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Thermal analysis — review and prospect

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Abstract

The history of thermal analysis is briefly reviewed, focusing on fundamental aspects, such as quantitative measurement by DTA, kinetics, purity determination, sample-controlled thermal analysis and temperature modulation. Several general trends, commonly seen in the history of thermal analysis, are also pointed out. Among these trends are new techniques, new application fields, diffusion of the techniques from research to quality assurance, computerization and robotics, infrastructure, such as standardization, etc. In this overview, new techniques and methods of thermal analysis are examined and directions of future progress are anticipated for its sound development.

Keywords: Thermal analysis; History; Trends; Developments; Methods

1. Introduction

Thermal analysis has now had more than eleven decades of history. During this long history, various techniques were invented and thermal analysis has been used in many fields. Nowadays, the application of thermal analysis spreads among minerals, inorganic substances, metals, ceramics, electronics materials, polymers, organic substances, pharmaceuticals, foodstuff and biological organisms. While application in each field began in research, it has been diffusing through development into control of processes and qualities. Today, thermal analysis is an essential tool for materials research and development, while quality assurance is now one of the 'hot topics' in thermal analysis.

In research into high-temperature superconducting oxide materials, we saw one of the most vivid examples of its versatility. Since the end of 1986, research was stimulated by the discovery of a new oxide material, and a boom occurred in research into these materials. In the course of this boom, various thermal-analysis techniques were used for a variety of purposes [1] as listed in Table 1, and from this the readership can realize versatility of thermal analysis. This is one typical example and the situation is quite similar in other fields of research and development.

Considering the long history of these steady developments, it is often thought that thermal analysis is already so mature that there is little room for further progress, as in the case of infrared spectroscopy. In this technique, progress has not been remarkable for a few decades, though it has been used in various fields as an analytical tool. However, this is not the case with thermal analysis. Just as new frontiers have been explored in magnetic spectroscopy, such as magnetic resonance imaging, new trends and further progress have also been made in thermal analysis and these will be discussed here.

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Table 1
Examples of application of thermal-analysis techniques for high-temperature superconducting oxide materials

Application fields	Applied techniques
Forming reaction and its kinetics	TG, DTA, EGA[a], MO[a], ETA[a]
Crystalline transition	DTA, TD[a]
Melting and glass formation	DTA, MO[a]
Oxygen content	TG (TPR[a]), EGA
Non-stoichiometry	TG, EGA, (TPR[a])
Sintering and crack formation	TD[a]
Matching of thermal expansion for thin-film formation	TD[a]
Critical temperature	TE[a], TM[a]
Phase diagram for single-crystal formation	DTA
Vapor pressure and volatilization for MOCVD[b]	TG, EGA[a], EGD[a]
Heat capacity	DSC

[a] EGA and EGD are recommended terms for evolved gas analysis and evolved gas detection, respectively. The following abbreviations are not recommended, but used for convenience here: ETA, emanation thermal analysis; MO. microscopic observation; TD, thermo-dilatometry; TPR, temperature-programmed reduction; TE, thermo-electrometry; TM, thermo-magnetometry.

[b] Metal organic chemical vapor deposition.

On the other hand, it is also observed that some of the progress is not grounded on sound physical bases. Therefore, critical reviews of these progresses are essential for furtherance and development of thermal analysis. The author has tried to make such reviews and to summarize them in this brief article. Naturally, it is made from the author's own viewpoint, mostly based on his experience, and, hence, it is neither comprehensive nor free from bias.

2. Short history of fundamental aspects

2.1. The very beginning and automation

It was in 1887 that thermal analysis experiments were first made by Le Chatelier, and it was related to the heating-curve method for clay minerals. The heating curve was automatically recorded by using a galvanometer, a photographic plate and a light chopper. Strips were printed on the photographic plate with the light chopper, and the interval of the strips corresponded to the heating rate. Tammann also did similar thermo-analytical work during the same period. Differential thermal analysis (DTA) was invented in 1899 by introducing a thermally inert substance (reference material) and measuring the temperature difference between the sample and the reference material in the heating-curve method. It should also be mentioned that, just as in a modem apparatus, the temperature and the temperature difference were automatically recorded in one of the apparatuses used at this time, as in an *X-Y* recorder, by using two galvanometers and a photographic plate with prisms.

