Thermochimica Acta, 110 (1987) 31–49
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REPORT ON THE WORKSHOP: ADVANCES IN THERMOANALYTICAL INSTRUMENTATION

Chairman: C.B. MURPHY

P.O. Box 631, Fairport, NY 14450 (U.S.A.)

Co-chairman: K. HABERSBERGER

Heyrovský Institute of Physical Chemistry and Electrochemistry of the Czechoslovak Academy of Sciences, Máchova 7, Prague (Czechoslovakia)

The workshop moderators (Dr. C.B. Murphy and Dr. K. Habersberger) were assisted by a scientific panel, Dr. W.-D. Emmerich (F.R.G.), Dr. P. Gill (U.S.A.), Dr. W. Ludwig (G.D.R.) and Dr. H.G. Wiedemann (Switzerland).

After the introduction, prepared by the moderators, free discussion of the relevant problems took place. The report of the workshop as recorded is reported verbatim by the Chairman.

INTRODUCTION

In instrumentation today, it is believed that we have two distinct types of issues. There are those that can be attributed to instrument manufacturers and a second set, unique to the specific equipment available to each of us and what we are attempting to do with it. It is important to keep these issues separate.

Thirty years ago the individual had to construct the apparatus that was used. Some components were available. In 1955, Robert Stone was building equipment for sale in the basement of his home with the help of craftsmen at the University of Texas at Austin. It took a considerable amount of time to obtain a unit after an order was placed for equipment described in 1952 [1]. Thirty years ago the literature was replete with DTA curves of calcite, gypsum, and cupric sulfate pentahydrate to show the merits of one piece of equipment over another. In thermogravimetry, calcium oxalate monohydrate was a popular material for comparative testing. Dr. Robert Mackenzie, 1985 Du Pont–ICTA Award winner, and Farquharson [2] recommended back in 1952 that a heating rate of 10 ± 1°C min^{-1} should be employed so that comparisons would have significance.

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

0040-6031/87/$03.50

Twenty years ago, in 1965, the first ICTA was held in Aberdeen, Scotland. A number of instrument manufacturers were represented: Netzsch, Du Pont, Mettler, Perkin-Elmer, Stanton and Shimadzu, and several papers were presented based on work with the Derivatograph (MOM). Within the ten-year period commercialization had become a fact of life. Twenty years later, 1985, the advent of readily available, manufactured equipment has freed the literature from papers comparing one apparatus with another. The manufacturers have done a good job and have given us apparatus with appropriate sensitivity, accuracy, reproducibility, reliability, etc.

While many individuals have purchased state-of-the-art equipment, it is felt that there still is a problem with the trend equipment is taking. Equipment costs are high. The most recent ICTA News [3] indicated that one of our group was retiring from the field because of this. In the same issue, Professor Banerjee questioned whether outmoded equipment could be provided to needy institutions. Yesterday, the panel on Education, Publication and Standardization essentially asked the same question. How do you get reasonably priced, good equipment in the schools?

Previously, producers of thermoanalytical instrumentation concentrated on the construction of sample holders and furnaces, as well as the problems of temperature programming, the latter often being solved by mechanical means. Parallel evolution of recorders solved display and output data-registration problems. Today, effort is being concentrated in a direction we could call integration of thermoanalytical instruments into the computer age. This trend is common to all instrumental analytical methods. The new devices are characterized by several main points:

— electronic control of furnace (complex temperature programs),
— electronic sample temperature correction,
— processing and registration of data output,
— some give desired answers, e.g., ΔH or T_g.

We should not forget that the main objective of a good instrument should be *quality*, not only *comfort*. A good instrument should deliver reproducible data with high sensitivity and resolving power.

Modern thermoanalytical instrumentation is very versatile, especially with respect to temperature programming and data processing, both thanks to computerization. However, only a small part of their capabilities are used in practice in most cases, the usual heating rate, e.g., being no faster than 20°C min^{-1} or slower than 5°C min^{-1}. The unused capabilities were paid for in vain, unless they were economically legitimate through mass production of a universal device.

Coupling DTA or DSC with a mass spectrometer or X-ray diffraction unit brings purchasers into the realm of two pieces of capital equipment. While in many cases research can afford this, quality control cannot. It appears that there is some need for low-cost as well as higher priced equipment. In justice to the manufacturers, they respond to demands. They cannot sell what is not needed. Low-cost instrumentation would have to be made in large volume with minimum options and marketed with minimum sales expense.

Equipment must become modular with changes being simple and made by the operator. Simultaneous measurement modules could be incorporated inexpensively. Effluent gas detection would be one such simultaneous measurement that would help to interpret phenomena occurring during experiments. Simplified pressure–vacuum systems could also be provided without major expense.

Unique problems always will be with us. They are not totally equipment related, but also encompass the materials being investigated and the materials of construction of the equipment. While the following problems are known, they provide the means to distinguish between equipment related and materials interaction problems.

(1) Equipment related:
    (a) microsample holder for explosive investigations [4];
    (b) thermocouple sample holder for single crystal examination [5].
(2) Materials interactions:
    (a) catalytic NH_3 oxidation by Pt thermocouples [6];
    (b) polyhydroxyalcohols (sugars) reacting with borate glass sample holder [7];
    (c) halogenated polymers reacting with Al_2O_3 diluent [8];
    (d) pyrite-rich clays gave different results with Ni and stainless steel sample holders due to Ni_2S_3 formation [9].

The amazing facet of thermal analysis is the scope of its application. Thirty years ago the biggest users were ceramists and mineralogists. Today, there is not much that has not been examined by DTA, DSC, and TG; therefore, it is not unusual that unique problems are encountered. It also must be remembered that while the panel represents an extensive breadth and depth of experience, even they could not have developed expertise in the total scope of thermal analysis. Therefore, for some problems one can only hope to get the best available advice.

