Thermochimica Acta, 150 (1989) 93–99
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL ANALYSIS FROM A NUMERICAL ASPECT

G. LIPTAY

Department of Inorganic Chemistry, Technical University of Budapest, H-1521 Budapest, Gellért tér 4 (Hungary)

(Received 25 January 1989)

ABSTRACT

This paper presents a study of the frequency of thermoanalytical investigations during the period 1975–1987. On the basis of information included in the *Thermal Analysis Abstracts*, analyses of the frequency of the methods applied the techniques used and the substances investigated were carried out.

In papers which survey the present state and development of thermal analysis, evaluation is generally subjective. We have already attempted to examine the state of this branch of science as reflected by numbers of papers; however, evaluation over a 3 year period [1] or over a 6 year period [2] does not truly reflect the development of the subject. Wendlandt has also analysed the state and development of thermal analysis over a shorter period on the basis of method [3] and publications in *Thermochimica Acta* [4].

Our present investigations are based on the *Thermal Analysis Abstracts*. Publications abstracted by this journal between 1975 and 1987 were analysed, and tables were composed on the basis of these data. During the major part of this period publications appearing in the U.S.S.R. were not included; however, since 1985 the *Thermal Analysis Abstracts* have also included these publications. We believe that the longer period investigated (13 years) gives a true picture of the situation and development in this branch of science.

Figure 1 shows the number of publications included since 1972 (the start of abstracting) in the *Thermal Analysis Abstracts* as a function of year. After an initial constant increase, the number of publications reported remained constant, and has tended to fluctuate in recent years. It seems that there will be no sudden increase in the number of publications in the coming years.

We also studied at what frequency certain methods (instruments), techniques and types of substance investigated occur in the publications reported (taking the sum of these publications as 100%). It should be noted that only the methods, techniques and substance which occur most often are given: if several methods, techniques and substances are dealt with in one

0040-6031/89/$03.50

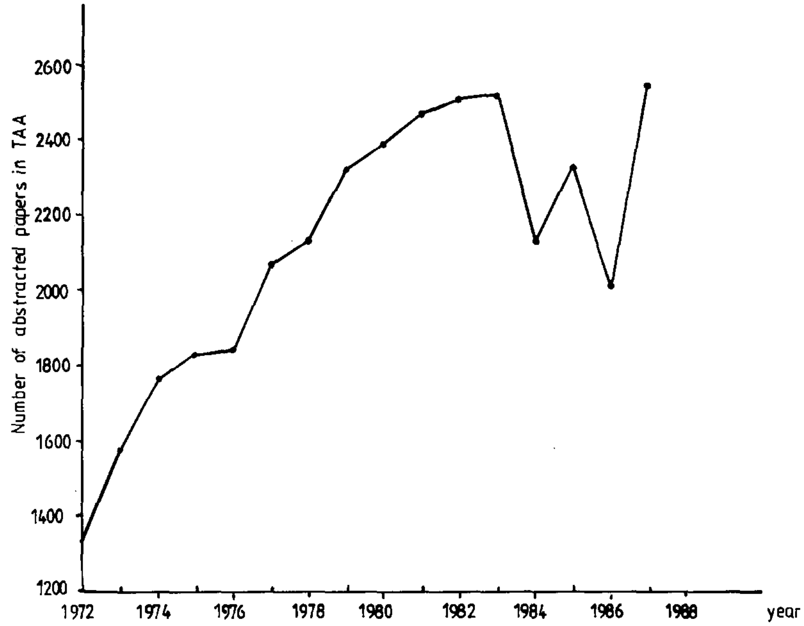

Fig. 1. Number of publications abstracted in *Thermal Analysis Abstracts* since 1972 as a function of year.

publication, this is taken into consideration for all applications. Thus the percentage values do not add up to 100%.

