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DATA ACQUISITION AND ANALYSIS FOR THERMAL ANALYSIS, BASED UPON THE FLUKE 2452 SYSTEM *

PATRICK K. GALLAGHER
AT & T Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)
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ABSTRACT

A system for the collection and analysis of data from a wide range of thermoanalytical instruments is described. The system is capable of simultaneously collecting data for evolved gas analysis, thermogravimetry, differential thermal analysis, differential scanning calorimetry, and dilatometry while manipulating, listing, displaying, plotting or storing data from previous experiments. The system is based upon a Fluke 1722A controller which off-loads programs to various microprocessors. These collect and store data from each instrument. The stored data can then be retrieved and processed at the operator's convenience. Therefore, it is possible to concurrently process data from previous experiments utilizing the extensive computational capabilities of the 1722 and its peripherals.

INTRODUCTION

The general class of techniques encompassed in the generic title of thermal analysis has risen dramatically in prominence over the last quarter century. Because of the generally methodical nature of the associated data collection and analysis coupled with the occasional complexity, such as for kinetic analysis, these techniques have represented ideal candidates for the application of computers and microprocessors. This marriage of computers and thermal analytical instrumentation has further accelerated the growth of these methods. Not only has the operation of the instrumentation become more convenient but the quality and quantity of the data are significantly enhanced. It therefore becomes feasible to undertake studies that would have been impractical prior to these times.

During the courtship period (the late 1960s and early 1970s) of this relationship between thermal analysis and computers, investigators developed their own unique hardware and software for the purpose. Some of the earliest reports described A/D converters which read two channels of data

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sequentially onto punched paper tape [1]. This was later improved to read four channels simultaneously onto magnetic tape [2] which represented an improvement in speed, reliability and quietness. In these early efforts the data were merely collected and stored in the laboratory while large in-house, main-frame computers were relied upon for the analysis, plotting, and storing of the data.

By the mid 1970s the major manufacturers of thermal analytical instrumentation had deciphered the handwriting on the wall and began to offer combination packages of their instrument with another supplier's programmable calculator and some software. This has, of course, progressed and evolved into the sophisticated packages currently available from virtually all manufacturers of thermal analytical equipment. Simultaneous with this practice of incorporation by the manufacturer, was the continued trend by some thermal analysts to proceed independently. By the 1980s there were many commercially available data acquisition systems and dedicated computer systems which could readily be adapted to provide flexible and powerful support of most analytical instrumentation. It is the purpose of this paper to describe one such possible system.

DESCRIPTION OF THE SYSTEM

A block diagram of the overall computerized thermoanalytical system is presented in Fig. 1. The six thermoanalytical instruments which are connected to the system are indicated across the top and bottom of the figure. The lines in pairs represent analog inputs, usually those which would have gone to an analog recorder. Single lines represent digital connections via either an IEEE-488 or RS-232-C link. The dashed lines indicate the physical transport of the 5-1/4 in. floppy disks between the dilatometer in a separate laboratory and/or the archive collection of disks.

The heart of the data acquisition and computer system is the Fluke Model 1722A Instrument-Controller which is a 12 MHz, 16-bit computer based upon the Texas Instruments TMS99000 microprocessor. As configured herein, the computer includes dual IEEE-488 and dual RS-232-C ports; a 400 Kbyte, dual-sided, 5-1/4 in. floppy disk drive; 1.4 Mbyte of RAM; a real-time, non-volatile calendar and clock; and a touch-sensitive, high-resolution-graphics CRT display. Software enhancements include a basic compiler with word processing and an elementary graphics package. The major external peripherals are a Hewlett-Packard 9872C plotter, Winchester 5 Mbyte firm disk, and a Fluke 1776A printer.