It is believed that there is a market for good, low-cost, modular instruments. It is represented not only by laboratories in schools or in developing countries, but also by those who would like to try thermal methods in the solution of their problems. There are laboratories where speed of analysis or ease of operation are not primary objectives.

Prof. B. Wunderlich, U.S.A.: I agree that there is not much need for very fast analysis for a slow process but I would like, and I have asked for a good number of times for the development of an equipment which goes "superfast". I would like to see 10000 K min^{-1} heating rates. We have pushed it ourselves to about 1000 K min^{-1} using commercial equipment and with self-built equipment to about 10000 K min^{-1}; if you calculate the rate per second, then it does not sound so impressive. But the reason for this is that with such fast heating rates you can simulate industrial processes, especially in things like the textile industry and thin film industry, which uses an enormous number of thermal analyses for their end-product use analysis. Then you can simulate processes that show what happens on quick quenching, what happens on quick heating, how fast do the kinetics of a process go? I think it is true. You do not want to measure equilibrium processes very fast because you might lose your equilibrium, but if you want to measure kinetic processes, and DTA can do so in real time, that means you can follow a process and there you might want to go fast.

Dr. H.G. Wiedemann, Switzerland: May I call your attention to another branch of thermal analysis, analytical pyrolyzers. You know it is a question as to whether analytical pyrolyzers is a branch of thermal analysis. All the people with analytical pyrolyzers feel thermal analysis is part of analytical pyrolysis. These people have the same wishes to have heating rates, not like Prof. Wunderlich, but up to 100000 K min^{-1} for quick analysis. At the Gordon Research Conference about $1\frac{1}{2}$ months ago, some thermal analysts participated and felt very lonely showing their work at this meeting. They were very astonished because of all of the biomass analyses. This thing of the wood analysis is extremely interesting today for energy production; they were astonished when I presented the thermoanalysis separation of the cellulose and lignin peaks with a heating rate of 0.1 K min^{-1}. It was selected not just for the lecture but for a very special aspect of Egyptian papyri aging. They want to do very quick analyses and cannot separate very exactly with a slow procedure. So, it is very good that we now discuss the high heating rate, a thing we must have in our own field. However, that depends on the sample size: how large is the sample and what is the heat distribution in this sample? Who knows the heat distribution in these samples at these heating rates?

Dr. C.B. Murphy, U.S.A.: There was a paper that came out of Los Alamos [10,11] and another from the west coast [12,13] on RF heating systems that went to elevated temperatures, but I am not sure of the heating rates. The other thing that you might think of is the use of a laser beam to get extremely fast rates. Someone suggested some time ago that if you used a laser beam that you could use the sample as the sample holder because it would be so intense at the moment and at the site that the effect would be recorded, but it would not radiate fast enough so that the material would be its own sample holder.

Dr. W. Ludwig, G.D.R.: My question is what will you measure at such high heating rates, rates of the order of 1000°C min^{-1}? You have a sample with high heat transport.

Prof. B. Wunderlich, U.S.A.: We measure a lot with it. The problems you would like to analyze are both on heating and on cooling. You would like to do both as quickly as possible. On cooling, I think it is obvious; but on heating, polymer samples rearrange quickly. Polymer samples have transitions which have a time constant. You would like to outrun these. For example, it can be partially polymeric material: we measured, for example with heating rates up to 1000°C min^{-1}, the conversion of monoclinic to trigonal Se. You can determine monoclinic Se, a ring compound, and when you heat it while it is melting, it continuously changes.

Further conditions that you would like to know: can you be sure that you can eliminate thermal lag? There is a very simple calculation which I make with my students in the thermal analysis course: if you use milligram samples with polymers, you are limited, for polymers, to a heating rate of about 100 K min^{-1}, if you allow a thermal lag within the sample of about 1°C. If you go to 10000 K min^{-1}, you have to reduce your sample to 1 μg and you have the same lag as with 1 mg and 100 K min^{-1}. So, a small sample, which is like a speck of chalk on the black-board, it has no bulk any more if you have 1 μg; you have a very thin thermocouple which has practically no lag; you have a very fast recorder. It is a very different technique.

If you want a high heating rate, we go in steps: gram quantity, milligram quantity, and microgram quantity. The old mineralogists' samples were up to 1 g and you had better not use a heating rate faster than 1 K min^{-1}. If you go to 1 mg, you can go to 100 K min^{-1}. If you go to 1 μg, then you can go to 10000 K min^{-1} and 1 μg is still what you consider theoretically a macroscopic sample. If it is one single crystal, it has no surface effects; it gives you bulk properties. So, 1 μg is the limit between the macroscopic and microscopic sample. Below that, you have large surface effects.

Dr. P. Gill, U.S.A.: I would like to state the position, at least from a manufacturer's viewpoint, and from my own and Du Pont's interests. Our attempt in developing new instruments, new technologies, or advancements of the capabilities of existing instruments is to solicit our users or potential users to find out what they specifically need and to try to address the need that is obviously most encompassing. In other words, what can we do to satisfy the largest number of people, and also is it something that is technically feasible and can it be developed in a reasonable amount of time at a reasonable cost, and are enough people going to have interest to add it to their system? We agree that there is a need for rapid heating and cooling. I have not heard, other than from Prof. Wunderlich, a great deal of interest from the polymer community in general, which I think is where this particular approach might be addressed. However, I also solicit inputs in other areas, other than improving the specifications of existing devices, as to what your interests might be in terms of new technologies or commercialization of technologies that now exist but are becoming increasingly used. What are the needs in the way of additional ease of use, or high quality results? We tend to look to you to give us input so that we can do the research and development and, hopefully, satisfy those needs. Obviously, the manufacturer that best satisfies those needs is the one that is going to be successful. So, obviously, we need a concerted input as to what direction we should be approaching. Where are manufacturers not providing you, as a user, with the kinetic of capability that will best serve your interest?