Table 1 shows the frequency of the methods (types of instruments) most commonly used. It can be seen that one of the oldest thermoanalytical methods, thermogravimetry, plays an important role and accounts for 20% of all the methods investigated. Use of the differential thermal analysis (DTA) method shows a slightly decreasing tendency. Use of the differential scanning calorimetry (DSC) method increased decisively up to the beginning of the 1980s, compensating for the decrease in the use of the DTA method. The use of simultaneous methods definitely shows an increasing tendency. The use of dilatometric analysis shows a slight decrease. After an initial increase, the use of thermomechanical analysis shows a decrease. The importance of calorimetric (other than DSC) measurements has increased. The wider use of mass spectrometric analysis is limited by the high price of the instrument. The application of the isothermal technique shows an increasing role after a temporary regression. The number of publications involving some kind of diffraction have increased significantly.

Table 2 shows the distribution according to techniques. It can be seen that the process of decomposition (degradation) is most often used, accounting for about 20% of the publications. Methods based on the investigation of dehydration, dehydroxylation and on the measurement of the heat of reaction have markedly increased in use. The number of publications dealing

TABLE 1

Percentage of publications dealing with certain types of instruments during the period 1975–1987

	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Number of publications	1827	1838	2069	2131	2321	2387	2469	2501	2513	2124	2328	2012	2544
Thermogravimetry (TG)	10.4	22.7	18.7	18.2	19.0	23.4	19.8	22.6	20.9	20.4	19.0	19.3	18.4
Differential thermal analysis (DTA)	21.1	22.5	21.6	18.7	19.0	18.7	19.6	17.8	16.5	18.2	17.2	15.7	14.6
Differential scanning calorimetry (DSC)	11.7	13.4	10.9	11.8	13.3	15.9	18.3	18.5	13.5	20.2	15.9	20.7	13.3
Simultaneous TG–DTA	5.1	7.7	8.9	7.8	6.3	8.5	8.8	7.6	7.6	9.1	7.1	11.5	9.2
Dilatometry (TD)	4.8	5.7	5.6	3.3	4.7	5.2	2.6	4.0	4.3	3.3	3.7	4.2	3.5
Electrical measurements	10.7	10.4	11.8	8.6	7.1	8.0	7.9	8.1	10.7	10.1	6.4	8.1	8.7
Thermomechanical measurements	4.6	4.1	5.3	5.4	6.7	6.0	4.5	3.6	2.2	2.2	1.3	1.8	1.5
Calorimetric methods other than DSC	8.1	7.0	6.1	5.6	8.2	6.3	8.3	8.8	12.4	11.1	11.1	13.0	13.3
Magnetic spectroscopy (NMR, ESR, Mössbauer)	2.6	4.0	5.3	6.6	3.2	3.8	2.6	2.2	2.0	3.5	2.5	4.8	4.8
Mass spectrometry (MS)	1.4	2.2	3.0	3.5	2.8	3.6	1.9	2.5	2.2	3.8	2.4	3.3	3.5
Isothermal techniques	13.4	20.0	16.7	18.0	13.2	8.2	5.4	5.1	5.4	5.5	7.3	8.9	10.9
Magnetic measurements	2.8	4.8	5.7	5.2	5.5	3.6	3.3	3.1	5.1	5.9	4.3	4.1	4.8
X-ray, electron and neutron diffraction	2.9	3.3	5.1	5.2	5.5	5.8	5.3	4.6	5.5	12.1	16.1	17.1	17.5
Microscopic methods	1.9	4.4	4.0	3.4	4.0	3.1	3.1	2.3	2.7	2.8	2.1	3.2	2.8

NMR, nuclear magnetic resonance; ESR, electron spin resonance.

