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REPORT ON THE WORKSHOP: THE USE OF COMPUTERS AND DATA STORAGE IN EVERYDAY THERMOANALYTICAL PRACTICE

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INTRODUCTION

The workshop was organized under the four topics, used as headings in this report. Each was summarized briefly by the chairman and then discussed in general. There were about 75 participants in the audience. The following is a synopsis prepared from the tape produced during the discussion. Statements which may be used as suggestions for future consideration by ICTA are printed in italics. The large interest and lively audience participation has shown "use of computers" to be close to the heart of many thermal analysts. *If the format of workshops is to be continued in future meetings, this topic should be placed high on the list of possible discussions.*

DATA ACQUISITION AND DATA HANDLING

B. Wunderlich, RPI, Troy, NY, U.S.A.: Heat conduction and electrical compensation DSCs are ideally suited for computerization. Both the temperature signal (given as a thermocouple output, a resistance bridge balance, or an analog or digital programmer output) and the measured amplitude (always an analog output proportional to ΔT) must be properly digitized over fixed time intervals for handling by the computer. The first effort at Rensselaer to design a computerized DSC (Perkin-Elmer DSC 2) was made in 1974–1976 with a simple Hewlett-Packard 9821A electronic calculator [J. Therm. Anal., 13 (1978) 71]. A series of slides of the more advanced Laboratory Microsystems 1000-DSC data station were shown as illustration of data acquisition and data handling [J. Polym. Sci., Polym. Phys. Ed., 22

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(1984) 379]. The system is based on a 16 bit A-to-D converter and a Z-80 based Chromemco microcomputer with a 65 kbyte random access memory. Presently we are, again with help of Laboratory Microsystems (P.O. Box 336, Troy, NY 12181, U.S.A.), going to the third generation computer for the same Perkin-Elmer DSC, using an IBM microcomputer. The major progress in these developments are faster and more convenient data handling, not more precise measurement. The major problem is illustrated by the sequence of slides. Every possible alternate evaluation of the data must be provided for and run through each time. The final, hard copy output must be able to satisfy the different needs for reports, slide representations and publications. Now let us start with questions, problems, comments, etc.
M.E. Brown, Rhodes University, Grahamstown, South Africa: Is a 16 bit A-to-D converter necessary or would a 12 bit one be satisfactory, and what about the sampling rate?
B. Wunderlich, RPI, Troy, NY, U.S.A.: A 12 bit A-to-D converter should be satisfactory. [Added comment: 16 bits can yield a precision of 1 in 65 536; 12 bits, 1 in 8192, since typical DSC precision is at best 0.1% (1 part in 1000) and 0.5 K out of 1000 K (1 part in 2000) 12 bit systems should be satisfactory.]

Sampling rate is one of the points I would like to suggest for discussion. Since an A-to-D converter samples only over a short time interval, it is necessary to collect many data points to reduce the statistical error and then cut-down the large volume of data by averaging appropriately. For heat capacity measurements, for example, it may only be necessary over wide temperature ranges to provide one point every 10 K, but this point must contain *all* experimental information, a fact often overlooked by researchers and programmers alike. We could show [J. Therm. Anal., 13 (1978) 71, 179] that with a computer averaging system an error reduction for the data by 1/3 to 1/5 is possible. Naturally this improvement is limited to the statistical sampling error and does not affect systematic errors.
N.J. Manning, Stanton-Redcroft, London, U.K.: Are there any comments on the use of voltage-to-frequency converters? We find that a voltage-to-frequency converter averages the signal over a time period [since the digital output is just a count of cycles per time unit]. Also, the resolution can be very high, one part in 10^6 is possible. Adding a voltage-to-frequency converter to each input, one approaches the analog system and has a continuous monitoring of the inputs, but such an ideal system may be expensive.
E. Gmelin, Max Planck Institute, Stuttgart, F.R.G.: First, a general comment, one could call this first topic also a "Hardware" (data acquisition) and "Software" (data handling) discussion. Now, let me draw attention to the point that there are immense numbers of computer systems generated in company laboratories, universities, and by equipment manufacturers. In most of these systems to date, data acquisition and data handling are

combined. *For the future development, especially in light of increasing development of networks of computers in and between larger institutions, it is important to produce hardware which can be combined with any type of software. This means that the strong trend to standardization of hardware and also computer operating systems should be extended to the software.* I would wish to be able to take programs from any software library which are able, for example, to calculate Debye functions, thermodynamic functions, curve fitting parameters, Bessel functions, etc., and combine them with instrumentation developed by various manufacturers. Furthermore, one would like to avoid the enormous cost and inconvenience involved in updating computer systems due to non-compatible software. Note that we have in the last seven years been using three different computers on the same calorimeter because of the fast hardware development.