In 1915, the second technique of thermal analysis, i.e. measurement of mass change (thermogravimetry TG), was invented by a Japanese physicist, Honda. It is also worthy of note that, in 1925, TG data was first analyzed for kinetic purposes by the Japanese electrical engineers, Kujirai and Akahira [2], who performed the kinetic analysis of thermal deterioration of electric insulating materials to predict their thermal life. The third method invented before the Second World War was thermo-dilatometry.

Thus, three major techniques were already available in those days. However, the automatic recording and control were rarely available and usually two persons were required for carrying out experiments, i.e. watching the meters, recording the data and controlling the temperature, for a long time without intermission, so that thermal analysis was tedious and hard work and needed patience. These techniques were mainly applied to minerals, metals, inorganic substances, ceramics and refractory materials. The application to natural polymeric materials by Kujirai and Akahira was a rather exceptional case.

After the Second World War, the technology of automatic recording and control had been developed, and this equipment became available, especially after 1950. In Japan, for instance, the author assembled a DTA apparatus in the mid-fifties. An automatic recorder, a temperature controller and a d.c. amplifier were used in the apparatus, all of which were made in Japan. A similar apparatus was made by Suga, while another DTA apparatus was setup by Otsubo and Kato using U.S.-made equipments. These were the only three fully automated DTA apparatuses in Japan in the mid-fifties [2].

Fully automated apparatus, however, became commercially available at the end of fifties [2], while automated thermo-balances and power compensation DSC (pc-DSC) were also commercialized at the beginning of the sixties. Thus, people were eventually relieved of tedious and hard labor when performing a thermal analysis experiment. The automation led to a flourishing period of thermal analysis in the sixties and seventies. It should also be mentioned that the First International Conference on Thermal Analysis was held in 1965 at Aberdeen, Scotland.

In this period, the parts of thermal analysis assembly were formulated. They consisted of a furnace, a temperature controller, a transducer to measure the sample physical property and a recorder, which records the transducer output signal as a function of the temperature or time. In most cases, the temperature was controlled at a constant rate of heating or cooling. The common features of thermal analysis in this period are a constant rate of heating or cooling and the recording of the transducer signal, but not the physical property itself.

2.2. *Quantitative measurement by DTA*

Although DTA has a long history as mentioned above, quantitative measurement by DTA, such as the measurement of heats of transition and fusion, and theoretical studies were started in the 1940s. In the beginning, the temperature distribution within the sample was ignored so that the temperature was implicitly assumed to be uniform. The possibility of quantitative measurement was postulated on this assumption [3]. However, taking accounts of the temperature distribution within the sample, it was proved by rigorous theoretical study that quantitative measurement by DTA is "*inherently impossible*" [4]. In a conventional DTA, the sample plays two roles:

1. the heat source in which heat of reaction, fusion, transition, etc. are evolved or absorbed, and
2. the thermal barrier in which temperature gradient occurs in proportion to the heat flow to the sample, because the thermocouple junction was inserted into the sample.

Thus, the proportionality coefficient between the peak area and the heat of reaction, fusion, or transition, etc. is dependent on the sample, namely its apparent thermal conductivity depending on its nature, packing density, etc. This is the reason for the above-mentioned postulate of impossibility.

This assertion of the inherent impossibility was denied on the same rigorous mathematical basis by introducing a new structure into the conventional DTA apparatus [5,6]. In the new design, the thermocouple junction was set outside the sample, and the thermal barrier for the heat flux measurement was inserted between the sample cell and the furnace (or the metal block for temperature uniformity). Thus, the above two roles of the sample are separated and the measurement of heat became possible. It was made clear that quantitative DTA, which is the former term for heat-flux DSC (hf-DSC), is a dynamic operation of a conduction calorimeter, such as a Calvet calorimeter [6]. Thus, calorimetry by hf-DSC and pc-DSC commenced in the mid-sixties, and these gradually gained acceptance in the field of calorimetry.