Dr. E. Gmelin, F.R.G.: A short note to clarify the previous discussion and perhaps one answer to the question as to whether or not it is possible to achieve heating rates of several thousand degrees per second. There is a simple formula:

$$\text{general relaxation time} = \frac{\text{specific heat}}{\text{thermal conductivity}}$$

The thermal conductivity is fixed, you cannot change it at room temperature or higher temperature. So the only way to achieve higher heating rates is to make smaller samples and the only way that Prof. Wunderlich must go is to submicro samples.

Prof. B. Wunderlich, U.S.A.: Not for 10000 K min^{-1}.

Dr. E. Gmelin, F.R.G.: We are working in another field on the interaction of laser and solids. In physics today, it is well established that by shining a laser on a solid you can have extremely high heating rates. However, what is also known is that thermal conductivity given by the equilibrium of phonons and the thermal conductivity of electrons is no more the classical thermal conductivity. The physics is completely different and, therefore, I think you cannot calculate with normal classical formulas. So I think that there is a limit of perhaps several thousand degrees per minute.

Dr. M.J. Richardson, U.K.: I would like to reinforce what Prof. Wunderlich has said about making sure that your samples, as you reduce them in size, are representative because in addition to the physical aspects of thermal diffusivity, etc., there is crystallographic information which changes very often in fact. If you cool small samples, you get a structure which is not that of the bulk material, and that starts to become very serious very often at certain milligram samples.

Dr. J. Chiu, U.S.A.: I agree with all the speakers so far. My opinion is that the use of extremely high heating rates is useful in certain applications, but for a small percentage of the users. It seems to me that all the speakers concentrated on DSC or DTA, but there is another area which might require high heating rates which have not been commonly used. That is the area of TG. During the 5th ICTA in Japan, I heard quite a few papers [14] and also there are two Japanese manufacturers that actually have high heating rates in TG analyzers. The purpose for using high heating rates in TG is to substitute traditional pyrolysis-GC by a GC and to get the additional weight-change information. This is a unique advantage of high heating rates. In addition, you can have controlled heating rates (high, medium, or low) or isothermal operation. So I think there is a territory there that might be useful. The technique used by the Japanese was an infrared imaging technique. You have an infrared beam focused into the sample for extremely fast heating rates. I believe the rates they used were in the region Prof. Wunderlich was talking about. However, if we would like to apply the same type of knowhow to DSC, I anticipate a problem. Not because the heating source is not adequate; we can heat as fast as we can using an infrared imaging device or a laser beam. The problem is the detecting device. When we heat that fast, how do we know the actual temperature? How do we control heat transport reproducibly and meaningfully and make theoretical calculations from that? That is the problem. I think that there are no faster heating DSC units available at this moment, other than those in private use in laboratories of their own. Since some people touched on the use of laser fast heating, I did have such an idea, but I have not been able to do it successfully. The idea was to copy the same concept of Fourier Transform at use in IR and NMR. This relies not entirely on the detection system, but on the computerization. It uses the computer to compute rather than an electronic device to monitor. So my concept was to use a laser beam to heat up, to introduce a pulse into the sample; whether it was large or small did not matter and then you use the computer to reach in to retrieve the information just like you do for Fourier Transform IR and NMR. However, writing a specification will be somewhat different. You have to produce entirely new set of theoretical calculations in order to compute what the results mean and to reconstruct the thermogram from that. I would like to pose this as a challenge to all to ICTA members present. Who can generate the first Fourier Transform DSC?

Dr. V. Mathot, The Netherlands: I would like to know what other companies or universities have faced the same trend. In our company there is a growing interest in microcalorimeters, not only in my field, which is polymers, but also in fertilizers. In polymers I know at least one reason for that and that is because we are doing fractionation. That is a rather old technique, but there is a revival now, and connected with the revival is microcalorimetry because you would like to know what is happening during the fractionation. We are fractionating in solution, so we crystallize the polymer in solution and dissolve it, and so on, and we would like to see the whole process in our calorimeter. We would like to stir and maybe add things and so on, so, at least in our company, we are buying microcalorimeters. But then we are faced with the problem that there is only limited availability of microcalorimeters, at least in the temperature range we would like to have, that is from low temperatures to high temperatures.

Dr. Philip Gill, U.S.A.: There are a number of commercial devices that you look at, and you look at the demand for those devices. If it is growing, then we need input from people like yourself. What is the application? How is it used? Can it be developed into a technique that would make it simple, quick and give high quality data in the industrial or academic environment? I think right now, with what is commercially available, that there is a question as to whether there is a need and whether the need is satisfied.

Dr. V. Mathot, The Netherlands: Most of the industrial apparatuses have linear cooling rates, but in the most practical industrial applications you have an exponential for your temperature. Most apparatuses do not have the possibility for controlled cooling at exponential temperature rates, so we have to do it ourselves by computer. What we are missing, however, is the possibility to do this on commercial equipment to study crystallization rates, for example, on linear polyethylenes, which crystallize over a big temperature range, and to study it under practical conditions.