TABLE 2

Percentage of publications dealing with certain types of technique during the period 1975–1987

	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Number of publications	1827	1838	2069	2131	2321	2387	2469	2501	2513	2124	2328	2012	2544
Dehydration and dehydroxylation	5.5	7.2	6.9	5.3	7.4	6.2	6.4	8.8	9.7	9.8	10.3	11.9	9.9
Heat of reaction	6.3	6.4	5.2	6.7	8.2	5.3	3.2	8.1	16.0	10.0	12.3	15.7	17.1
Kinetics	13.1	14.5	14.5	16.2	13.5	12.6	11.0	16.9	15.6	14.5	15.7	13.9	16.5
Low temperature	9.5	14.6	14.9	14.0	11.0	11.0	9.9	9.0	13.5	13.0	9.1	10.5	12.0
Melting	7.0	7.7	8.3	8.9	8.7	12.2	10.7	8.7	5.9	10.4	7.0	11.3	7.7
Phase diagram studies	9.9	7.8	7.7	8.2	10.0	7.0	7.4	7.7	7.4	7.6	7.4	6.5	5.8
Pressure	4.2	2.8	4.2	3.9	2.5	4.5	3.9	4.0	3.8	3.7	3.7	2.9	3.9
Specific heat	3.1	2.6	2.7	1.6	1.8	3.2	3.5	3.8	7.8	5.7	6.7	7.4	7.0
Solid state reactions	3.9	3.1	3.1	2.7	3.1	1.7	2.6	4.3	4.7	2.6	2.8	3.0	4.3
Thermodynamic constants	7.8	8.3	7.9	9.4	10.0	8.4	12.4	12.5	11.8	9.4	13.6	13.6	16.3
Very high temperatures (> 1500 ° C)	2.6	1.1	1.9	1.4	0.6	2.8	1.5	1.9	2.0	1.0	6.1	2.1	1.9
Characterization studies	5.4	12.4	10.3	14.9	17.0	18.2	19.3	22.1	28.0	12.9	5.3	6.4	6.0
Crystallization and crystal structures	9.4	16.4	17.7	17.7	14.0	13.5	12.8	10.4	9.7	13.6	15.1	17.5	14.9
Decomposition and degradation	14.0	18.8	18.3	18.4	18.7	19.9	18.9	20.0	21.2	20.3	17.7	21.7	21.1
Glass transition	5.8	7.7	5.8	7.7	7.8	9.0	8.0	7.0	4.2	7.1	4.4	5.9	3.5
Phase transition	9.5	7.0	9.8	7.7	8.0	9.6	10.7	10.4	13.0	12.0	13.1	14.2	12.7
Apparatus design or modifications	4.4	4.9	6.1	4.2	5.5	5.6	5.8	5.7	5.3	4.9	5.4	8.0	6.9

TABLE 3

Percentage of publications dealing with certain types of compound during the period 1975–1987

	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
Number of publications	1827	1838	2069	2131	2321	2387	2469	2501	2513	2124	2328	2012	2544
Alloys	7.3	6.0	7.1	4.0	3.6	5.0	5.3	5.5	6.2	6.1	5.7	6.0	6.1
Catalysts	1.6	3.9	3.2	3.2	3.4	2.8	1.9	3.1	2.5	5.2	4.4	4.0	3.3
Ceramics	3.7	3.2	2.3	2.9	4.3	3.8	2.9	5.3	4.3	4.5	4.4	3.4	4.8
Clays	1.6	3.1	2.1	1.5	1.8	2.0	3.5	2.1	2.3	1.8	1.8	2.1	1.4
Glass	3.5	2.1	3.0	3.8	3.6	2.1	3.8	3.2	3.1	3.6	4.3	4.5	4.3
High polymers	15.9	22.3	16.1	22.1	19.8	26.2	22.6	18.3	9.7	15.0	11.1	19.7	9.1
Inorganic (simple)	25.0	24.3	26.6	26.5	27.9	26.1	26.8	29.4	34.2	23.8	25.2	24.1	34.2
Inorganic (complex)	6.2	7.3	7.3	8.3	7.0	5.2	7.0	6.2	7.4	6.2	4.3	5.9	4.7
Metals	5.4	6.6	4.2	2.9	3.4	4.8	3.5	3.1	3.6	4.0	4.2	3.8	4.2
Organometallic compounds	3.9	5.3	4.0	5.5	3.8	1.5	0.8	1.3	1.0	3.4	1.2	1.1	0.6
Minerals	6.7	6.2	7.1	7.4	6.4	6.1	9.4	6.2	7.2	6.6	7.4	4.0	4.4
Organics	10.5	15.0	9.3	11.7	10.5	10.2	12.0	15.2	16.1	12.1	13.4	11.9	15.0
Electrical and electronic materials	3.8	4.0	3.0	1.7	2.7	1.8	2.6	1.7	2.6	6.9	8.8	11.5	9.8
Medicines	0.2	0.3	0.3	0.1	0.3	0.3	0.5	0.3	0.2	0.7	1.4	1.7	1.2