B. Wunderlich, RPI, Troy, NY, U.S.A.: I think this important point should be impressed by the users onto the hardware producers. Present trends are still to offer mainly fully integrated hardware/software systems, incompatible to other software and often even inaccessible to easy modification. In our case we quite similarly are working on the third computer for the same calorimeter because of quick advance in technology.

N.J. Manning, Stanton-Redcroft, London, U.K.: A further point concerns calibration. Many people used to calibrate their recorder systems only very few times a year. In the computer systems it is easy to *include quick calibration routines*. It is important to make sure that the results are as accurate as possible.

G. Varhegyi, Hungarian Academy of Sciences, Budapest, Hungary: We are using a thermobalance/mass spectrometer system with the MS under full computer control. During the MS settling time the computer averages the data flow from the analog-to-digital converter (pressure, temperature, and weight) so that every point is composed of several thousand data. This gives a very good curve for kinetics evaluation, for example. If we need numerical differentiation for DTG, however, we need further smoothing. My question is: *What is best, using digital filters or smoothing using the more complicated spline functions*?

J.C. van Miltenburg, University of Utrecht, Padualaan, The Netherlands: I am not a mathematician but am very satisfied with the numerical Savitzky–Golay method. Using it for smoothing our first- or-second-order differentiation the results are very good [Anal. Chem., (1964) 1627].

E. Koch, Max-Planck Institute, Mülheim/Ruhr, F.R.G.: I must agree with this statement. We also have good success with this method and see no need to go to others. Concerning the amount of data, we take about 2000 counts per signal, but in the subsequent integrations and calculation of rate constants it is not too good to have too small intervals; we restrict the calculation to only 150 points per experiment for optimum results.

P. Fellner, Inst. Inorg. Chem., SAV, Bratislava, Czechoslovakia: One cannot

just find one procedure for all cases. As we said before, it is important to collect as many data as possible, then if your computer is fast enough, more sophisticated data handling procedures are called for. But, one should not overprogram, otherwise it may not be possible to understand what one gets out of the computation.

B. Wunderlich, RPI, Troy, NY U.S.A.: In our data bank efforts we use spline functions to fit the large variety of differently reported data to a uniform temperature interval data table [J. Phys. Chem. Ref. Data, 10 (1981) 89]. In measurements by DSC, one makes three separate runs and these are to be combined by the computer. One must watch that all three are properly calibrated and averaged. Recently we found that it may be possible to get perhaps to a precision of $\pm 0.1\%$ in heat capacity, but this calls for continued supervision of the instrument by the operator [J. Therm. Anal., 29 (1984) 1369]. Conditions like the thermal history of the instrument cannot be handled by the usual software, it must be possible to override in such cases the normal, programmed operation.

M. Richardson, National Physical Laboratory, Teddington, U.K.: Perhaps the best advice I can give is not to use any of the manufacturers' programs. I myself would be delighted to push just a few buttons to analyze, for example, a peak. I see programs which permit me, by setting two cursors, to get an area. I am sure this area is correct, but what does this area mean? It may have no thermodynamic validity. Thermodynamics is a simple science, although it often turns people off; it is, however, much less complicated than many procedures which go into computer programming. With little effort *it should be possible to get quantitative data which have thermodynamic significance and produce not only pictorial representations. Such analysis is needed to convince chemical thermodynamicists that thermal analysis is a genuine science.*

G. Varhegyi, Hungarian Academy of Sciences, Budapest, Hungary: Is it of interest to compress a thermal gravimetry curve into 25 data points? We worked out such a simple program using a 25th degree polynomial 12 years ago, but did not publish it in a journal in English. To avoid the spurious waves in the curves caused by the experimental errors, which give problems in evaluating DTG, we chose the polynomial which is close to the actual points, but has maximum smoothness as defined by the second differential quotient.

