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RESEARCH,
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**DEVELOPMENT OF COMPUTER-CONTROLLED
THERMOGRAVIMETRIC INSTRUMENTATION
FOR MEASUREMENT OF ENVIRONMENTAL AND
HIGH TEMPERATURE VOLATILIZATION AND
DESORPTION OF CONTAMINANTS
FROM POLYMERIC MATERIALS**

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A conventional thermogravimetric analyzer was modified and computerized to provide an environmental chamber adequate for comparative measurement of diffusion and evaporation of liquids from polymers. The computer-instrument system supplements complex and expensive environmental wind tunnel research for preliminary measurements of relative rates of processes at both environmental and high temperatures and under atmospheric conditions. The diffusion and evaporation transport properties of liquid-state chloroesters, diesters, organophosphates, and ether-acetates were measured in or on urethane, polyester, and methacrylate polymers. The results obtained that are of general interest to computer-oriented chemists demonstrate the enhancement of instrument performance by the computer system; the important system components are signal analysis software, kinetic computations, graphic display of rate data, and data base generation. <i>(Continued on reverse)</i> <i>Keywords:</i>					
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In addition, correlations of physical and solvent properties with transport rates would be of interest to polymer and environmental chemists. The system consists of a number of modular hardware and software subsystems that can be adapted by other investigators to obtain desired capabilities.

PREFACE

The work described in this report was authorized under Project Number 1L162706A553, CB Defense and General Investigation. This work was started in October 1983 and completed in March 1986. The experimental data are recorded in laboratory notebooks 82-0137 (4 June 1982) and 83-0095 (16 June 1983).

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DEVELOPMENT OF COMPUTER-CONTROLLED THERMOGRAVIMETRIC
INSTRUMENTATION FOR MEASUREMENT OF ENVIRONMENTAL AND HIGH
TEMPERATURE VOLATILIZATION AND DESORPTION OF CONTAMINANTS FROM
POLYMERIC MATERIALS

1. INTRODUCTION

1.1 Background and Purpose.

Investigators are employing a physical chemical transport framework with increasing frequency^{1,2} to study the sorption and desorption of organic liquids and pesticides from solid surfaces. Desorption, volatilization, and persistence under environmental conditions are emphasized in some studies.³ There is growing literature on contaminant removal and decontamination from mostly polymeric or metallic surface materials.^{4,5,6} Several publications have addressed the removal of toxic compounds from polymeric coatings.^{7,8} Limited research is also under way on the influence of temperature on the evaporation, transport, and sorption-desorption of liquid contaminants onto or from polymer surfaces; examples include studies of environmental volatilization, desorption during high-temperature processing, and temperature-controlled volatilization during thermal destruction. The transport behavior of liquid organic esters within a polymeric matrix has also been considered with respect to environmental contamination and persistence.⁹

One purpose of the studies reported here is to continue in the direction of the research cited above, with respect to the effect of temperature on vaporization and desorption of organic contaminants from polymeric materials. The scope of the investigations includes both environmental and temperature-induced removal of contaminants from polymeric surfaces. The present studies are concerned with the development of experimental methods for these evaporation and desorption measurements based on the adaptation of a conventional thermal microbalance and implementation of computer control of the experiment.

Recent research in our laboratory has led to the solution of a wide range of experimental problems by adapting or modifying a conventional, commercial microthermobalance.^{10,11} In most of these instances, the use of custom, computerized instrumentation provided the necessary capability or enhanced the microthermobalance capability such that the problem could be solved.^{12,13} Computerized experimentation has also been employed by others in mass spectral measurements of surface desorption from inorganic catalytic substrates.^{14,15}

Computer interfacing allows one to augment the use of the conventional microthermobalance to perform slightly unconventional experimentation in nontraditional areas for thermogravimetric analysis (TGA).¹³ Therefore, the purpose of this study was to develop new capabilities by interfacing a conventional microthermobalance to a laboratory computer to measure unusually fast or slow transport processes. Several examples of these experiments with a computer-thermogravimetric system are as follows:

- a. Evaporation of liquids as a function of liquid properties using the TGA furnace tube as a mini-environmental chamber or wind tunnel.
- b. Diffusion of liquids from polymeric substrates.
- c. Flash thermal desorption of liquids sorbed into or adsorbed on specific surfaces.
- d. Thermal desorption during complex, nonlinear, time-temperature profiles.

1.2 Scope of the Variables Investigated.

The dependent variable in most of these experiments is usually a rate of desorption or diffusion, or other time-temperature-mass function for a mass transport process. One can group the independent variables investigated into at least two types:

- a. Transport variables; including relative mass, liquid shape, velocity of gas over liquid (or wind speed), relative humidity, turbulence, and geometry of the gas-liquid-solid interface. In general, these variables can be adequately studied over a limited range relative to the broader range allowed by the more complex and expensive dedicated apparatus usually employed. For these experiments, a Gilmont Model No. F-1200 (Serial No. H-280) flowmeter was used, and the wind speed over the sample was maintained at approximately 350 mL/min. Converting from volume to two-dimensional velocity and employing dimensional values for the TGA furnace tube geometry, the wind speed was approximately 1.63 cm/s (0.036 mph or 0.058 kph). Mass and humidity can be either controlled or varied as accurately as they can in most systems. For these experiments, the purge gas used was technical grade nitrogen directly from a cylinder (water-pumped, minimum 99.5 vol %). In addition, this system has the advantage of being able to hold simply the remaining mass transfer variables at a constant value.