The ability to run the various instruments separately and simultaneously with data processing is achieved through off-loading the appropriate program for each instrument into the Fluke 2400A microprocessors. These devices each contain the A/D converters (resolution of 1 part in 10^5, e.g., 1

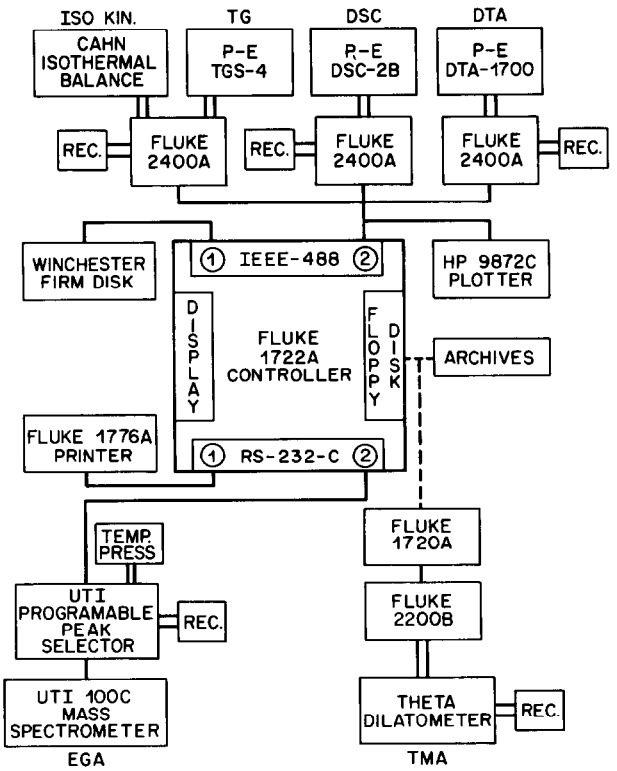

Fig. 1. Block diagram of the computerized thermal analysis system: (=) analog connections; (———) digital connections; (- - - - - -) physical transport via floppy disks.

μV in 0.1 V), thermocouple linearization and compensation, D/A converters, scanners, clock, storage (21 Kbyte user defined), status alert, etc., necessary to collect the analog signals and convert them to the desired units while simultaneously outputting the desired analog signals to a recorder for real-time monitoring of the experiment. The desired data are available for transfer to the 1722A computer at any time. This transfer is normally made at the operator's convenience after the experiment has been terminated. In general, the raw data files are archived on floppy disk for future recall as desired.

The EGA apparatus has been described in detail elsewhere [3,4]. The UTI Programmable Peak Selector acts in the same capacity as the Fluke 2400, collecting and storing the desired data. Rather than being programmed from the Fluke 1722A, however, it has its own keyboard and programming controls. The dilatometer is located in a different laboratory and has its own self-contained but less powerful data acquisition system. The expansion/temperature data are collected on a floppy disk if desired which can then serve as an input into the 1722A computer and its peripherals for subsequent processing. For those who do not require subsequent data

processing, the output is available on printed tape from the Fluke 2200B and as an analog trace on the x–y recorder.

SOFTWARE CONSIDERATIONS

The Fluke 1722A can be obtained with either (or both) a FORTRAN or BASIC compiler. The particular system described herein is operated in the manner where the source files, written in BASIC, are maintained on floppy disks in archive and the compiled versions are stored on the firm disk along with the operating system ready for instant use. Whenever possible the data files are manipulated in the RAM where access times are fast and there is no disk wear.

Naturally, a prerequisite for choosing the independent route over the packages supplied by the manufacturers of thermoanalytical equipment is the ability to generate the appropriate software or at least that part directly associated with the thermoanalytical applications. Considerable effort is necessary initially to reach a satisfactory operating level. The advantage is that of providing exactly what the specific operator or application requires along with a better understanding of what is going on during the operation. The computer will nearly always provide a numerical answer, but it remains for the operator, with his experience in the subject and the understanding of how the numbers were derived, to assess the reliability of the answer. Clearly, having generated the software adds immeasurably to your assessment of such a process.