B. Wunderlich, RPI, Troy, NY, U.S.A.: The question of representation of data in the literature must naturally be left to the author (and the editor). I would like to comment that on reviewing even only few years old literature, one finds that much of the discussion is already outdated, but the data may be useful for a much longer time. Unfortunately one finds today the trend to take much less care in description of instrumentation and data than in discussion. *It would be useful to develop standards for representation of instrumentation and data.* Even "well-known manufacturers" in one country or at one time may be impossible to trace somewhere else or at a later time.

B. Wunderlich, RPI, Troy, NY U.S.A.: In a series of slides the workings of the heat capacity data bank and its development into the Advanced THermal Analysis System was illustrated. A summary, concentrating on the computer aspects of this system was printed in Am. Laboratory [14(6) (1982) 28]. The data bank in its printed form is published in the J. Phys. Chem. Ref. Data (1981–83). Once in existence, the data are used to improve our understanding of the theory and develop empirical as well as theory-based prediction schemes. *The enormous benefits from such a critical collection of the effort of the whole community of researchers in the field should make the support of data bank efforts in thermal analysis a major topic for ICTA.* Computers are indispensable for its working and continuous updating.

E. Koch, Max Planck Institute, Mülheim / Ruhr, F.R.G.: The main goal of our activities in the field of thermal analysis is to find the best reaction mechanism in all-liquid systems from TA curves. Our efforts started in 1970 with an analog computer and progressed through digital calculators to the present WAX11 system. To establish a data bank for kinetics we developed a strategy to store up to 50 parameters, divided into general parameters such as amplitudes, peak areas, baseline, and characteristic temperatures; activation data based on simple first- or-second-order kinetics; and special data; i.e., shape indices, etc., related to mechanisms. These parameters are then derived for many different experimental conditions such as different concentrations. To answer the question of the best model, the computer is asked to generate for all possible reaction models the same general parameters. Rules for extension to $N + 1$ reactants are being worked on. By comparison with the data bank it is possible to classify reasonable mechanisms within a given reliability. Only then, after one knows what a reasonable model is, are useful activation energies computed.

B. Wunderlich, RPI, Troy, NY, U.S.A.: This looks like the development of a double data bank for kinetics. Experimental information and data on models are stored separately and can be made to match for computation of activation parameters and evaluation of best mechanisms. I think this is perhaps a reasonable approach to a kinetics data bank. Without a universal model, kinetics data banks would be quite useless.

P.D. Garn, University of Akron, Akron, OH, U.S.A.: One of the problems which faces us when dealing with kinetics is the variety of processes, in need of description. It is not that polymers and inorganic processes must be separated, but reversible, and partially irreversible processes, in general, must be considered differently. The situation is and remains confused until simple, straightforward problems are solved. I cannot think of a more useless data bank than one of activation energies. It is, however, possible to design a proper menu to call up activation energies for different models from the experimental data. We can look forward with some hope towards a

useful system. Clarifying the problem is of importance for this meeting [see also the workshop on kinetics].

J. Šesták, Czechoslovak Acad. Sci., Prague, Czechoslovakia: I would like to call attention to the fact that there are two applications where computers are of use. First, for the pure data bank, and a good number of these exists already for thermodynamic data. Then, for the mathematics used to evaluate the data. The computers are so powerful today that we can calculate practically whatever we like, and we should discuss what methods are available, rather than discuss kinetics models. Different methods of statistics, for example, may lead to different answers.

L. Kubicar, Slovanska Akademia Vied, Bratislava, Czechoslovakia: We have set up a data bank in our laboratory for heat capacity, thermal diffusivity, and thermal conductivity since we measure 600 points in 8 h and have the equipment running 24 h a day. The data base is structured to contain characterization of sample and measurement, region of measurement, characterization of data, and data.

G. Varhegyi, Hungarian Academy of Sciences, Budapest Hungary: A comment about statistics *as we use in our data collection averaging over perhaps thousands of points, I do not believe that statistical methods are applicable any more to further data treatment* because the random error does not exist any more. Now the errors are practically only systematic, such as baseline errors, etc.