- b. Material variables; including liquid vapor pressure, molecular cross section, solvent parameters (dispersion, dipole, hydrogen bond, and total solubility parameters) of liquid and polymeric substrate.

One might expect that the computer-TGA system would excel at performing the material comparisons and provide a rapid and convenient selection of the transport variables. The importance of determining the relationship between contaminant-material properties and transport and persistence in the environment has already been emphasized by Freed and co-workers.¹⁶ The properties of the polymeric materials that influence their sorption of contaminants and their ease of thermal decontamination are of interest, as well as the solvent properties of the liquid contaminants.

The scope of this study is further influenced by the available characterization of physical and surface properties of the model contaminants employed. The factors controlling the loss of liquid from a drop on a surface are the vapor pressure and total surface area. The factors determining the surface area are the drop shape, contact angle, and extent of adjacent liquid monolayer formation and its dynamic renewal during evaporation.

Studies are under way to provide concurrent photographic recording of liquid contact angles. However, these data are not relevant to the initial purpose, and the immediate scope is limited to comparative measurements on related liquids with other conditions held constant. Observation and timing of liquid spreading behavior showed essentially similar spreading and contact angle properties.

2. EXPERIMENTATION

2.1 Instrumentation.

The thermogravimetric instrumentation, computer hardware, and software are presented in Figures 1 and 2. Figure 1 shows a schematic of the sample holder on the microbalance unit. The horizontal slide-mounted mass transducer assembly allows considerable versatility in experimentation. Gas flow over the sample can be:

- a. Directed from either end of the chamber tube.
- b. Either totally enclosed or vented into atmospheric or reduced (vacuum) pressure.
- c. Smoothed by insertion of vanes.

Selecting the gas atmosphere type (dry nitrogen, air, oxygen, etc.) and flow rate (wind speed) can be done in the same manner used in conventional TGA operations. Relative humidity can be adjusted to any level between ambient and zero by mixing dry cylinder gas and ambient air to the desired ratio using multiple flow controllers.

The suspended polymer substrate upon which the liquid samples are placed is shown in Figure 1. The figure also displays a closer view of the transducers; first, the sample thermocouple; second, the mass transducer; and third, the analog derivative of mass change (within the module electronics, not visible in the figure).