Dr. P. Gill, U.S.A.: I disagree that equipment is not commercially available. I do not want to make a plug, but I think with a computer now you can devise an exponential cooling curve with a device that will provide you with the coolant capacity by simply putting in multisegment steps and putting in the various weights. Obviously, depending on the slope of the curve, you are going to have to design a multipoint exponential curve, but that can be done. You have many, many segments, all of which can be built together to give you an exponential curve, if that is what you like, or you can put it on automatic and put it on blast cool. Then you do not have any control, but you will have the same exponential each time. You get control with multisegment steps put into the computer, as long as you do not exceed the specifications of the device.

Dr. K. Habersberger, Czechoslovakia: We have considered the discussion that took place in the workshop on education yesterday—the question of the need of more inexpensive, basic thermoanalytical instruments. I do not feel that there is any need to go into that, but we would like to know if anyone here would desire instruments with less comfort available for schools or for first trials of the method. Would some of you be interested in such an apparatus?

Prof. B. Wunderlich, U.S.A.: I would be interested in 32 of them for freshman chemistry.

Dr. W.-D. Emmerich, F.R.G.: What should the cost be?

Prof. B. Wunderlich, U.S.A.: About 250 dollars.

Dr. K. Habersberger, Czechoslovakia: Dr. Mackenzie mentioned in his lecture just about an hour ago that maybe this is the time again to concentrate the efforts of the producers not only on the processing of the signal, but on obtaining the signal sought, the sample holder, and things like that. Speaking about programs that straighten the baseline, maybe it would be interesting to develop a sample holder that would require less straightening.

Prof. B. Wunderlich, U.S.A.: You now suggest that $250 can be added altogether to possibly achieve something like this. What we would need is a DTA block which contains a built-in heater and the necessary thermocouples and then bring out, with a proper interface, everything to a personal computer. The personal computer that I use at the moment for my teaching costs $59 and that could be easily programmed to give a beautiful output on either a TV set or on a printer. So, I think it is possible and one should not think of being primitive; one can these days be quite sophisticated. That little personal computer has 64K memory and you can write awfully sophisticated programs for the input. I think that there exists for this computer a kit for doing thermal experiments so that it should not be too difficult to go the added step.

Dr. W.-D. Emmerich, F.R.G.: I am interested in this low-cost DTA or DSC system. From my understanding, you have to distribute it and you have to advertise it. Therefore, $250 is somewhat off, but I think you are talking about the correct order of the price. Fast quenching or fast cooling was one attraction in the steel industry in the case of dilatometry. Discussing fast heating or cooling in DSC one should study, before he starts his own work, how the steel people did it. One could get useful information from them. In discussions with Dr. Murphy and others before this session I asked what the topics would be. One subject mentioned was that for potential customers the equipment has become too expensive or they are too expensive. I agreed. As I remember, and I have now worked 15 years for an instrument company, during this period we have only about 10 to 12 letters altogether stating that my budget is this and this and I need this and this, so I know what I am talking about now. I know that is a risk and I do not want all of the prospective users to agree with me. As a potential customer you could do a good job to try to, lets say, advocate the manufacturers. You lose the competition, but there are also other possibilities. Send us letters and say I would like to do this and this and this and this is my limitation and I need only this linearity, only this sensitivity and only this temperature range. Now my budget is this and this. But, I am sorry to say, what the clients normally say is I need this minimum sensitivity and this temperature range, but the manufacturer should provide this and this and this. I hope you understand what I meant and this could be done from the customers side. If we cannot fulfill it, which is not a solution, it trains us to offer instruments which are in the system, available, which are more adapted to the need of the users. We will go through laboratories, and I did it because my mother company is doing a lot of projects around the world in the ceramic field, and see that they are equipped with tremendous amounts of fantastic instruments. On discussing with the people whether they can really use them because of manpower, spare parts, concentration, etc., 50% are not used in the full range they can cover and this is the main problem. Our job is, as a manufacturer, to produce the instrument, to sell it, and to get as much money as possible for it. So, you can use the competition and you can use the relationships with the manufacturers and tell him I can use this and this and my budget in this and this.

Dr. P. Gill, U.S.A.: I agree 100%. If you are looking for low-cost equipment, then it is necessary to sacrifice something in specifications and performance. To do that it is possible to take out something that has been added. Usually those features have been added because somebody has asked for it and when somebody wants to have an instrument, they usually do not want to sacrifice any performance. They want the maximum performance capability; temperature range, linearity, sensitivity are not going to be sacrificed. Some of the software capabilities can be sacrificed and then it is possible to meet budgets as Dr. Emmerich stated. But I think the initiative has to come from you and to force the manufacturer into the position where he, indeed, is directed to satisfy that need in terms of price and performance, to compromise, to meet the needs of your particular use. I would agree that most people would buy at a specification that is much greater than the needs of 90% of their application because they feel that maybe there is a need outside beyond their current capabilities. But if there are budget limitations, then compromise somewhat in specifications I think that the instrument can be tailored to those needs by most manufacturers.

Dr. W.-D. Emmerich, F.R.G.: We are trying to be flexible, but the company also can lose its reputation. You are asking for specialty style equipment and you calculate the price and you know you can only sell it once, or maybe twice in five years. Then you come up with a price that is so tremendous that you are not able to publish it. It is better, and let us say more diplomatic from my side of the fence, to say we cannot do it or we do not want to do it, instead of saying yes, we can do it but the price would be this and this and this. Up to a special point, it is possible, it depends on the instrument itself. When it is only a certain modification, for example, it can be done, but for the final contained instrument, let us say DSC specific heat measurements up to 3000°C, then you have to charge roughly a minimal $500000 for us to develop it and keep it running. If I published this price, you would say this company was crazy.