E. Gmelin, Max Planck Institute, Stuttgart, F.R.G.: I would like to propose as a project to ICTA or one of its committees to report critically on the number of existing data banks on thermophysical data, how to use them, their availability, etc.

B. Wunderlich, RPI, Troy, NY, U.S.A.: I would like to suggest that a data bank in itself serves only half its purpose if it is not coupled to prediction schemes. If we can use data on, let us say, 1000 materials to predict unavailable data on 10000 others, the value of the data bank is greatly enhanced. In the polymer field with practically unlimited copolymerization possibilities for industrially important materials this is particularly important.

P.D. Garn, Univ. of Akron, Akron, OH, U.S.A.: Certainly a data bank which includes as many basic data as possible will be a great help in the prediction of properties, but I would look with great fear upon any data bank which would also try to perform the prediction. The prediction is still in the foreseeable future best left to the human mind. We have some superiority.

B. Wunderlich, RPI, Troy, NY, U.S.A.: This brings us to the discussion point: who makes the mistakes, the computer of the operator. The answer is that the mistakes are always the fault of the operator. If there is no prediction scheme, well founded in theory, then one should not have a computer predict data. There are, however, many such examples of well-known prediction schemes (see for example A. Bondi, Physical Properties of

Molecular Crystals, Liquids and Glasses, Wiley, New York, 1968; D.W. van Krevelen and P.J. Hoftyzer, Properties of Polymers, Elsevier, Amsterdam, 1972).

P.D. Garn, Univ. of Akron, Akron, OH, U.S.A.: This is not prediction, this is simple calculation.

COMPATIBILITY OF COMPUTERS AND COMPUTER NETWORKS

B. Wunderlich, RPI, Troy, NY, U.S.A.: We have heard already some remarks about compatibility or the lack of compatibility of computer programs. This becomes particularly serious as one wants more and more to link computers and take part in ever-increasing networks of computers. I think that turn-key systems, which include measuring instrumentation and data handling, but are inaccessible to the user for modification, will be losing their appeal as one needs more flexibility and more systems become available which permit changes by the user.

R.M. Flynn, Science Appl. Research, Goddard Space Flight Center, Greenbelt, MD, U.S.A.: We work primarily with main-frame computers, such as WAX 11780, IBM 3081 and 4341, and XEROX Sigma 9. Many of the problems of compatibility between these have been worked out; the computers can talk to each other. Certainly one must make changes in the bit configuration, but there are programs written to do this. The individual does not have to do the same work again. The problem may be to get at these programs since they are not universally available. The trend is, indeed, to have different computers speak to each other. Unfortunately, the computers are not changing themselves to be completely compatible.

Another point along the earlier comment of Dr. Richardson (above). Some present-day software systems are already commercially available which permit you to make software changes. This is what many experimenters like. Others may not want to get involved in such changes, perhaps they do not have the expertise to do so. There are movements in the direction many of us want.

G. Varhegyi, Hungarian Academy of Sciences, Budapest, Hungary: What program language is best used? I am writing in an old form of Fortran, but would like to write in such a language that others can use the programs.

E. Gmelin, Max Planck Institute, Stuttgart, F.R.G.: Perhaps the question one should ask is not what programming language to use, but which operating system. Compatibility is much more connected with the operating system than the programming language. Most personal computers today can be run in any of the common languages. In our institute, which is one of about 600–700 people, we have decided, for example, not to buy any instrument which has no IEEE-bus compatibility and no computers which do not have a standardized system. Which system to choose for an institution may be

individually different, but some of the present common systems will probably remain supported for a long time.

G. Varhegyi, Hungarian Academy of Science, Budapest, Hungary: To the topic of computer networks, I do not see any need for the connection of a data bank to such network. We find that receiving, for example, an annual update to our mass-spectra library by floppy disc through the mail is quite sufficient.