The first boom for thermal analysis, especially DSC, came in the 1960s with the applications to polymers, for which melting behavior was mainly observed in relation to morphology. In this field, quantitative research was done by full calorimetric application of DSC, and its theoretical basis was established prior to this boom in the course of its history as mentioned above.

2.3. *Kinetic applications of thermal analysis*

With fully automated thermo-balances, researchers explored new fields of thermal decomposition. The natural goal of research in this field is kinetic study. After the work of Kujirai and Akahira, kinetic application of thermal analysis was not carried out until the end of the 1950s, probably because of a lack of need. Freeman and Carroll [7] applied TG to the kinetic study of thermal decomposition and Kissinger [8] proposed a method to estimate the activation energy from DTA peaks.

Their methods were, however, based on an assumption of *n*th order reaction mechanisms. There are other cases, as clearly seen in some solid reactions, such as Avrami-type reaction, and also in some polymer decompositions, such as random scission in the main chain. Today, it is well known that the most reliable kinetic methods are iso-conversion methods [9], such as the Friedman plot [10,11], the Kissinger–Akahira–Sunose plot [8,12,13] and the Ozawa–Flynn–Wall method [14,15]. Friedman and Kissinger derived their method on the same assumption of *n*th-order reaction as above, but their wide applicability was made clear by Ozawa later [11,12], while Akahira and Sunose [13] independently found wide applicability of the Kissinger plot. Thus, the main kinetic methods had been established also in the sixties.

Among these three methods, the Friedman–Ozawa method [10,11] has advantages over the other two, because the constant rate of heating is not a prerequisite for this method and no approximation is made in derivation of the method. It is also worthy of note that this method became more easily applicable when computers could be used fully, because data for both, the conversion and the rate of conversion are needed for kinetic analysis by this method. The former can be calculated from the latter or vice versa with a computer.

It was shown that the iso-conversion methods can also be used for other processes, such as diffusion [16]. Non-isothermal kinetics for Avrami processes in crystallizations and solid reactions was derived [17,18] in the beginning of the seventies. In non-isothermal kinetics, the difference in the temperature dependence of the rates for nucleation and growth is taken into account. This difference in the temperature dependence is a very important point needed to derive non-isothermal kinetics of a reaction consisting of multiple elementary processes.

For relaxation processes, such as glass transitions, methods for kinetic analysis of thermal analysis data were also derived [19,20].

2.4. Sophisticated interpretation of thermal analysis data

For analyzing thermal analysis data, knowledge of the heat flow around the sample in DSC was another key point. O'Neill [21] pointed out that the rates of melting, transition, etc., in pc-DSC are controlled by the heat flow rate in the apparatus and that the heat flow rate is controlled by the temperature gradient between the micro-heater and the sample. On this understanding of the temperature distribution and the heat flow around the sample, the curve of the molten fraction vs. the temperature may be derived from a DSC curve for purity determination. There was a contradictory postulate that deconvolution can be done for analyzing a DSC curve using the transfer function based on linear theory of measurements or superposition principle [22]. This postulate is inconsistent with the method used in the purity determination, and its reason was made clear later by experiments [23,24]. The superposition principle or convolution and deconvolution hold only in electrical heating in the sample cell or infrared irradiation to the sample cell. These are all linear processes. On the other hand, the sample transformations, such as melting, transition, etc., are non-linear processes. For instance, in the melting process of pure substance, as in purity determination, the sample temperature is almost kept constant during the melting. Thus, the deconvolution or the linear theory of measurements does not hold in these non-linear processes.

This is also very important in temperature-modulated DSC (tm-DSC) mentioned below [24].