Dr. H.G. Wiedemann, Switzerland: I would like to raise another problem. The conditioning of the sample is, in many of the instruments today, not given too much attention. Because many of the samples are used as they come in and are not conditioned before or, if they are conditioned before and transferred to the apparatus, they have to be conditioned again, I mean the surface layers of water or gases which are at the sample. I do a lot of measurements and have shown that the differences between a conditioned sample (cleaned by drying in the instrument before the run or by a molecular beam) and non-conditioned sample are large. Does anyone do it? We are all interested in the results: what the substance does in clean or not clean conditions.

Dr. C. Murphy, U.S.A.: There was a paper by Barrall and Rogers [15] in which they got three distinct peaks from Al_2O_3 that had been exposed to laboratory vapors. After the Al_2O_3 had been run, the peaks disappeared on rerunning. If you condition a polymer sample you change things in the polymer. A recommmendation was made that you pour molten polymer into the sample holder and you cannot do that with all polymers.

Prof. H.-J. Seifert, F.R.G.: In my opinion the purity of the samples is not a problem of the producer of instruments, but is a problem of the scientist who is dealing with it. If I am doing X-ray crystallography and I have four samples, then I measure one result and I cannot say afterward it is the people that sold me the equipment, but what I have put into it. It is good in my opinion that the producers give information with the instruments coming from the scientific world, ICTA for instance, somewhat like "For Better Thermal Analysis". But in my opinion the purity of substances is a problem of the people who are measuring. What would be very important is the knowledge of the accuracy of the reproducibility of the instruments. For instance, if I am doing some thermodynamic work and I want to publish my results in a journal somewhere, say the Journal of Thermodynamics, they do not print results from me if I do not give the statistical error and say something about systematic error. You know I miss these numbers in all announcements of the producers. In connection with the Standardization Committee, we have discussed, for instance, a question of enthalpy standards. Let us assume we have five companies and from each company five apparatuses are tested. Now let us assume testing yielding results with a reproducibility for company A 10% worse than that for company B, which could happen. We have asked what should we do in the Standardization Committee. What would happen if we published that? One company would be very angry with us. And so, it would be a question of honesty with the companies from the beginning to give us these values. That is to say you are measuring under this and this conditions with this and this and this components, then you will have a statistical error of this degree. I would ask the representatives of the companies whether this is possible, or what is the meaning to this problem?

Dr. P. Gill, U.S.A.: I think your suggestion was one in which ICTA develops the enthalpy standards and then submits to each of the manufacturers to run under standard test conditions that either they define based on their standard instrument, or ICTA defines, or some agreement is reached as to what indeed are optimum conditions and then they report back to ICTA the results and precision.

Prof. B. Wunderlich, U.S.A.: The company is off the hook. I do not think it is the companies way or that they can specify what you want. What the companies specify is perfectly all right. They give you the millivolts and what the instrument can do, the rest is your job. We have done with instruments of various companies represented here measurements and I can tell you that depending upon how we used the instrument, not the instrument maker making it, we could give you a factor of 100 in the accuracy. We have done with the same instrument measurements which were precise in heat capacity to 0.1% and others which were precise to 10%, and if the company accidentally has a good operator they may give you good data. If they have their second generation technician running it because they are busy, then they will shorten their own instruments. So, I think that this is not something you can ask the company to do, and I do not think that this is something a "round robin" will ever do. If you got the wrong birds, it will not do well. So, I think that this is an important question, but this must be answered by doing research and having people who have experience tell you what the best conditions are. You see the questions on heat capacity, I can run on 1 mg or I can run on 100 mg. Already, I have a factor of 100 which is not influenced by the instrument parameters. I get 100 times the precision out of it. For heat capacity, for most samples, that is very easy and it has nothing to do with the instruments, it has only to do with me, how I make the measurement.

Dr. H.G. Wiedemann, Switzerland: Prof. Seifert, you failed to get my point. What I mentioned was not the purity of the sample itself. It was conditions to start a sample or the homogeneity of the conditions where I started the sample. I mean the atmosphere in my experiment is a substance in addition to the substance in my crucible. If I have different conditions in the atmosphere or the water layer on the substance, I can get different results with the same sample. In most of the instruments today, you are not able to condition the sample for equal starting points to compare the results with one another. That means not only the water, but $O_2 : N_2$ ratio or very pure N_2 can change a run of the same sample with the same purity very drastically.

Dr. J.S. Crighton, U.K.: We take your point, Hans. We have in fact done work using a clean environment in which we also can change the humidity and we find quite significant variations. Our main samples tend to be fibers with a very large specific surface area so your point is very relevant in our particular context and we do find very significant variations. We were forced to build, because there wasn't any other facility available, a special clean box. Our sample holder was installed inside the clean box.

Dr. H.G. Wiedemann, Switzerland: You allowed the sample to attain the same starting conditions?

Dr. J.S. Crighton, U.K.: Yes.

Dr. L. Kubicar, Czechoslovakia: I can make some remarks about accuracy. First we must distinguish between measurements of two kinds: measurements of thermophysical parameters of materials which are used for construction, for studying aging of materials, for organization of technology and so on; and then the measurements of kinetics of transformations. The accuracy for measurements of kinetic parameters must strongly depend on thermophysical parameters of materials which are studied.

Prof. W. Eysel, F.R.G.: I want to go back to one of the items discussed by Hans Seifert and this was round robins. Somehow this may turn out very much to the disadvantage of the manufacturers because always people have to select participants and we have heard (and I do fully agree) that the performance of an apparatus is not only dependent upon its properties, but also on the capability of the user and the skill of the user. Nevertheless, I think that these round robins are necessary, for example, to test, as we tried to do on a small group basis, standard materials, reference materials and potential reference materials. I think that there are big difficulties, even if the people doing that round robin try to be honest and consider everything and, if they try to stay away from comparing instruments, the results of the round robin carried out on various instruments will always contain results on the quality of the instruments, you cannot get away from that. This is a big difficulty, but I think it cannot be prevented. This is a question to the users here because I am involved in such a round robin experiment at the moment. How should we handle that?