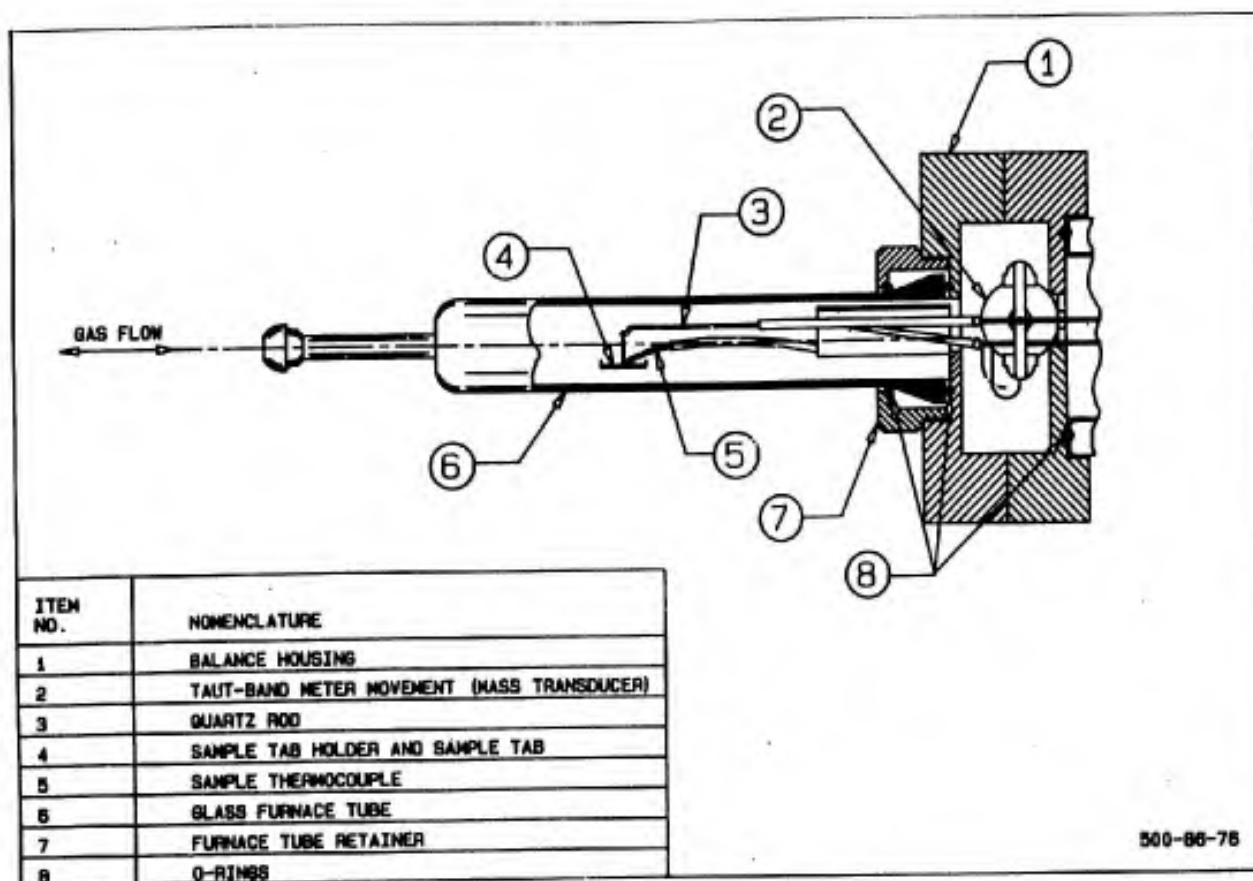


Figure 1. TGA Balance Assembly

2.2 Computer Interface.

Temperature, mass, and derivative signals are interfaced to differential amplifiers, a multiplexed **sample-and-hold**, successive approximation, analog-to-digital converter, and a real-time clock. Figure 2 presents an instrument diagram interfaced to a versatile dual-CPU disk network system. The signals are digitized, temporarily stored in the memory of one CPU, transferred to disk, analyzed on the other CPU, and displayed and/or printed on a switch-selected input/output device. Reduced data files are transferred under minicomputer control to a time-share mainframe for production of high resolution graphics hard copy.

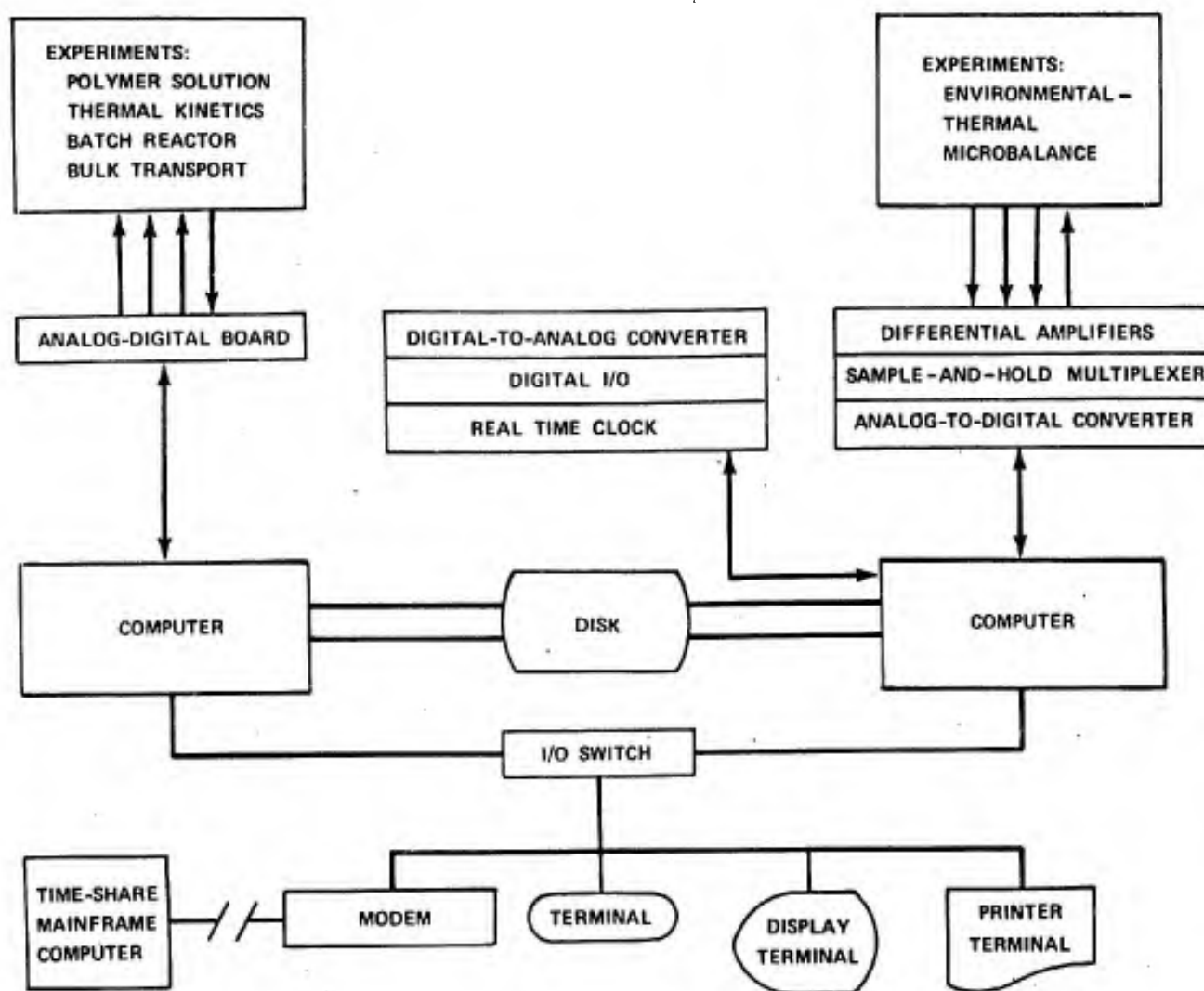


Figure 2. Dual-CPU Disk Network System for Experimentation in Environmental and Polymer Chemistry

