shown in Fig. 2.

The numbers of publications issued in the different years are presented in Table 1. The sum of these publications is taken as 100%. The percentages of the methods with regard to each year and the 6-year period are shown in Table 1. It should be mentioned that only the more important methods are listed in Table 1. Furthermore, when several methods were used in a paper, then this particular paper features in each row in question.

It is seen from Table 1 that one of the oldest thermoanalytical method, thermogravimetry, continues to play an important part at present, with 18.9%.

DTA remains the most frequently used thermoanalytical method, with 20.1%. However, it seems to show a slight tendency to decrease. This may by connected with the fact that DSC has been increasingly used during the last 15 years (12.9%).

Table 1

Methodology	Year	1975	1976	1977	1978	1979	1980	Σ	%
	Number of publications	1827	1838	2069	2131	2321	2387	12.573	100
Thermogravimetry		10.4	22.7	18.7	18.2	19.0	23.4	2.381	18.9
Differential Thermal Analysis		21.1	22.5	21.6	18.7	19.0	18.7	2.532	20.1
Differential Scanning Calorimetry		11.7	13.4	10.9	11.8	13.3	15.9	1.627	12.9
Simultaneous TG—DTA		5.1	7.7	8.9	7.8	6.3	8.5	927	7.4
Dilatometry		4.8	5.7	5.6	3.3	4.7	5.2	618	4.9
Electrical measurements		10.7	10.4	11.8	8.6	7.1	8.0	1151	9.2
Thermomechanical measurements		4.6	4.1	5.3	5.4	6.7	6.0	683	5.4
Calorimetric methods other than DSC		8.1	7.0	6.1	5.6	8.2	6.3	864	6.9
Magnetic spectroscopy (NMR, ESR, Mössbauer)		2.6	4.0	5.3	6.6	3.2	3.8	538	4.3
Mass spectrometry		1.4	2.2	3.0	3.5	2.8	3.6	354	2.8
Isothermal techniques		13.4	20.0	16.7	18.0	13.2	8.2	1847	14.7
Magnetic measurements		2.8	4.8	5.7	5.2	5.5	3.6	582	4.6
X-ray, electron and neutron diffraction		2.9	3.3	5.1	5.2	5.5	5.8	598	4.8
Microscopic methods		1.9	4.4	4.0	3.4	4.0	3.1	438	3.5

A simultaneous combination of the two most important thermoanalytical methods (TG and DTA) was used in 7.4% of all the publications. This method also shows a tendency to rise, the reason for this probably being the spreading of simultaneously working instruments.

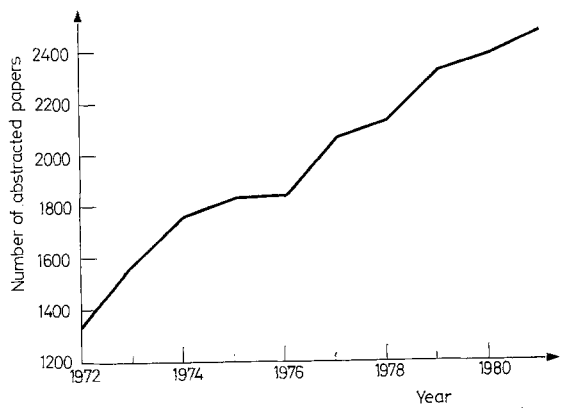

Fig. 1.

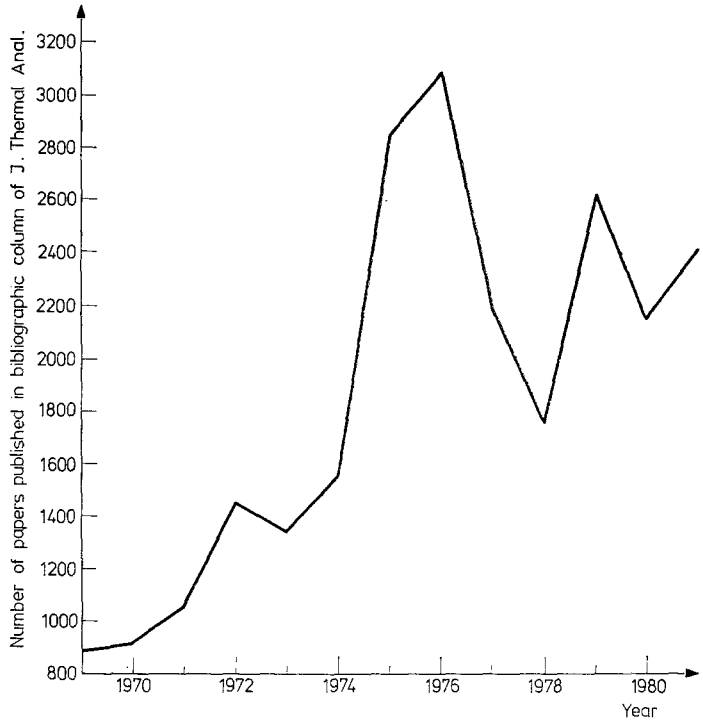

Fig. 2.