Dr. C.B. Murphy, U.S.A.: I will answer you in part. I think one of the things you have to do is that you are going to have to get more participants in the framework of that analysis because doing it with the number employed to devise standard materials, where all you were looking for was a point on a curve and taking a temperature, was easier than this. Now you want to measure the area under the curve and get the heat content, but it is not just that. It goes back to how I weighed my sample. A lot of things are going to affect this and if it is all going to reflect back on the manufacturer, I think in justice that you must have a statistical number of equipments from each manufacturer. I know you do not have that now and I know you have some equipments where the individuals have made them themselves and they are still using them because they are very good. How do you weigh that one result against a statistical array of results from Du Pont equipment, for instance?

Prof. W. Eysel, F.R.G.: We have considered that point of course, but if you have to do the work of such a round robin it is a lot of work for the organizers. We did not want to have a statistical result of all users. We want to see how far we can go and which is the utmost precision and the best performance of the instruments. So, your have to look for those people (and we have tried to find them) who can really use the instrument and not those who are not aware of all that you can do with them. Somebody said before that many users are of this type. They buy instruments and do not know about their capability, so I think the pure statistical number is not sufficient for what you want to do your own round robin and that is the trouble. We have approached manufacturers, perhaps not at the time when we started, and not all had instruments for this type of measurement, but we are continuing this. We did not want the laboratories of the manufacturers to make the measurements themselves. We wanted to do them ourselves and be independent. For those instruments where we did not know somebody who was good, we asked the manufacturers can you tell us who is a good customer of yours and is capable of working with your instrument. In some cases, we did not receive answers. So you see the dilemma is not so easy. We should not have a completely statistical evaluation, because it will just give you an average about errors and you will never know where you will end up.

Dr. P. Gill, U.S.A.: The American Society for Testing Materials should be communicated with. They have conducted many, many round robins on thermal analysis to determine precision and accuracy for specific methods for doing purity, enthalpy, heat capacity, etc; these data are available. I know they had a lot of difficulties. They used NBS standard materials as their starting point. The data are public and the standards are published in ASTM so you may want to establish communication. Dr. Blaine from Du Pont can probably help you there, he is chairman of that committee.

Prof. B. Wunderlich, U.S.A.: I think one has to be very careful in standards and standardization because there are a good number of quantities which we want often to standardize which are fixed and that means where a round robin only brings out very little, like this polystyrene work. Unfortunately I am also a member of this and I sent in my data and I just do not believe anything decent will come out of this because this is nothing else than a temperature calibration and a temperature calibration set since 1964. We have a temperature scale and we know that water melts at 0°C to a precision much beyond all thermal analysis equipment. There is no need for any standards which are not related to that scale. The same way heat capacities have been measured to a precision of at least 0.1% by adiabatic calorimetry for a good number of samples. I think that what is necessary is to get this information available to everyone and I think that many manufacturers give you the heat capacity curves of Al_2O_3, indium, etc. The same way as heats of fusion, these are fixed quantities and there are methods which are more precise than DSC usually and we know these numbers. That means that we can concentrate on the ones which are not known and one gets closer and closer to the true value. There is no need to have many people make measurements on samples which may not be well characterized due to sample characterization, the instrument, etc. When we do DSC measurements our biggest problem always is a baseline. It was mentioned before, but I have not heard a suggestion as to how we can eliminate the baseline. The only way I know of to eliminate a baseline on present commercial equipment is to make three measurements, and almost nobody does it. Everybody is happy to make one measurement, but not three. Nobody makes a sample, a blank and a standard. Why do not the instrument manufacturers get to work and make those three measurements into one. Then automatically, the baseline is gone and much of the round robin is not necessary because then everything is very nicely enclosed in one measurement and you cannot help but be a good thermal analayst, not put by the pleasure of doing measurements three times. I think it is possible and I have suggested that a number of times. So, this is one suggestion. The other suggestion I think should upset all the instrument manufacturers, but maybe points out the difficulties of our present situation. Dr. Murphy mentioned modularization. I think that this is a very key word. At the moment, I think that the instrument makers want to do it all, make the cell, make the linear temperature device, make even the computer, write the program and let nobody else put their hands in it. Would it not be nice if we all could use a standard computer of our own choice, like the $59 one I was mentioning or the $3500 big IBM computer which seems to be more popular or any other computer, and let an independent company write the programs. Personal computers gained enormously when hundreds of people could have a hand in writing their own programs. But in most company equipment you have to buy the whole thing for, I do not know, $10 000, $20 000, $40 000, $60 000, depending on how much you want to have, and you get it all and you cannot shop around. That excludes all the small instrument makers who have a good idea for a fast DSC, or a slow one, or one which goes to low temperature, or one that goes to high temperature, which you can plug into the X company computer or Y company linear temperature programmer and so on. I think that if this modularization would be a little more common, it would be quite useful. I have the hope that with the availability of more and more personal computers this will probably develop. I don't know whether you have any comments, or whether this is outrageous to suggest.