B. Wunderlich, RPI, Troy, NY, U.S.A.: Although it may look cheaper to get a data bank update by mail, one must consider that this is only so in the specific chosen circumstances. A computer network could serve you with all data banks. In addition, it can put abstracts such as Thermal Analysis Abstracts (in the future), Chemical Abstracts and increasing numbers of journals in a searchable form at your fingertips. One can then have a "superlibrary" and all data banks at an inexpensive terminal. Furthermore, present planned new computer networks would charge only computer-connect time, i.e., the time during which actual data transfer takes place, omitting the long times needed to read transferred data and to make decisions. This allows a very economical information transfer even to the poorest nations and will certainly be cheaper than transfer of hard copy or computer discs of all the data banks and literature which may be needed only occasionally. The development of such networks for science information is, however, somewhat slower than we hoped when we designed our data bank some years back. *ICTA should perhaps provide an awareness bulletin of development of networks of interest to the thermal analyst.*

TEACHING WITH COMPUTERS

B. Wunderlich, RPI, Troy, NY, U.S.A.: The computer provides a new tool for teaching. I feel its importance may be at the same level as the first introduction of the mass-produced book in the 15th century. At that time the teaching profession must have felt threatened (as one may feel perhaps today) because all material worth learning was, in time, available in form of books. As it turned out, only a very small fraction of the population was able to develop into autodidacts, instead, the book became the most important tool to learn in conjunction with a teacher. Similarly, I think that the computer will become a most important teaching tool. The computer lecture is not equivalent to a live lecture or discussion, but, if it is used well, can lecture to the student using audio tape, can have limited dialogue with the student, providing questions and answers, can teach the student only what he/she needs to know by multiple level lectures and exercises, can check the performance by evaluating student input, and provides a one-to-one study situation. Specially this private learning step, where, depending on personal factors, the student may have to go over certain portions many times and

may skip over others quickly, is suited for computer guidance. I think the computer, especially in the form of the personal computer, will revitalize and expand the learning. It might even generate an expanded group of autodidacts. The computer is also capable to combine all audio-visual techniques in the lecture room. I use, for example, a small personal computer system (64 K RAM, 6502 MPU) which can combine all audio-visual needs for a large lecture room. The output is displayed by a series of standard 25-inch TV monitors. Demonstrations, overhead texts, etc., are shown by the computer directly with the possibility of partial reveal of text, scrolling and side-way shift, as well as introduction of a pointer. Movie clips and still-photographs are shown by an integrated, 1/2-inch video recorder. The computer, by appropriate programming, offers a practically unlimited flexibility. Being a "personal computer" it is also possible to quickly incorporate changes into the program, let us say the evening before, by adding a new text-overhead, a new video-clip, or via video camera a new photograph. Programming a new demonstration or simulation may take more time. It is of importance to not use exclusively prepackaged programming for such teaching efforts because these are, at least presently, repetitive. As one learns to develop ones own programs, one can see the possible educational advantages and make use of them while programming. Extending such systems on which I have worked now for only about three years, one can easily dream of instant calls to data banks and libraries in the study room and of immediate access to lectures by any authority. It should even be possible to have the expert working in a research lab not connected to a teaching facility provide his/her knowledge world-wide via computer network. I am sure such development will change our ways of learning. In particular, it will ease the continuous learning and updating process in todays quickly advancing society. One of the best things is that in order to take part in this perhaps biggest advance in teaching, you need only an inexpensive personal computer and a telephone line. For the first time, all countries can take part in this information exchange.

At the end of the discussion an example excerpt of the computer-assisted audio course on "Introduction to DSC" was displayed on the overhead monitors. The video tape of the computer output was made available through the courtesy of Dr. H. Wiedemann of Mettler. The full course in an early version was on display at the 7th ICTA in Kingston. Details are available upon request from my office.

CONCLUSION

The workshop produced a number of suggestions, aired a number of fears and hopes, provided some expertise, and enabled the exposition of some dreams. I hope to speak in the interest of all participants when I wish for an update in Jerusalem in 1988.

REMARKS ON COMPUTERIZED STATISTICAL ANALYSIS

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Modern computerized techniques have proved to be efficient in bringing an improved quality to the measurement process, data collection and pretreatment, in creating technically oriented data bases, etc. On the other hand, their impact on the methods of extracting information from experimental data is still negligible. Up to the present day there are methods employed on modern fast computers that have their origin in manual calculations under idealized assumptions. This has resulted in the statistical treatment of experimental data being the weakest link in the logical chain "project of experiment–measurement–information extraction—interpretation of results".