2.3 Procedures.

Prior to loading a sample, the computer data acquisition system and the thermobalance system are both properly calibrated. The FORTRAN program is started and all requested input is entered, except the final prompt for data acquisition to commence. At this point, the sample is loaded onto the sample tab.

The individual components that are referenced are illustrated in Figure 1. The basic procedure to operate the TGA is found in Section 9.4 of the Du Pont 990 Thermal Analyzer and Modules instruction manual.

The furnace tube retainer (#7) is unscrewed, and the balance housing (#1) is moved to the right. The balance housing assembly consists of the mass transducer (#2), the quartz rod (#3), the sample tab holder and the sample tab (#4), and the

sample thermocouple (#5). The sample tab holder and sample tab can be changed, depending on the nature of the experiment being performed.

Once the correct sample tab holder with sample tab is properly positioned on the quartz rod, the balance housing is moved to the left and snugly secured to the furnace tube (#6) with the furnace tube retainer. With reference to Section 9.4 of the Du Pont 990 Thermal Analyzer and modules instruction manual, the appropriate purge gas flow is started, and the tab/holder weight is offset to zero. The furnace tube retainer is then unscrewed again, and the balance housing is moved to the right. The sample is then carefully loaded onto the tab using a Finnpiquette Positive Displacement Pipette (PDP); a stopwatch is started when the sample first touches the sample tab. The balance housing assembly is carefully moved to the left again and secured to the furnace tube. The computer is then given the command to begin data acquisition, and the elapsed time on the stopwatch is noted.

Typically, elapsed time between sample application and initiation of data acquisition was 30 s. Estimates of spreading diameter and cessation of spreading were noted as a function of time. The rapid initial spreading usually ended after 2 to 3 min.

The preceding procedure applies to experiments in which the sample weight-loss is being studied either as a function of time at an isothermal temperature or as a function of temperature at either a constant or computer-programmed rate of heating. In a flash thermal desorption experiment, the sample is suddenly exposed to a very high temperature of about 100 to 300 °C for several seconds. Because the reliability of the initial weight is very important, the quartz rod or the sample tab holder must not be disturbed in any way. Any disturbance of the rod or holder will change the zero reference of the sample, and thus prevent any quantitative data from being obtained.

For this flash thermal desorption experiment, the furnace tube is inserted into the furnace as far to the left as possible and preheated to a temperature above the target temperature. The balance housing assembly is positioned such that the sample tab is about 1 cm to the right of the open end of the hot furnace tube; a cork stopper is fitted into the furnace tube to insulate the sample from the heat source; a temperature increase of the sample thermocouple was not detected with or without the stopper in place. There is no heat transfer to the sample at this distance. After the liquid is loaded onto the polymer surface, the cork stopper is removed, and the hot furnace tube is moved to the right to a predetermined distance from the furnace and completely surrounds the sample. Care is taken not to touch the quartz rod or the sample tab holder suspended from the rod. The furnace tube is kept in this position for a precalibrated time interval to produce the desired temperature versus time profile and then carefully withdrawn from around the sample.

Various reproducible time-temperature profiles can be developed by calibrated movement of the furnace tube or balance housing. The most frequent application produces exponential time-temperature profiles that are characteristic of a temperature source passing over a surface to remove contaminants.

2.4 Materials.

The following instruments were used: Du Pont 951/990 Thermal Analysis System; Labsystems Finnpiptette Positive Displacement Pipette; Fisher Scientific Company Memory Digital Stopwatch, three Honeywell 218 Bridge Amplifiers; Honeywell 123 DC Amplifier; PDP 11/10 and 11/24 Minicomputers with Terminal and Printer; and modem transfer of data to Univac mainframe for graphics.

The following liquids from Aldrich Chemical Company were used: chloromethyl 2,2-dimethylpropanoate, (chloromethyl pivalate) (CAS# 18997-19-8); 4-chloro-n-butyl acetate (CAS# 6962-92-1); diethyl 2-chloropropanedioate (diethyl chloromalonate) (CAS# 14064-10-9); dimethyl hexane-1,6-dioate, (dimethyl adipate) (CAS# 627-93-0); and 2-hydroxyethanol, (ethylene glycol) (CAS# 107-21-1). Also used were dimethyl 2-chloropropanedioate, (dimethyl chloromalonate) (CAS# 28868-76-0)--Fluka Chemical

Company; an acrylic terpolymer¹⁷ from Rohm and Haas Company; and aluminum tabs with either an aliphatic polyurethane or an alkyd polyester coating (Chemical Coatings Laboratory, Fort Belvoir Research, Development and Engineering Center).