Dr. W.-D. Emmerich, F.R.G.: I do not have a direct answer. I do not know whether it will satisfy you. Fifty percent of our sales people ask for a turn key job. Depends on different reasons whether it is the system in which we deliver, or is a project, or anything else. If we could sell thermal analysis equipment at the shop around the corner, this would be the right way, like the computers are sold now. But if you look at the market now, if the instrumentation is clear, they discuss software. Who has the better software? What is going on here? What do you have next year? How much will be the new generation of software? These are the questions. In the internal report, people are writing I prefer this and this manufacturer because of this and this and that and these arguments come up and they do not say I would recommend that we buy this temperature linearization module from that company and the computer there and the software we will do by ourselves and the furnace we will buy from XY company. Before they decide, there should be more fair and open discussion from the customer. The manufacturer should say we can do it or we cannot do it. The client should say we like this and not say this when they really want a different thing. They play with us; that is useless.

Dr. P. Gill, U.S.A.: A comment in that regard too that expands a little bit further upon what Dr. Emmerich just said and that is that users that require this kind of custom building—if they did it on their own and there was some data output and it was not quite what they expected, then they would come back to the manufacturer and say this is not right: tell me what is wrong with your instrument? When you investigate further, in fact, it is what they have done to the data subsequent to what the instrument generated. So, we have some obvious reasons for wanting to keep the software and hardware in a package. We have to support it. We have to provide application support, technical support, and theoretical support. It is critical that we are able to know exactly what is going on so we can analyze if there is a problem. We know it is the manufacturer's responsibility to correct and not some outside organization that changed it.

Dr. V. Mathot, The Netherlands: I propose that we should found a new subcommittee of ICTA to work out a unified program for the different DTA, DSC, and other equipments which may be used by every company and with the corresponding hardware interfaces. I do not agree completely with the comments of Prof. Wunderlich. There are a lot of measurements in adiabatic calorimetry made with a precision of 0.1%. It is no problem, but it is not possible for any user to get such a characterized sample to check their own apparatus and I think this is a problem. So what you need is really well-characterized materials. Let me say NBS is melting 10 tons of indium and is distributing it over the whole world to everybody who wants a sample. At this point, it is not very important whether the indium is pure to 1, 10, or 100 ppm, if it is the same charge of sample. This gives security to the user to reproduce the calorimetric scale. I think that the calorimetric scale is much more problematic than the temperature scale. The temperature scale is better established than the calorimetric scale. Sapphire is probably the best reference material.

Dr. N.J. Manning, U.K.: I would like to make a couple of comments with regard to specifications and such like. One of the problems that we have when we talk about specifications is that we have to be realistic with regard to real locations. For example, if you take a microbalance to ten different locations, you will probably be able to get results which vary quite differently in those ten locations. We have, for example, found where buildings were built on rubber mountings and they swayed with the wind; where they are built on sandy foundations, you get a lot of vibrations; where there is a type of machinery in the place, you get vibrations transmitted. What we tried to do as a manufacturer is to get some idea of what people can reasonably achieve, not necessarily what we can achieve under ideal conditions within our laboratories with extremely good balance benches and such like. What I think you want to know as users is what you can reasonably expect to achieve in your own laboratory. I think maybe that the round robin approach will give you that information.

Dr. C.B. Murphy, U.S.A.: We have heard some problems and some desires in this discussion. It is obvious that some users have needs that are not being fulfilled by the instrument manufacturers. Also, it was made patently clear that the user could not afford the cost to produce one or two of a given instrumental type. Prof. Wunderlich was not fooling when he said graduate students are not paid very much. Maybe this is an area where industry can help academe. Give a university a grant for the construction of singular equipment. The question of modularity remains. There was no resolution of this problem in this discussion. The suggestion was made that another ICTA subcommittee be established to cope with this problem. However, to give the subcommittee a manageable task, I would recommend that they consider only the task of computerization of thermal analysis equipment. A meaningful solution for this issue, satisfactory to both the users and the manufacturer, would constitute success under any set of conditions.

REFERENCES

1 R.L. Stone, J. Am. Ceram. Soc., 35 (1952) 76.
2 R.C. Mackenzie and K.K. Farquharson, C.R. Acad. Sci., Session, Congr. Geol. Int. (Algeria), 14 (1952).
3 G. Lombardi, letter to P.K. Gallagher, ICTA News, 18(1) (1985) 1.
4 R.N. Rogers, Microchem. J., 5 (1961) 91.
5 C. Mazieres, C.R. Acad. Sci., 248 (1959) 2990.
6 J.L. Martin Vivaldi, F. Girella Vilchez and P. Fenoll Hach-Ali, Clay Minerals Bull., 5 (1964) 401.
7 L. Segal and D.J. Stanonis, Anal. Chem., 35 (1963) 1750.
8 J.F. Lee, Alumina Dilution Effects in DTA, Tech. Rep. CHA-1401, Boeing Airplane Co., Seattle, WA, U.S.A., 1960.
9 W.F. Cole and D.N. Cook, Am. Mineral., 51 (1966) 499.
10 G.N. Rupert, Rev. Sci. Instrum., 34 (1963) 1183.
11 G.N. Rupert, Rev. Sci. Instrum., 36 (1965) 1629.
12 N.L. Baldwin, S. Langer, F.L. Kester and C. Hancock, Rev. Sci. Instrum., 41 (1970) 200.
13 S. Langer, N. Baldwin, P. Gantzel, F. Kester and C. Hancock, in J.T. Walker, P. Chiotti and W.N. Miner (Eds.), Proc. Int. Conf. Compounds of Potential Interest in Nuclear Reactor Technology, Edward Brothers, Ann Arbor, MI, 1964, p. 359.
14 A. Kishi, K. Takaoka and M. Ichihashi, Therm. Anal., Proc. 5th Ing. Conf., 1977, p. 554.
15 E.M. Barrall, II and L.B. Rogers, Anal. Chem., 34 (1962) 1106.