2.5. Controlled-rate thermal analysis

The above-mentioned strategy for analyzing thermal analysis data is sophisticated and based on deep insight into the processes proceeding in the thermal analysis apparatus. More fundamental progress was made a few decades earlier, but its importance was not fully appreciated, though now it has been gradually recognized. That is the sample-controlled thermal analysis (SCTA, or controlled-rate thermal analysis, CRTA) [25], in which the rate of the sample property changes (or the rate of the reaction) is controlled in some modes by controlling the sample temperature. This is the reverse concept of the conventional thermal analysis. This concept was proposed in the sixties and experiments were made since then, but it did not become popular because of the difficulty in the control. Recently, commercial instruments have become available, but this method is still new and its potential capability will be explored fully in the future.

One of its clear advantages over the conventional constant-rate heating thermal analysis is a higher temperature-resolution. For instance, successive dehydration processes of copper sulfate pentahydrate can be separately observed by this new method. One of most important practical applications lies in pharmaceuticals, such as quinine hydrate. There must be many other unique features of this method, and for making full use of this technique, they will be made thoroughly clear in the future.

2.6. Temperature modulation

Another epoch-making innovation was the introduction of temperature modulation in DSC in 1992 [26,27]. Because Fourier analysis is used for analyzing the temperature oscillation, linearity of the process is the base for this analysis, so that sound application of this new technique should be limited in heat-capacity measurements at the present [24]. Moreover, amplitude decrement and phase shift are caused by the heat capacities inevitably occurring in the apparatus as well as by the thermal contact between the sample cell and the cell holder [28]. They are also occurring within the sample itself due to its thermal resistance and heat capacity [29,30], so that insight into temperature wave propagation is essential fur understanding temperature-modulated DSC (tm-DSC). These effects should be taken into account even in heat-capacity measurements. However, measurement of complex heat capacity is one of the remarkable advantages of this new technique, and it is reasonable to suggest that applications for other purposes will also be made in the future on sound physical base.

2.7. General trends in progress of thermal analysis

Beside progress in the fundamentals of thermal analysis, there are many other trends in the progress of thermal analysis, and they are classified in the following.

2.8. Development of new techniques

After DTA, TG, thermo-dilatometry and DSC, many new techniques have been devised, and various physical properties have been measured by thermal analysis. One of the remarkable developments in thermal analysis techniques is the 'three-dimensional thermal analysis'. 'Three-dimensional thermal analysis' is a phrase coined by the present author, and it is intended to express new techniques, such as thermophotometry by Fourier transform infrared spectroscopy (FT-IR), in which measured results are shown in three dimensions, such as the temperature, wave number and absorbance. This contrasts with conventional thermal analysis, such as DTA, DSC, TG and TMA, in which the results are shown in two dimensions. EGA by mass-spectrometry, thermo-analytical X-ray diffraction and thermal analysis by FT-NMR come within this category. It should be stressed here that, by these techniques, we can obtain more information than by the conventional two-dimensional techniques, and, moreover, we get microscopic information, such as chemical and crystal structures. This is a very important point, because we can detect only macroscopic changes by the conventional techniques. Simultaneous measurements by these new techniques and the old ones, such as simultaneous measurement of TG and EGA by mass-spectrometry and that of DSC and X-ray diffractometry, bring us new insight. Thus, the new three-dimensional techniques and their simultaneous measurements are becoming new powerful tools by which we can know more precisely what kind of process is going on in the sample.

2.9. Extension of application fields

As mentioned above, application of thermal analysis hitherto has spread from clay minerals to various substances, industrial materials and biological organisms. One of the remaining fields is the application to thin films, for which extremely high sensitivity is required. It is also very interesting, because thin-film properties might be different from those of bulk sample due to surface effect. Therefore, it is hard but challenging.

2.10. Decrease in sample mass

In the beginning of thermal analysis history, the sample mass used was of the order of a gram or more, but nowadays it is usually of the order of 10 mg or less. Therefore, it becomes possible to measure small, valuable samples, such as pharmaceutical substances under research, by thermal analysis. The benefit of this development is not only in this point. It brings us another benefit, i.e. decrease in the response time of the apparatus, and hence improvement of the temperature-resolution. Rapid temperature scanning can also be made with the short response time. We should not ignore these improvements, and we should explore further the possibility of reducing the sample amount.