3. RESULTS AND DISCUSSION

3.1 General Features of Environmental Desorption Data.

Figure 3 is an example of one type of graphics obtained as the output of the combined data acquisition, signal analysis, computational kinetics, and plotting software. Time is plotted on the horizontal axis as the independent variable with residual mass fraction on the right axis and computed rate constant on the left axis as dependent variables. The sample is a sessile drop of a chloromethyl ester polymer solution containing about 5% of the dissolved polymer. A software option allows nulling of the weight of such nonvolatile additives. The weight-loss curve shows the expected rate decrease as the liquid loss proceeds from the evaporation-controlled to the diffusion-controlled regime. This transition usually occurs at a time when the liquid-to-polymer ratio

approaches 1:1,¹⁸ which would occur at about 40 min in this example. However, the material system investigated here is a very adhesive, polymer-containing drop on a solvent-resistant polyurethane surface. Therefore, some unknown quantity of liquid will diffuse into or onto the polyurethane from the acrylic terpolymer while concurrently experiencing evaporative loss (Figures 4 and 5).

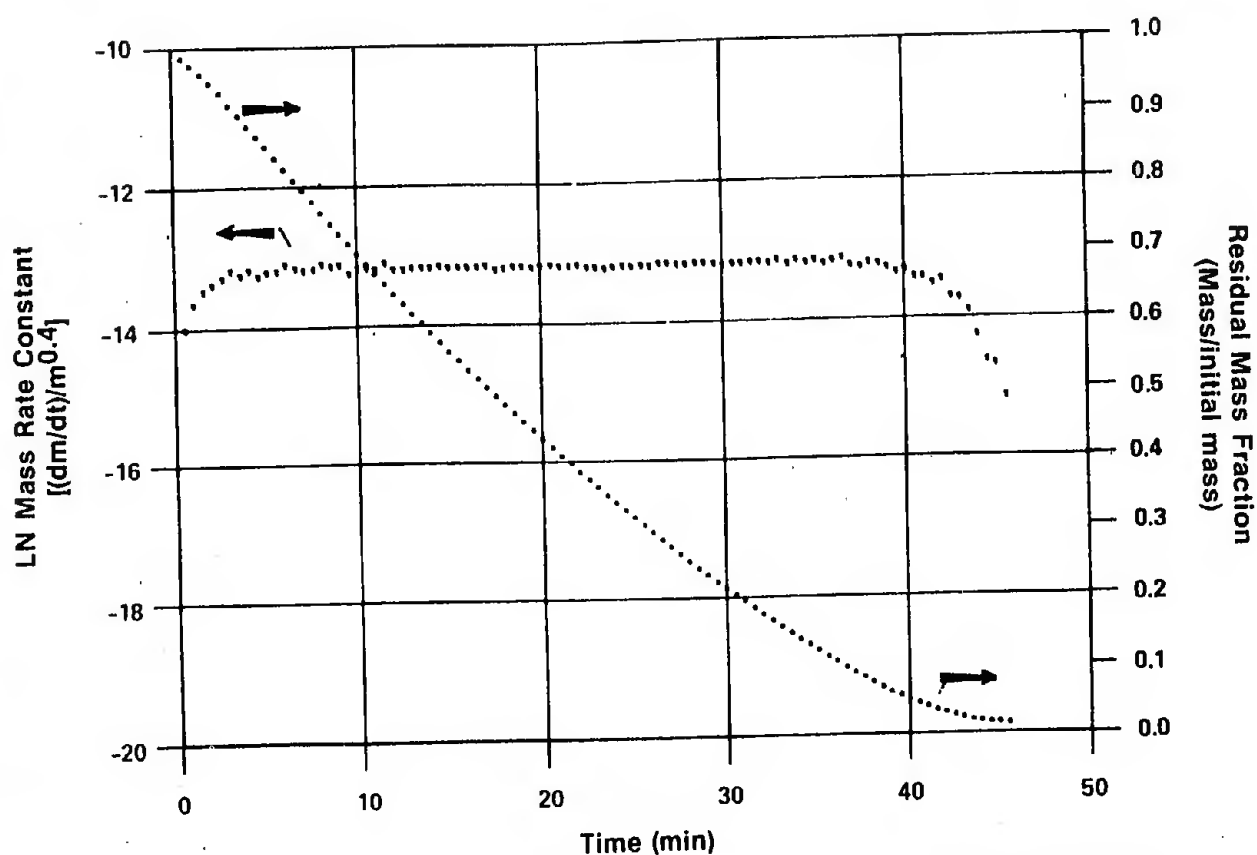


Figure 3. LN Mass Rate Constant and Residual Mass Fraction as a Function of Time on a Polyurethane Substrate for a Sessile Drop of a Polymer Solution: POLY(MMA/EA/BA) in Chloromethyl Pivalate.