General categories of the necessary software are listed in Table 1. The general-purpose computing programs are considered in the utility category while each thermoanalytical instrument would have at least one program in

TABLE 1

General types of software

LOAD	Charge microprocessor to collect, normalize and store data—analog output to recorder
READ	Input stored data—format data file
MANIPULATE	Average, smooth, or eliminate data—curve fit and background subtraction—expansion coefficients—derivatives—kinetic analysis—etc.
DISPLAY	Present segments of plotted or listed data on the screen
PRINT	Formatted output of data and information
PLOT	Plot segments of data
UTILITY	Storage and transfer of files—general purpose calculations—word processing—etc.

each of the other categories. It was found convenient for identification and subsequent file manipulation to have the first two letters of the program's or file's name represent the instrument and the latter four letters the program's function, e.g., TGREAD, DTPLOT, EGDATA, DSPRNT, etc. The raw data files are then archived under the sequential run number (T0764, E1107, etc.) and entered into a log book along with the archive disk number. These data files, as they are created, include brief title information and values of important parameters as well as the array of raw data.

Load programs which determine the details of the data acquisition process generally make use of time averaging. The A/D converters themselves work at two rates, 3 or 30 readings/s. The slower rate has much better noise rejection and is always used since the experimental parameters are changing relatively slowly. In addition, if the process is particularly slow (e.g., isothermal kinetics at lower temperatures or dynamic experiments at slow heating rates), the opportunity to time average multiple readings as a single data point can be used. The only disadvantage of this is the added wear on the A/D scanner relays which must make many more switchings. Since the scanner specification calls for $> 10^8$ switches prior to failure, this averaging is generally employed to reduce the noise further. The alternative is to allow for a fixed delay time between readings.

The display and plotting routines utilize sub-programs supplied by Fluke to do the automatic scaling, generation of the axes, and control of the plotter. Using the compiled version of the BASIC programs shortens the run time by a factor of 3–5. The compiled version provides a number of programming advantages as well. A general text editor is provided in the compiler software package and serves for routine word processing functions as well as for writing the programs.

EXAMPLES OF OUTPUT

Probably the best way of evaluating the overall system is to examine some representative samples of output. Figures 2–4 are direct copies of the plots output for TG, DTA, and EGA, respectively. The original plots had different colors for each curve on the multiple plots. The DTG curve in Fig. 2 was obtained by taking each point (i) and the point on either side ($i \pm 1$), fitting it to a parabola (e.g., 1), and analytically taking the derivative (eqn. 2)

$$(\mathrm{mg})_i = a + b(\mathrm{min})_i + c(\mathrm{min})_i^2 \tag{1}$$

$$\frac{\mathrm{d}(\mathrm{mg})_i}{\mathrm{d}(\mathrm{min})_i} = b + 2c(\mathrm{min})_i \tag{2}$$

Smoothing can be achieved by taking more points and using a least-squares fit to eqn. (1).