Dilatometry, which is used preferentially as a fairly routine method for studying clays, minerals, metals and their alloys, figures in 4.9% of the scientific publications.

There is a surprisingly high number of publications (9.2%) dealing with changes in electrical properties (conductivity, dielectric properties). This method has shown a tendency to decrease in recent years.

Publications based on the measurement of thermomechanical properties are showing a definite tendency to rise (5.4%). This is also explained by the spreading of adequate instruments.

A great number of publications (6.9%) deal with calorimetric data measured by methods other than DSC.

Magnetic spectroscopic methods were applied by thermoanalysts in 4.2% of the publications.

The application of mass-spectrometers to thermal analysis is showing a steady tendency to increase, amounting to 2.8% on average for the 6-year period. However, this is not a great number in absolute terms. These instruments are usually expensive, their price may be 5–10 times higher than that of a simple thermoanalytical instrument. Nevertheless, the rising trend indicates the growing significance of this method, since much new information is provided by simultaneous mass-spectrometry of the products of decomposition evolved.

The isothermal method is used widely (14.7%), mainly for the investigation of kinetic and technological problems.

Thermomagnetic properties are studied in 4.6% of the publications.

X-ray, electron and neutron diffraction measurements, which are supplementary methods in thermoanalytical studies, show definite tendencies to rise, and they amount to 4.8% of the publications.

Optical microscopy features in 3.5% of the papers, mainly as a supplementary method.

Methods other than those mentioned above, are also used in special cases, but their significance (at least when expressed as a percentage) is less appreciable.

Different techniques are presented in Table 2, according to the scheme described above. 6.3% of the publications are based on the measurement of dehydration and de-hydroxylation processes.

Investigations regarding heats of reactions account for 6.4% of the publications.

Kinetic measurements occupy a fairly outstanding position, with 14.0%. It seems, however, that decreasing attention is being paid to kinetic measurements in recent years.

Low-temperature measurements are somewhat surprisingly frequently used (12.5%). A considerable proportion of these measurements involve low-temperature specific heat determinations.

The phenomenon of melting is studied in 9.0% of the publications.

Table 2

Techniques	Year / Number of publications	1975 1827	1976 1838	1977 2069	1978 2131	1979 2321	1980 2387	Σ 12.573	% 100
Dehydration and dehydroxylation		5.5	7.2	6.9	5.3	7.4	6.2	789	6.3
Heat of reaction		6.3	6.4	5.2	6.7	8.2	5.3	801	6.4
Kinetics		13.1	14.5	14.5	16.2	13.5	12.6	1766	14.0
Low temperature		9.5	14.6	14.9	14.0	11.0	11.0	1567	12.5
Melting		7.0	7.7	8.3	8.9	8.7	12.2	1123	9.0
Phase diagram studies		9.9	7.8	7.7	8.2	10.0	7.0	1058	8.4
Pressure		4.2	2.8	4.2	3.9	2.5	4.5	466	3.7
Specific heat		3.1	2.6	2.7	1.6	1.8	3.2	310	2.5
Solid state reactions		3.9	3.1	3.1	2.7	3.1	1.7	362	2.9
Thermodynamic constants		7.8	8.3	7.9	9.4	10.0	8.4	1091	8.7
Very high temperatures (< 1500 °C)		2.6	1.1	1.9	1.4	0.6	2.8	217	1.7
Characterization studies		5.4	12.4	10.3	14.9	17.0	18.2	1682	13.4
Crystallisation and crystal structures		9.4	16.4	17.7	17.7	14.0	13.5	1863	15.0
Decomposition and degradation		14.0	18.8	18.3	18.4	18.7	19.9	2283	18.2
Glass transition		5.8	7.7	5.8	7.7	7.8	9.0	929	7.4
Phase transition		9.5	7.0	9.8	7.7	8.0	9.6	1085	8.6
Apparatus design or modifications		4.4	4.9	6.1	4.2	5.5	5.6	649	5.2

Thermoanalytical methods are used in 8.4% of the publications, to determine phase diagrams or certain of their details.

Measurements performed with pressure change are used in 3.7% of the papers.

2.9% of the publications deal with "solid-state reactions".

A surprisingly large number of publications (8.7%) use different methods in connection with the calculation of thermodynamic constants.

The high-temperature technique (the only measurements considered here are those beyond 1500°) amounts to 1.7% in Table 2. However, it should be mentioned here that this temperature region is of importance with only a small proportion of substances; further this technique involves numerous experimental and apparative difficulties. Nevertheless, its share of almost 2% may be considered to be significant, and the use of the method is essential for the solution of numerous technical problems.

Characteristic properties are used in many publications (13.4%) for thermoanalytical investigations.

15.0% of the publications are based on the study of crystal structure.

The most frequently investigated phenomenon is decomposition and degradation. This is quite natural, since the thermoanalytical interpretation of these phenomena provides scientists with a number of possibilities. These phenomena are studied in 18.2% of the publications.