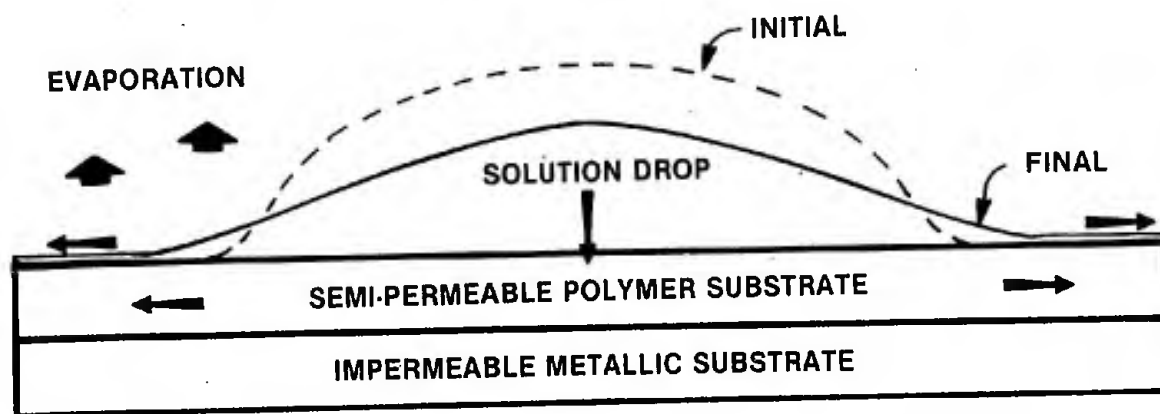


Figure 4. Geometric Configuration of Polymer Solution Drop Transport on a Polymeric Substrate

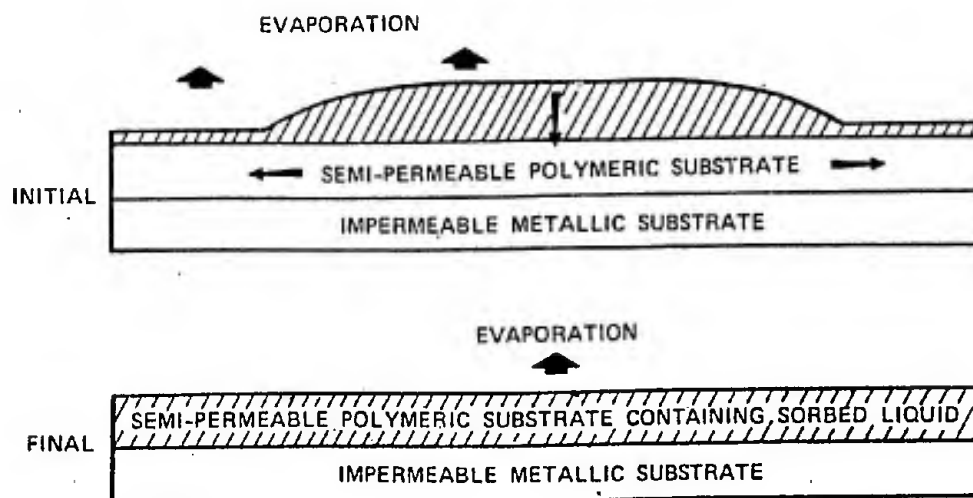


Figure 5. Geometric Configuration of a Liquid Drop Transport on a Polymeric Substrate

Identifying the onset of diffusion-controlled transport and the actual quantity of a polymer interacting with the liquid becomes more complex. Of course, the 1:1 ratio is no longer too useful as a guideline. Furthermore, linear extrapolation of the time versus residual mass fraction curve to a time of initial deviation is also not useful; the mass transfer process of a sessile drop involves a change of shape (and surface-to-volume ratio) in the first few minutes, and this change produces a continuously curved relationship over this initial time interval. In the next section, an interactive computational kinetics program is used to separate these processes.

3.2 Transport Kinetics.

Considerable progress in modeling the kinetics of sessile-drop evaporation has been made recently by Coutant and Penski.¹⁹ Thermal kinetics software was adapted to employ aspects of this model and to provide the rate constant plot as a function of time in Figure 3. The rate at zero velocity is omitted in this analysis. The model employs a theoretical exponent of $1/3$ in the mass term and our least-square analyses corroborated this value, producing optimal linear relationships at exponents of 0.3 to 0.4. The plot of rate constant versus time yields a horizontal line over the linear region of 0.9-0.1 residual mass fraction, at 5-35 min, respectively. Therefore, the onset of the deviation occurs at about 0.1 not 0.05 (5 wt %), and fully developed linear Fickian diffusion is observed only over the last 2 to 3%.

Using computer data acquisition analysis also aids in interpreting deviations from purely sessile-drop evaporation at the onset of evaporative mass transfer. The deviation is not

readily discernible by visual inspection of the data plot but can be readily seen in the rate plot at 0-5 min. Potential causes of deviations are:

- a. Rapid evaporative loss of more volatile impurities (higher rates).
- b. Humidity effects from evaporative cooling and water vapor condensation.
- c. Initial drop motion or spreading, indicating a dynamic contact angle and then an approach to an equilibrium angle. This explanation, suggested by Coutant and Penski,¹⁹ would yield lower initial rates.

3.3 Precision and Reproducibility.

Figure 3 identifies general features obtainable from the computerized analysis; Figures 6 through 8 demonstrate the computerized method's repeatability, precision, and ability to discriminate between materials or liquids.