In this contribution the area of regression analysis will be dealt with, where the discrepancy between the degree of knowledge and the practical techniques actually in use seems to be the most apparent. Most programs for regression analysis utilize the classical least-squares technique without verifying the assumptions leading to relevant results. It is known that the position of only one point from, e.g. fifty, can cause even a change in the sign of the regression curve (provided that the point represents an extreme). So far when robust techniques, e.g., the classical Huber M estimates, have been applied only the influence of outliers (in the y-direction) is eliminated and the extreme points in the x-direction (i.e., points with high leverage) remain influential. However, only modern robust regression techniques with bounded leverage satisfy practical requirements, being resistant to all types of influential points.

In our opinion, the robust regression methods are, to a certain extent, a matter of fashion. The reasons are as follows:

(1) they are robust to all types of influential points (even to those which are correct);
(2) with incorrectly specified models they do not run properly (it is known that points that are strongly influential in one regression model may be acceptable within another model);
(3) additional statistical analysis of models (interval estimates of test constructions) is complicated.

A more acceptable system appears to involve regression diagnostics, which permit both the identification of different types of failure of least-

squares assumptions (such as autocorrelation, heteroskedasticity, incorrect model specification and influential points) and the partial construction of regression models. However, these procedures are restricted to interactive data processing. In performing batch techniques, a number of advantages of regression diagnostics are lost. If follows that the benefits of regression diagnostics may be used efficiently with personal computers.

Practical problems lead predominantly to nonlinear regression models. However, even here selected methods of regression diagnostics may profitably be applied, the selection of a measurement model being a specific task in solving nonlinear regression problems.

The classical assumption of an additive measurement model (i.e., additive error action) is in many respects limited. The main reasons are that in many instances data cannot be negative (this is possible within an additive model even though the probability of such an eventuality is insignificant) and, provided that the measured quantities cover a range of several orders magnitude, the assumption of homoskedasticity can usually be held with difficulty (rather the relative accuracy is kept constant).

The application of a multiplicative measurement model suppresses both of the above restrictions (the data remain positive and the relative measurement accuracy remains constant). Further, from a numerical viewpoint, the treatment of a regression problem for the multiplicative measurement model does not appear be substantially more complicated.

In our poster presentation we outlined a simple technique that enables one to distinguish between the additive and multiplicative measurement models [1].

The last problem area connected with regression analysis is the choice of the type of regression model. In many instances this stage of regression analysis is a priori being solved and rather the consistency of the model with the data has to be judged. Here many approaches may be chosen, according to the aim of the regression analysis. Provided that data smoothing with subsequent integration (derivation) is carried out, the use of piecewise regression models, such as spline polynomials, is of merit. Even though the advantages of spline polynomials in comparison with classical polynomials are known, they do not occur in standard software for data regression analysis, hence their limited practical use. However, spline polynomials are extremely suitable for applications where the accuracy of measurement at individual experimental points is known. Moreover, one may profit from their properties in constructing adaptive models of a complex dependence for subsequent derivation and integration analysis.

From what has been said, it follows that there are a number of useful regression procedures that meet the requirements placed on experimental data treatment. In order to extend these techniques in practice, the following should be undertaken: completion of user-oriented software of all computer types for the laboratory with corresponding programs (software for profes-

sional experimenters) and familiarization by the experimenters with the logical principles of improved statistical methods and the presentation of results. This is the only way towards an adequate implementation of computers in the field of statistical analysis of experimental data.

REFERENCE

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NOTE ON THE DISTORTION OF TA CURVES BY TRANSPORT PHENOMENA

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Attention has been drawn by Holba [1] to the unfairly neglected distorting effect of the apparatus on the curves of EGA and related methods. Some special cases of this problem have already been considered, e.g., by Vachuška [2]; however, there seems to be no explicit and general approach at hand so far.