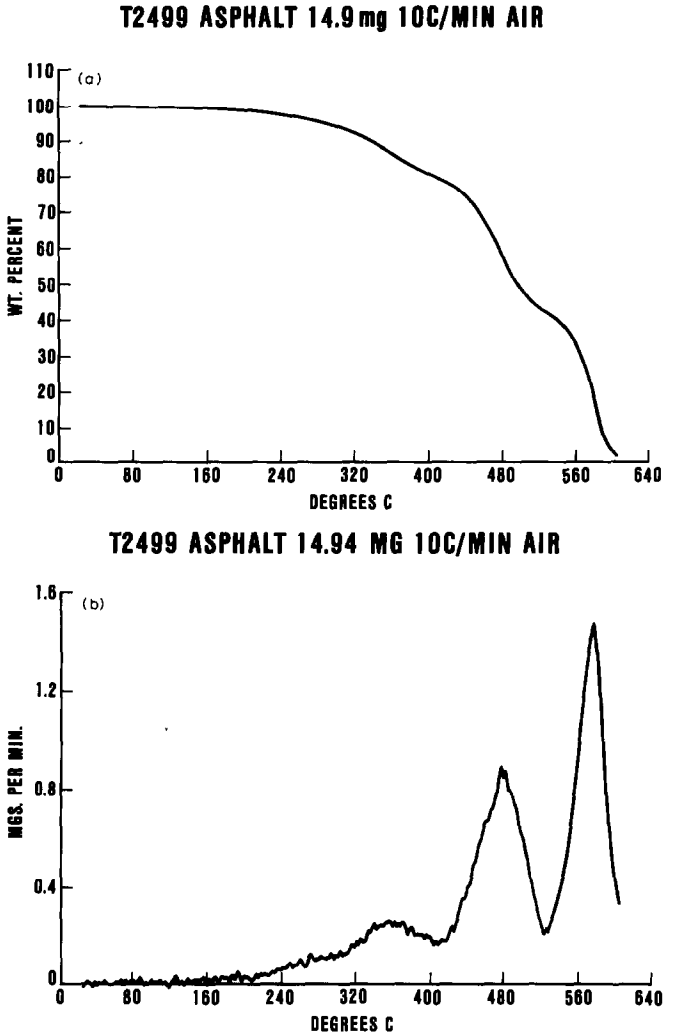

Fig. 2. Graphical output of a thermogravimetric experiment. (Asphalt sample courtesy of Dr. M.W. Rowe, Texas A & M University.): (a) TG; (b) DTG.

Sections of DTA curves for the heating and cooling of a crushed crystal of lithium niobate are presented in Fig. 3. The portions of the DTA curve surrounding the Curie temperature (T_c) are displayed to show the lack of temperature hysteresis associated with the event provided that the sample is not heated above 1200°C where further Li loss occurs [5]. The thus grown crystals have the congruent composition $Li_{0.972}NbO_{2.986}$ and the value of T_c is a good indicator of the degree of stoichiometry [5].

Nitrogen evolution from a sputtered film of InN deposited on SiO_2 [6] is used an example of EGA and shown in Fig. 4. The curves are for the intensity of the AMU = 28 peak recorded simultaneously at three different

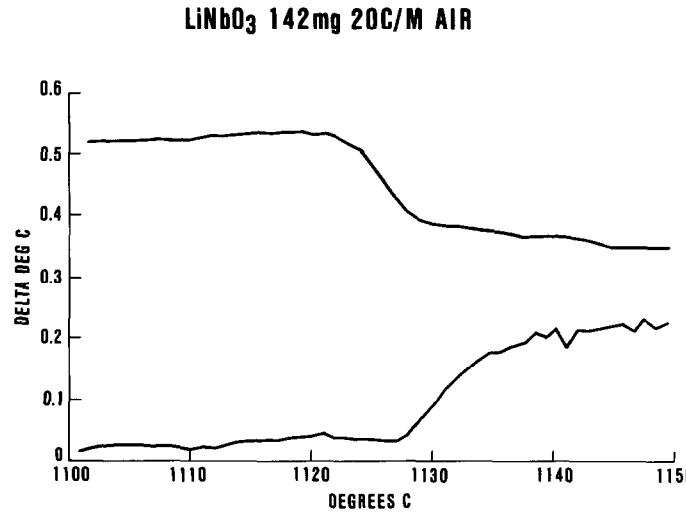

Fig. 3. Graphical output of a differential thermal analysis experiment of a congruently grown crystal of lithium niobate.

amplification settings (10^7, 10^8, and 10^9) on the mass spectrometer. The dependence of the apparent onset of a reaction upon amplification is clearly evident. It is also obvious that measuring an extrapolated onset is only effective if the entire curve without saturation is available. A value of 500°C would be obtained for all three curves if their entire contours were available, but, as they appear in Fig. 4, a pronounced shift towards lower temperatures is suggested with increasing amplification.