Figure 6 presents a residual mass fraction versus time plot for 4-chloro-n-butyl acetate, again containing a polymeric additive; five repetitions of the experiment were overplotted to demonstrate the good repeatability of the procedures. Figure 7 displays the narrow 95% confidence interval obtained from the five combined experiments (a second order polynomial was used to provide a statistical analysis over the entire range of polymer-liquid ratios that were independent of transport regime).

Figure 8 presents a residual mass fraction versus time plot of three experimental repetitions each of both diethyl chloromalonate and dimethyl chloromalonate. The three repetitions show the good repeatability of the computer TGA measurement system, and this low degree of scatter allows discrimination between these two closely related liquids after less than 40 min.

Figure 9 displays examples of rate constant versus time plots for the diethyl chloromalonate and dimethyl chloromalonate and the system's capability to further discriminate between:

- a. Relative rates.
- b. The time at onset of diffusion-controlled transport.
- c. Relative diffusion rates (by comparing negative time versus rate curves at 20-30 hr).

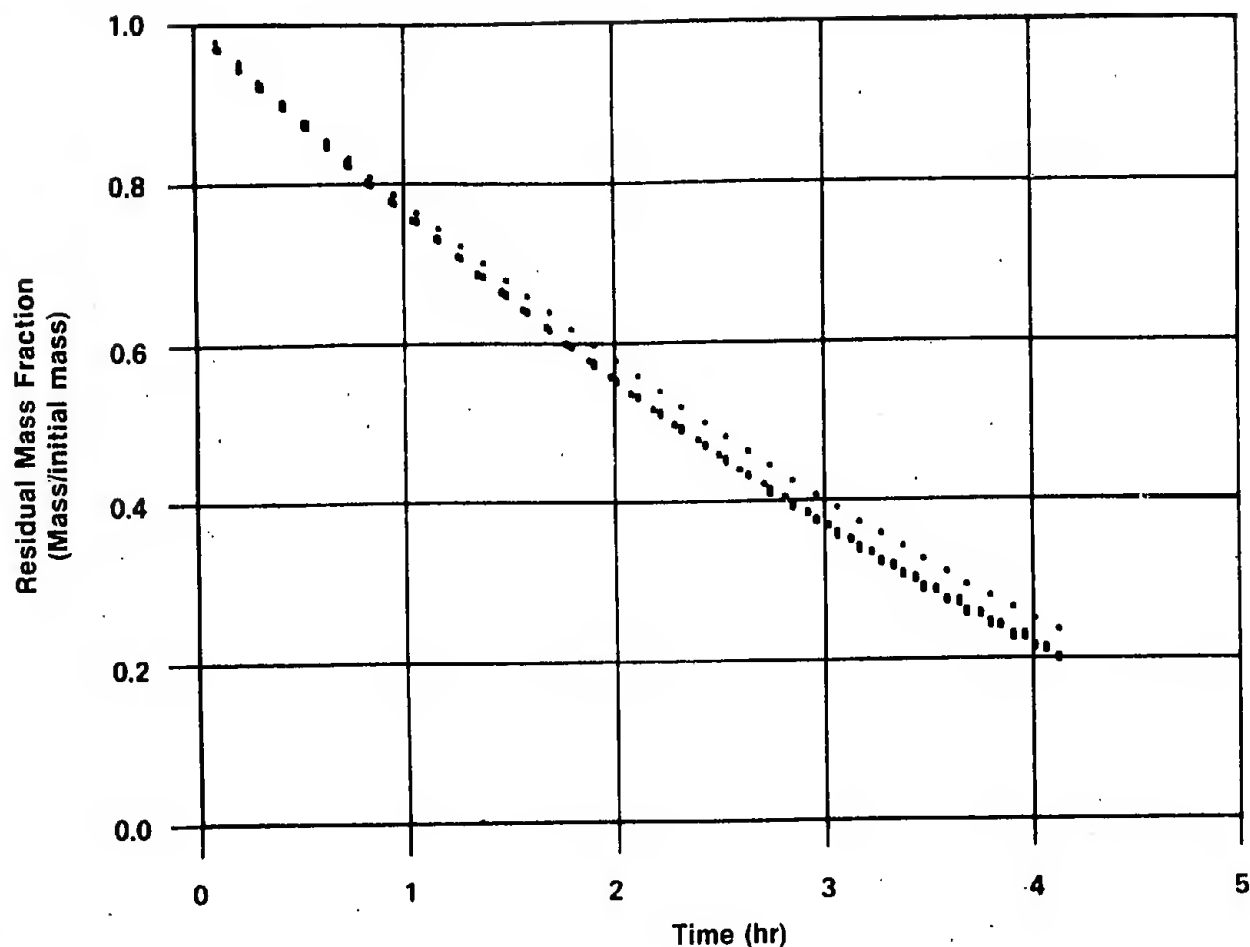


Figure 6. Reproducibility of Five Repetitions of an Environmental Evaporation Experiment from a Polyurethane Substrate for a Sessile Drop of a Polymer Solution: POLY(MMA/EA/BA) in 4-Chloro-n-Butyl Acetate

The system has the ability to provide a plot of residual mass fraction versus time to the negative one-half power, a form of a Fick's Law plot. This capability allows one to extract a portion of the data file displayed in Figure 4 and analyze a subsection of a process for alternate relationships; in all the examples, the last few milligrams (ca. 0.2 mg) of sample did not fit the sessile-drop evaporation, and the data relationships were being evaluated with a Fick's Law plot more appropriate to liquid diffusion from a polymer at low liquid to polymer mass ratios.