2.11. Sophisticated application

The simplest application is ‘finger-print test’ in which the shape of a thermal analysis curve per se is used, for instance, for identification and quality control. From this level of qualitative application through quantitative use, more sophisticated applications have been developed. Kinetic analysis, purity determination, heat-capacity measurement and transformation heat measurement are examples. However, some problems still remain unsolved. For instance, we do not have a kinetic method for analyzing consecutive reactions, although study of these reactions has become much more feasible with the introduction of EGA by FT-IR and mass-spectrometry. For competitive reactions, a few methods for kinetic analysis have been proposed, but here are few examples of their application. Similarly, much more information would be obtained by SCTA and tm-DSC, if some suitable methods could be devised.

2.12. Diffusion and penetration into production lines

As we have seen, thermal-analysis techniques have been transferred from research through development to quality control, process control and quality assurance, and it is a sign of maturity. Thus, we have now some International Standards for plastics by TG, DSC and TMA [31]. This natural diffusion and penetration will be observed in other fields of technology, and one of the examples can be seen in the pharmaceutical industry, and, for instance, the fact that thermal-analysis techniques are now being introduced into the Japanese pharmacopoeia.

2.13. Computerization and robotics

As mentioned above, automated apparatuses were used even in the very beginning of thermal-analysis history, so that computerization and robotics are natural consequences of the development of thermal analysis. However, it should be pointed out that computerization has a dangerous tendency to lead to misuse. For instance, smoothing of a thermal analysis curve is often done with a computer, and this is done to decrease the noise from the signal, but it sometimes deletes small real changes in the sample. It should also be mentioned that mechanistic application of software for data treatment sometimes leads to false conclusions. A careful and thoughtful application is required for sound development of thermal analysis.

As mentioned above, automation brought us a definite way of experiment, i.e. the constant rate heating or cooling and the direct recording of the transducer output signal. The output signal can be transformed into the physical property or other information with a computer, and other modes of temperature change can also be easily done with a computer. The many possibilities for computerization should be fully explored. On the other hand, robotics is useful in improving the rate of operation and it is also useful to increase the reproducibility of setting the sample cell in the apparatus.

2.14. Infrastructure

As the measurement is made under varying temperature in thermal analysis, accuracy and precision of temperature measurement have been severe problems. Since the very beginning of the international organization of thermal analysts in 1965, standardization has been one of key problems in thermal analysis, and the International Confederation for Thermal Analysis organized the Standardization Committee. This committee took an active part in this problem, and several series of certified reference materials were established and distributed worldwide. Other activities of ICTAC, such as nomenclature, education, etc., also provide us with a good and valuable infrastructure for thermal analysis [32].

3. Further progress

Earlier, the author has described several trends in thermal-analysis history. These trends will also be continuing in the future. Among them, a few are remarkable for the progress toward the next century.

SCTA should be described first. Besides the better temperature resolution mentioned above, this technique seems to have some other unique features. In conventional thermal analysis, the sample is forced to heat up at a constant rate, ignoring whether a certain change occurs or not, so that the process occurring in the sample is observed over a relatively wide temperature range. In some cases, additional reactions are observed together in the higher temperature range, where these reactions become predominant over the reaction observed in the lower temperature range. This situation makes the observed results complicated and seems a drawback of the conventional constant-rate heating thermal analysis, though the constant-rate heating is an excellent way to observe phenomena occurring in the sample over a wide temperature range.

Through a round robin test of the application of TG to thermal-life prediction of electrical insulating materials [33], for instance, this drawback was indicated as one of causes for low reliability of constant-rate heating TG in this application. The kinetic data obtained by the constant-rate heating TG are used to predict the thermal life at a relatively lower temperature, where electrical machines and cables are operated. However, the reaction occurring in the practical operating temperature is different from that observed by the linear heating TG in some cases. This situation is the reason for the low reliability. Thus, instead of TG, stepwise heating-and-cooling EGA is adopted for this purpose [33].