Let the carrier gas flow with a velocity $\mathbf{v}(\mathbf{x})$ from the sample chamber (volume V_s) to the detector (volume V_d), the centre of which is placed at the point $\mathbf{x}_d$ relative to the centre of the sample chamber. The time dependence of the detector response, $f(t)$, can be expressed by the equation

$$f(t) = \int_{t-t_d}^{t} \int_{V_d} \sigma[c(\mathbf{x}, \tau)] \, d\mathbf{x} \, d\tau \tag{1}$$

where t_d is the time constant of the detector and σ is the appropriate function (e.g., in the simplest case, multiplication by a constant). For $c(\mathbf{x}, t)$, the following equation must hold:

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} + \operatorname{div}[c(\mathbf{x}, t) \cdot \mathbf{v}] = \operatorname{div} \mathbf{j} + \eta(\mathbf{x}, t) - \zeta(\mathbf{x}, t) \tag{2}$$

where $\mathbf{j}$ is the diffusion flow vector, $\eta(\mathbf{x}, t)$ is the source function determined by the kinetics of gas evolution in the vicinity of the sample and by the gas desorption anywhere on the path to the detector and the ditch function $\zeta(\mathbf{x}, t)$ is determined by the kinetics of, e.g., radioactive decay of the measured gas and of its adsorption on the surface of the apparatus.

In eqn. (2), the second term on the left-hand side:

$$\mathrm{div}[c(\mathbf{x}, t) \cdot \mathbf{v}] = c \cdot \mathrm{div}\, \mathbf{v} + \mathbf{v} \cdot \mathrm{grad}\, c \tag{3}$$

reduces to $\mathbf{v} \cdot \partial c/\partial \mathbf{x}$ at constant $\mathbf{v}$; this condition is rarely met, however, even for purely laminar flow [2] of the carrier gas. On the other hand, the term

$$\mathrm{div}\, \mathbf{j} = \mathrm{div}[D \cdot \mathrm{grad}\, c] = [\nabla D]\ \nabla c + D\, \nabla^2 c \tag{4}$$

reduces to $D\, \partial^2 c/\partial \mathbf{x}^2$ for a constant diffusion coefficient.

Ignoring the adsorption–desorption process, we find the source function to be zero everywhere except in the vicinity of the sample. Reducing the sample geometry to a point at $\mathbf{x} = \mathbf{x}_0$, we can write the source function in the form

$$\eta(\mathbf{x}, t) = \delta(\mathbf{x} - \mathbf{x}_0)\phi(t)/V_s \tag{5}$$

where $\phi(t)$ is the true gas-evolution function and $\delta(\mathbf{x} - \mathbf{x}_0)$ is the Dirac delta function.

Considering emanation thermal analysis, the ditch function is simply the radioactive decay of the measured gas, i.e.,

$$\zeta(\mathbf{x}, t) = \lambda c(\mathbf{x}, t) \tag{6}$$

In such a case, eqn. (2) can be written as

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} = D\frac{\partial^2 c(\mathbf{x}, t)}{\partial \mathbf{x}^2} - \frac{\partial c(\mathbf{x}, t)}{\partial \mathbf{x}} + \delta(\mathbf{x} - \mathbf{x}_s)\varphi(t)/V_s - \lambda c(\mathbf{x}, t) \tag{7}$$

and solved for the explicit form of $\rho(t)$.

An even more general if implicit approach to this problem has been proposed recently by Beckman and co-workers [3,4]. The detector response, $\mathrm{f}(t)$, to the true gas evolution from the sample, $\phi(t)$, is expressed in general by the Fredholm equation of the first kind:

$$\mathrm{f}(t) = \int_{t_0}^{t} K(t, \tau)\phi(\tau)\, \mathrm{d}\tau \tag{8}$$

where the kernel $K(t, \tau)$ represents the distorting effect of the apparatus. In the numerical approach, $\mathrm{f}(t)$ and $\varphi(t)$ are represented by column vectors of their N discrete values; $K(t, \tau)$ has then the form of an $N \times N$ square matrix, the elements of which can be obtained from the detector response $\mathrm{f}(t)$ to a known $\phi(t)$ (e.g., a 1-s pulse of the gas injected artificially into the sample chamber) using eqn. (8). The proposed method has the merit of generality and viability, provided that a solution of eqn. (8) does exist. It can shown rigorously, however, that this is not generally the case, which leaves some doubt about the physical meaning of eqn. (8). Nevertheless, the examples of curve reconstruction given in ref. 4 show the viability of the method and the dubious value of any kinetic analysis by EGA and related

methods neglecting the corrections to the curve distortion by the transport effects.

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