PRESENT STATE OF COMMERCIALLY AVAILABLE THERMOANALYTICAL EQUIPMENT

K. HABERSBERGER

Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2 (Czechoslovakia)

V. BALEK

Nuclear Research Institute, 250 68 Řež (Czechoslovakia)

In order to provide the readers with up-to-date information about the state-of-the-art in the field of commercially produced thermoanalytical devices, the editors have asked all manufacturers who have taken part in the exhibition of thermoanalytical instruments at the 8th International Conference on Thermal Analysis in Bratislava to provide us with documentation to the point. This request was met by the following firms:

Du Pont de Nemours International S.A. (European representatives: 50–52, route des Acacias, CH-1211 Genève 24, Switzerland);
Maple Instruments (Dr. G. van der Plaats, Philipsweg 1, 6227 AJ Maastricht, The Netherlands);
MOM Hungarian Optical Works (H-1525 Budapest POB 52, Hungary);
Netzsch-Gerätebau GmbH (P.O. Box 1460, D-8672 Selb, F.R.G.);
SETARAM (agency: 160, Bd. de la République, F-92210 Saint-Cloud, France);
Stanton-Redcroft Ltd. (Copper-Mill Lane, London SW17 0BN, U.K.);
Systag (CH-8803 Rüschlikon, Bahnhofstr. 76, P.O. Box 77, Switzerland).

Whereas only several years ago electronics was first applied in thermal analysis with solid-state temperature controllers, contemporary thermoanalytical apparatus is characterized by microprocessor control of the equipment and computer processing of the data. All those who attended the conference and visited the exhibition of thermoanalytical equipment on the occasion of the 8th ICTA will surely agree with us on this point. The application of microprocessors led to the introduction of a larger scope of temperature programs, including extreme, both low and high, heating and cooling rates. In order to ensure a constant rate of the investigated transformation, heating rate control by the investigated process itself has been used, e.g., in quasi-isothermal and quasi-isobaric thermogravimetry (MOM). The storage and processing of experimental data by means of a computer gives new possibilities for the evaluation of the results as well as for their monitoring and registration by modern techniques (video display unit, plotter). Electronic derivation of the measured thermoanalytical curves used by most manufacturers gives the possibility of resolving the smallest details of sample changes reflected by the curves.

The production program of the world-wide companies includes first of all the traditional thermoanalytical techniques like DTA (heat flux), DSC, and TG, as well as simultaneous combinations like DTA–TG or DSC–TG. Answering the demands of the scientific community some producers also offer an optional unit for simultaneous detection or analysis of evolved gas products (EGD or EGA) using a mass spectrometer, a gas chromatograph (Netzsch, SETARAM, Mettler) or a unit for the titration of gas absorbed in a suitable solution (MOM). In the program of Netzsch, a unit for the detection of radioactive inert gases (ETA) is also included.

The needs of material research are met by instruments for dilatometry and for thermomechanical analysis. Even more specialized techniques like high-temperature microscopy (Stanton-Redcroft) and X-ray diffraction (Mettler) are commercially available.

Of special interest to the potential users are the quantitative specifications, like, e.g., the temperature range of operation of the devices. Besides instruments working in the most common range, i.e., between ambient temperature and temperatures around 1000°C, devices with an extended range to either sub-zero or extremely high (even up to 2400°C, Netzsch) temperatures are available.

Practically all producers offer gas-tight systems with the possibility of carrying out the experiments either in vacuo or in a controlled atmosphere (or a gas flow). In some cases programmed change of the gas medium (SETARAM) or gas flow sensors (Maple Instruments) are provided. High-pressure measuring cells for DTA or DSC are also available (Du Pont, Maple Instruments, Netzsch).

The sensitivity of DTA, DSC and TG devices produced by renowned manufacturers is sufficient for even the most exigent experimenters. Calorimeters of various kinds are commercially available, calorimeters of the Calvet type being produced, e.g., by SETARAM. The safety calorimeter (Systag) is suitable for simulating operating conditions including the use of large samples (20–50 cm^3) and the investigation of explosive materials. This instrument uses special measuring cells (SEDEX, SIKAREX).

Instruments for measuring other thermophysical properties of solids are usually single-purpose devices. A special vapor pressure balance is designed for measurements in high vacuum (Netzsch). A smoke chamber for the establishment of smoke properties of materials (also on exposure to flames) as well as other flammability test equipment should be mentioned here (Stanton-Redcroft). Among the accessories, presses for the customized manufacture of sample pans (e.g., Maple Instruments) are available.

A much discussed question at the workshop on trends in thermoanalytical instrumentation was that of the modular design of the equipment. Such a design leads to the possibility of the successive completion of the equipment as well as to high versatility in its application. Examples of such a modular design are to be found, e.g., with Du Pont, SETARAM, Stanton-Redcroft.

Another need expressed at the workshop on education at the 8th ICTA should be mentioned, namely that of a simple low-cost thermoanalytical device (e.g., for DTA) for the training of students. Such devices would also be suitable for low-budget laboratories in developing countries, for routine quality checks, or for preliminary trials of the application of thermal analysis. A low-cost DTA device has been offered, e.g., by Netzsch and Maple Instruments.

This short note cannot be a comprehensive survey of the commercially available thermoanalytical instrumentation, its purpose being just to point out the present trends and the variety of the equipment available for thermal analysis and related methods. The authors would like to thank all the manufacturers who have kindly met our request by supplying us with information on their recent manufacturing programs.

A small part only of this documentation could be used for this brief note. However, interested readers will certainly find helpful assistance from the manufacturers when asking for detailed information directly.