This situation seems much the same in other materials as well. On the other hand, by SCTA the rate of heating is reduced when the reaction begins to start, so that high-temperature parallel reactions cannot occur. Therefore, it seems plausible that SCTA gives us more reliable kinetic data for these purposes than conventional constant rate heating thermal analysis [34].

Another possible advantage of SCTA might be in the atmosphere above the sample. Because the rate of reaction is controlled, the volatilization rate of gaseous products is also roughly controlled. Although it is not well confirmed, the kinetic parameters estimated by conventional TG, such as the activation energy, are sometimes dependent on the sample mass, but this dependence is not found by SCTA/TG. Difference in the atmosphere may be one of the plausible causes for this discrepancy.

There might be other unique features and advantages in SCTA, and we can anticipate that these features and advantages will be fully explored in the future.

Temperature modulation is also a new trend to be described. Besides DSC, this technique is applied to other thermal analysis, for instance, TG [35], dynamic thermo-mechanometry [36], thermo-dilatometry [37] and thermo-electrometry [38]. One of the common features of these temperature-modulated thermal analysis techniques is the possibility of distinguishing the non-equilibrium state from equilibrium state, because the kinetic nature of non-equilibrium state to equilibrium state appears in changes of the sample response to the temperature modulation, especially to its frequency dependence.

One of these advantages of this technique is well recognized in DSC; at least, by tm-DSC we can observe and measure the imaginary part in heat capacity, which is one expression of the above kinetic nature. If the reliable method for analyzing tm-DSC data for the sample transformation is derived on a physically sound base, it can be forecast that applicability of temperature modulated thermal analysis will be greatly appreciated.

In recent issues of scientific journals, we still see many papers on kinetic methods for reactions of a single elementary process, so that outsiders may misunderstand there are still serious problems to be solved. On the other hand, we see few papers on kinetic analysis of reactions in which multiple elementary processes are involved. As mentioned above, the latter processes are not now as difficult to observe as before, because the powerful new tools, such as the three-dimensional thermal analysis, give us detailed information on the formation of the various products.

Effort presently devoted to the former kinetics should now be switched to the latter. However, one of the difficulties for the study of these kinetics lies in the situation that the multiple elementary processes accelerate at different rates with changing temperature, because of their different activation energies.

The trend for decreasing the sample mass seems to be limited, probably because of difficulty in accurate sample mass measurements. However, there are great advantages in using a micro-amount of sample, i.e. the short response time for rapid temperature scanning and high-frequency temperature modulation. The short response time can be achieved also by using thin or slender specimens. The author is of the opinion that this problem is worthy of intensive study, and that it will have some connection with thin films. Because thin films are very important samples from the viewpoint of industrial importance and scientific interest, this is also a very important challenge.

It should be mentioned in relation to this that there are a few very interesting developments, such as the application of scanning tunneling microscope technology to thermal measurements of microscopic area of the sample [39,40]. Let us imagine what kind of things we can learn by this technique. What we have observed by thermal analysis till now is statistically averaged properties and phenomena, but when we enter the nano-scale area, they will not be statistical and we will probably see fluctuations. In this sense, this is another and perhaps the most futuristic trend in thermal analysis.

4. In conclusion

Hitherto, thermal-analysis history has been reviewed from the author's own viewpoint, and several trends have been seen in this history. We saw instances of physically sound developments in thermal analysis, such as quantitative DTA, purity determination, and non-isothermal kinetics. In these cases, the postulates of an illogical base were critically considered. From these observations, we can concentrate our efforts for sound development in thermal analysis, and we can find new possibilities of sophisticated applications of thermal analysis to our problems. We can also learn that, essential to these developments are insights into the details of the process and concrete consideration. The author hopes the remarks in this short article will be helpful for the readership in their work.

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