with kinetic methods varies around 15%. In a large number of publications crystal structure, low temperature techniques, phase transitions and the melting process are studied. A remarkably large number of publications deals with the description and modification of the instruments. This indicates that there is still a great demand for the elaboration of special application possibilities. Thus the description of new instruments and instrument modification plays an important part in thermal analysis. This shows a demand for an interest in further thermoanalytical methods, and ensures the further development of this branch of the science.

In Table 3 the distribution of the type of compounds investigated is summarized. The compounds studied most often are inorganic compounds. More than 25% of the substances studied are inorganic compounds! Interest in organic compounds has increased somewhat. The situation in the investigation of polymers is surprising. Up to the beginning of the 1980s interest in these compounds increased, reached a maximum of 25%, and has since shown a decreasing trend. The investigation of metals, alloys, catalysts, clays, minerals, glasses and ceramics has not changed significantly, but interest in some types of ceramics (high-temperature ceramics) substantially increased during 1986 and 1987. Complex compounds have been studied in a large number of publications (in our opinion possibilities are not exhausted in this field). Since the middle of the 1980s the investigation of the properties of electrical and electronic materials has definitely increased. The same tendency has been observed in the study of medicines.

It should be noted that the data in the three tables are concerned with research and publication. However, thermal analysis methods are also applied regularly in several industries; conclusions on these data can be drawn only indirectly.

Results of thermoanalytical research can be published in two ways: on the basis of the method used or on the basis of the substance used. Examples of the former are the *Journal of Thermal Analysis* (since 1969) and *Thermochimica Acta* (since 1970). The percentage of papers published in these two journals is shown in Table 4.

Papers published in journals with preference to use and application are less easily available for thermal analysts, but they furnish important information for appliers and users in the single special fields. However, about 30% of the published papers appear in the two specific thermoanalytical journals. (It is interesting to note that on the basis of earlier data about 50%

TABLE 4

Percentage of papers published in the *Journal of Thermal Analysis* and *Thermochimica Acta* with respect to all papers published on thermal analysis

1975	1976	1977	1978	1980	1981	1982	1983	1984	1985	1986	1987
15.0	13.7	11.5	12.9	19.3	19.2	18.4	23.8	27.4	49.2	31.1	29.4

of radiochemical research results appear in the two international journals of this branch of science.) The large amount of publications on thermal analysis in the *Journal of Thermal Analysis* and *Thermochimica Acta* has been increased due to the publication of the Proceedings of ICTA '85, ICTA '88, ESTAC '84 and ESTAC '87 in these journals.

The results obtained show past and present trends; conclusions on future trends cannot be drawn with accuracy.

REFERENCES

1 G. Liptay, Magy. Kem. Lapja, 35 (1980) 41.
2 G. Liptay, J. Therm. Anal., 25 (1982) 235.
3 W.W. Wendlandt, Thermochim. Acta, 36 (1980) 394.
4 W.W. Wendlandt, Thermochim. Acta, 50 (1981) 1.