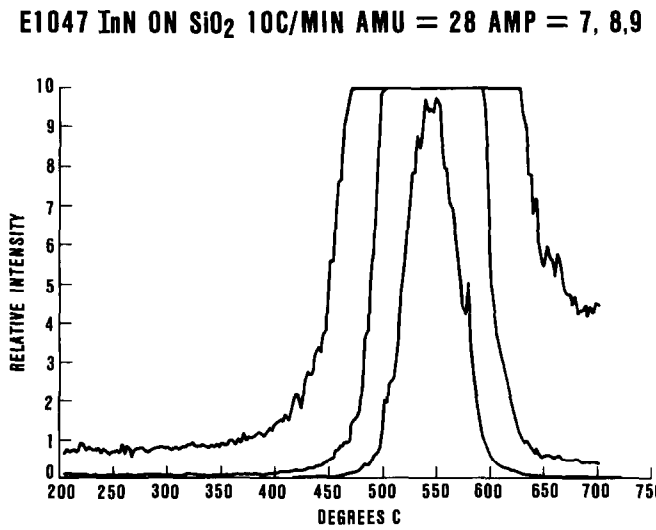

Fig. 4. Graphical output of N_2 evolution (EGA) from a film of InN on SiO_2 (mass spectrographic amplifications of 10^7, 10^8, and 10^9).

TABLE 2

Kinetic functions ($F(\alpha) = kT$) used in the computer analysis (α = fraction reacted)

Power law	α^n; $n = 1, 2, 1/2, 1/3, 1/4$
Contracting geometry	$1-(1-\alpha)^{1/n}$; $n = 2, 3$
Erofeev	$[-\ln(1-\alpha)]^{1/n}$; $n = 1, 1.5, 2, 3, 4$
Diffusion controlled, 2D	$(1-\alpha)\ln(1-\alpha)+\alpha$
Diffusion controlled, 3D	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
Jander	$[1-(1-\alpha)^{1/3}]^2$
Prout–Tompkins	$\ln[\alpha/(1-\alpha)]$
Second order	$1/(1-\alpha)-1$
Exponential	$\ln \alpha$

In general, there is not much mathematical manipulation required in the acquiring and plotting of conventional thermoanalytical results. The calculating power and speed of the computer, however, become much more important when performing either isothermal or dynamic kinetic analysis. Table 2 lists 18 of the rate equations commonly applied to solid-state reactions in the form of $F(\alpha) = kT$ [7]. A program has been developed which makes use of the array of weight, time, and temperature points that would normally be acquired from an isothermal gravimetric study. Keyboard inputs to this program are the weight corresponding to the start and finish of the reaction, the fraction reacted, α, over which the curve fitting is to be accomplished, and the particular equation numbers to be studied. The summary page of the printout is shown in Fig. 5 for a typical example. This example is for the oxidation in 0.1% O_2 in Ar of a film of NbN on SiO_2 to Nb_2O_5 [8]. The title information shows the experiment number (K0477), the particular sample designation (SG-97-3), the date, the time, and the input parameters. The number of points found in the designated range of α and the average temperature for those points are determined and are also listed in the title information. In this example all 18 equations were selected and the values of the rate constants, standard deviation of the least-squares fit in both α and percentage of $F(\alpha)$, and the extrapolated value of time at $\alpha = 0$. Since time is started when the sample nominally reaches temperature, the significance of negative values of t_0 is that a significant amount of reaction has occurred in reaching this point while positive values of t_0 would imply an induction period. In general, the sort of kinetic data analysis illustrated by Fig. 5 requires only a minute of computer time with compiled BASIC and adequate RAM.

The standard deviations are used to establish which rate law fits the data best over the selected range of α. It must be stressed, however, that mechanistic implications should not be made from such data alone [9]. Supporting evidence, such as microscopy, would be necessary. When the family of isothermal runs at different temperatures is used in an Arrhenius plot to evaluate the activation energy it has been generally found that nearly