The growing importance of the "glass transition" techniques is indicated by their share of 7.4% of the articles.

Phase transitions are studied in 8.6% of the publications. It should be mentioned however, that other supplementary methods are necessary in almost all cases in these studies.

5.2% of the publications deal with the description and construction, as well as with the modification of new instruments. The instrumental development is well indicated by this percentage, and it can be seen that specific new instruments are being constructed, modified and applied in appreciable numbers.

The distribution of the substances investigated in the publications is shown in Table 3.

It is clear that the greatest number of articles relate to inorganic chemicals (26%), these accounting for more than a quarter of all the publications.

The growing importance of the thermal analysis of polymers is indicated by the high percentage of these substances (20.7%).

Similarly, a large number of publications deal with the properties of organic compounds (11.1%). These latter two types of compounds have a significant role in the growing use of DSC. Differential scanning calorimetry provides a possibility for the more detailed study of polymers and organic compounds.

A surprisingly high number of papers deal with the thermal properties of complex compounds (6.9%). There are certainly greater possibilities in this topic, but scientists occupied with the chemistry of complex compounds do not make full use of the opportunities given by thermal analysis.

Minerals account for 6.6% of the thermoanalytical studies.

Table 3

Substances	Year	1975	1976	1977	1978	1979	1980	Σ	%
	Number of publications	1827	1838	2069	2131	2321	2387	12.573	100
Alloys		7.3	6.0	7.1	4.0	3.6	5.0	680	5.4
Catalysts		1.6	3.9	3.2	3.2	3.4	2.8	378	3.0
Ceramics		3.7	3.2	2.3	2.9	4.3	3.8	425	3.4
Clays		1.6	3.1	2.1	1.5	1.8	2.0	253	2.0
Glass		3.5	2.1	3.0	3.8	3.6	2.1	376	3.0
High Polymers		15.9	22.3	16.1	22.1	19.8	26.2	2603	20.7
Inorganic–simple		25.0	24.3	26.6	26.5	27.9	26.1	3275	26.0
Inorganic–complex		6.2	7.3	7.3	8.3	7.0	5.2	864	6.9
Metals		5.4	6.6	4.2	2.9	3.4	4.8	560	4.4
Organometallic compounds		3.9	5.3	4.0	5.5	3.8	1.5	488	3.9
Minerals		6.7	6.2	7.1	7.4	6.4	6.1	830	6.6
Organics		10.5	15.0	9.3	11.7	10.5	10.2	1391	11.1
Electrical and electronic materials		3.8	4.0	3.0	1.7	2.7	1.8	347	2.8

In 4.4% of the publications different metals are examined, while the percentage for alloys is 5.4%.

In addition to those mentioned above, the percentages for other important substances are also indicated in Table 3. Of these, two types deserve attention: the study of metallo-organic compounds and that of electrical and electronic materials are becoming of increasing significance.

Table 4

Year	1975	1976	1977	1978	1979	1980
Number of abstracted papers	1827	1838	2069	2131	2321	2387
Number of abstracted journals	235	169	140	140	159	161
Journals publishing more than 20 papers annually	20	24	25	28	36	35
number of these papers	795	930	1454	1469	1649	1713
and their percentage	43.5%	50.6%	70.3%	68.9%	71.0%	71.8%
Journals publishing fewer than 5 papers annually	163	98	73	71	82	79
number of these papers	302	215	151	165	201	157
and their percentage	16.5%	11.7%	7.3%	7.7%	8.7%	6.6%

Conclusion

The wide-spread use of thermal analysis is indicated by the fact that studies utilizing this technique are published in various journals, depending on the applicability. Nevertheless, a certain concentrating process may be noticed recently, as can be seen from Table 4. The number and percentage of journals publishing more than 20 papers a year on thermal analysis are showing tendencies to rise while the percentage of journals publishing fewer than 5 papers on thermal analysis annually is decreasing.

It may be mentioned as a matter of curiosity that publications appearing in the two journals of thermal analysis account for only a small percentage of all the publications, as seen from Table 5.

Table 5

Percentage of papers published in JTA and TA with respect to all the papers published on thermal analysis

1975	1976	1977	1978	1979	1980
15.0	13.7	11.5	12.9	19.3	19.3

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2. W. W. WENDLANDT, Thermochim. Acta, 36 (1980) 393.
3. W. W. WENDLANDT, Thermochim. Acta, 50 (1981) 1.

ZUSAMMENFASSUNG — In der Veröffentlichung wird ein Überblick über die gegenwärtige Situation der thermischen Analyse gegeben. Auf Grund von aus Thermal Analysis Abstracts entnommenen Daten werden die Anwendungsmethodik, die verschiedenen Techniken, die Untersuchungsmaterialien sowie die thermoanalytische Publikationen enthaltenden Zeitschriften zusammengefaßt.

Резюме — В сообщении со многих точек зрения рассматривается настоящее положение термического анализа. На основе данных Thermal Analysis Abstract обобщены используемые методики, методы, исследуемые вещества, а также те журналы, где публикуются статьи термоаналитического содержания.