KINETIC ANALYSIS OF ISOTHERMAL WEIGHT LOSS RUN K0477

SG-97-3
30-JUN-82
06:58

THE MILLIGRAMS CORRESPONDING TO ALPHA = 0 IS 6.4

THE MILLIGRAMS CORRESPONDING TO ALPHA = 1 IS 7.02

THE MIN. VALUE OF ALPHA USED AND ITS SECS. ARE 0.1437903 49.072

THE MAX. VALUE OF ALPHA USED AND ITS SECS. ARE 0.9038871 8400.16

THE NUMBER OF POINTS IN THIS RANGE IS 255

THE AVERAGE TEMPERATURE IN DEG K THROUGH THIS RANGE WAS 729.5981

THE RECIPROCAL OF THIS TEMPERATURE IS 0.137061E-02

EQ. NO.	RATE K (REC. SEC.)	ST. DEV.	ST. DEV. %(F(A))	TIME ZERO (SEC)
1	9.326E−05	0.0193	2.54	−1.72E+03
2	6.660E−05	0.0414	5.45	−6.68E+03
3	5.044E−05	0.0510	6.72	−1.17E+04
4	4.038E−05	0.0565	7.44	−1.67E+04
5	1.980E−04	0.0768	10.10	7.75E+03
6	7.354E−05	0.0172	2.27	−6.28E+02
7	5.772E−05	0.0270	3.55	−3.08E+02
8	2.446E−04	0.0566	7.45	2.65E+02
9	1.299E−04	0.0141	1.86	−2.95E+03
10	8.991E−05	0.0147	1.93	−6.25E+03
11	6.894E−05	0.0175	2.30	−9.57E+03
12	3.143E−06	0.3718	48.91	−5.96E+03
13	2.159E−05	0.4175	54.92	1.19E+03
14	3.169E−05	0.2998	39.44	1.44E+03
15	4.426E−04	0.0169	2.23	3.61E+03
16	1.008E−04	0.0974	12.82	6.67E+02
17	1.684E−04	0.0213	2.80	−1.32E+03
18	8.089E−04	7.3205	963.10	1.50E+03

Fig. 5. Printed output of an isothermal kinetic experiment of the oxidation of a film of NbN on SiO_2 in 0.1% O_2 in Ar.

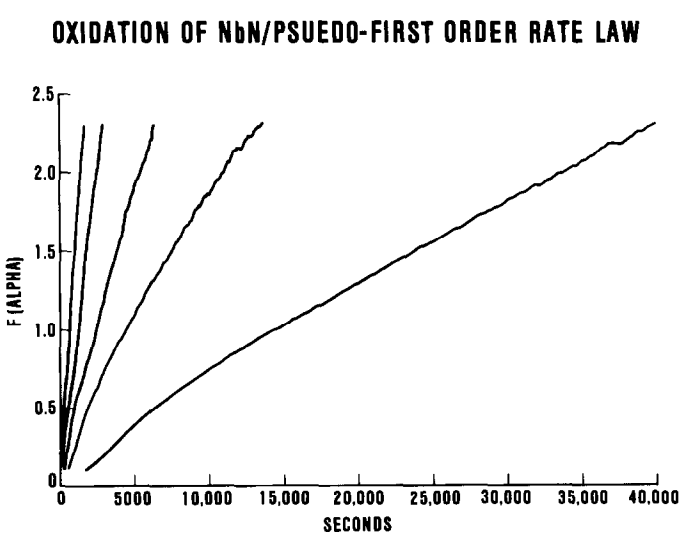

Fig. 6. Graphical output showing a series of isothermal experiments on the oxidation of bulk NbN in 0.1% O_2 in Ar ($F(\alpha) = -\ln(1-\alpha)$) ($T = 897.3$, 877.4, 855.7, 836.8, and 816.9 K).

identical values of activation energy will be derived from the consistent application of any of the reasonably well-fitting note equations [8–10]. A family of isothermal plots of $F(\alpha)$ versus time is shown in Fig. 6 for the oxidation of bulk NbN in 0.1% O_2 in Ar [10]. The plots for a pseudo first-order rate law, i.e., $F(\alpha) = -\ln(1-\alpha)$, are a direct reproduction of those made using the general system described herein.

A wide variety of other related capabilities exist, e.g., dynamic kinetic analysis, background fitting and subtraction, calculation of thermal expansion coefficients, etc. It is not feasible to illustrate all the applications. It is hoped, however, that this brief selection of examples will serve to demonstrate the power of this self-contained system to acquire, plot, manipulate, and store thermoanalytical data obtained from a wide variety of instruments. There is the added advantage that all the instruments can be running simultaneously along with the processing of earlier data. The speed of data manipulation and calculations is greatly enhanced by using compiled programs coupled with adequate RAM.

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