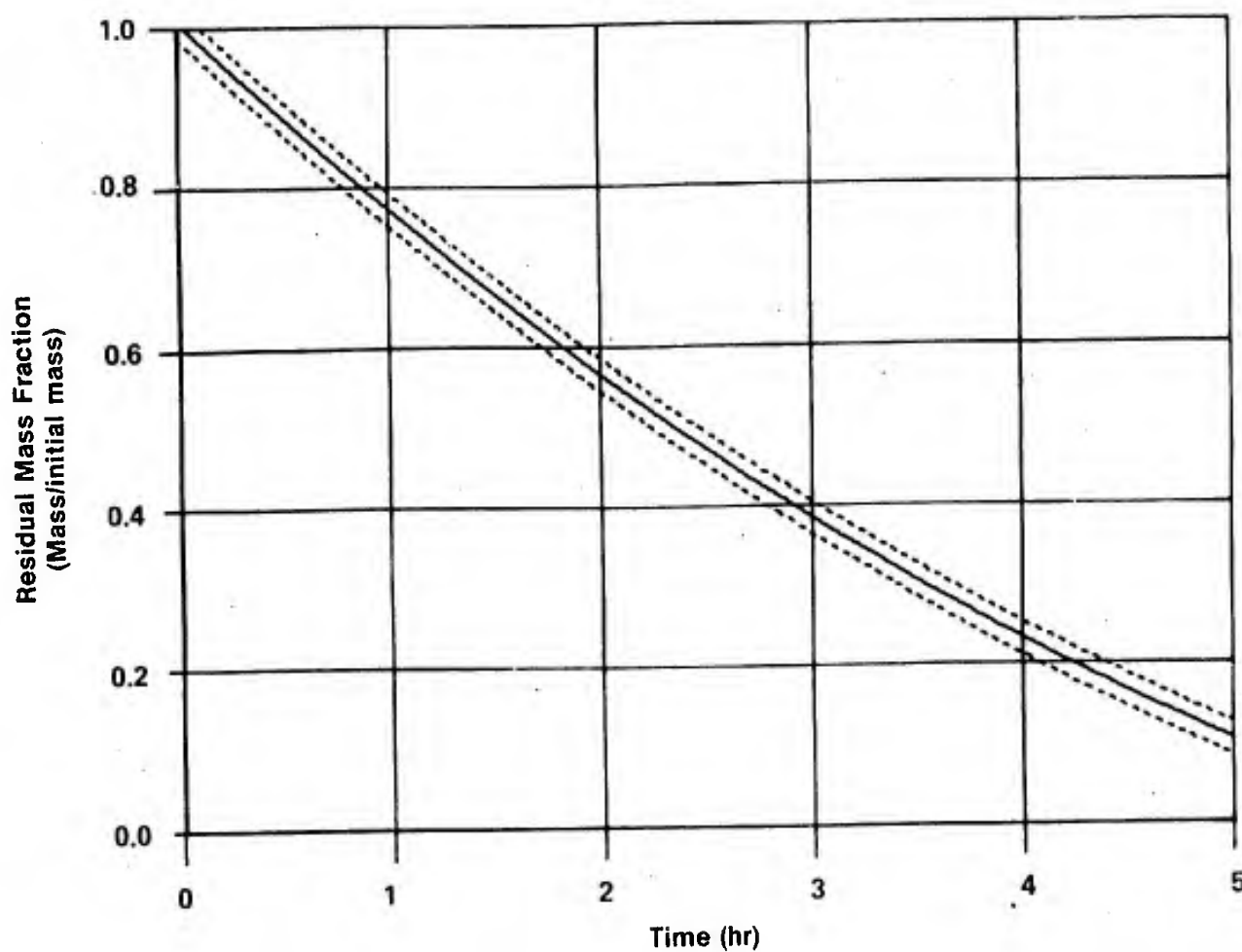


Figure 7. Confidence Limits (95%) for Five Repetitions of an Environmental Evaporation Experiment from a Polyurethane Substrate for a Sessile Drop of a Polymer Solution: POLY(MMA/EA/BA) in 4-Chloro-n-Butyl Acetate

3.4 Flash Desorption.

The ability to perform flash thermal desorption is another example of the versatility of using a research-oriented computer system with the thermal instrumentation. The rapid evaporation and/or diffusion of liquid can be measured with several types of experiments, that is, by exposing the polymer/liquid system to an exponential increasing then decreasing time-temperature profile or by exposing the system to a specific range of transient time constants (exponential plateau). These dynamic experiments are at the other end of the time scale from slow environmental measurements, and the availability of the successive approximation analog-to-digital converter gives one higher speed capability relative to most dedicated instruments with slower dual-slope converters.

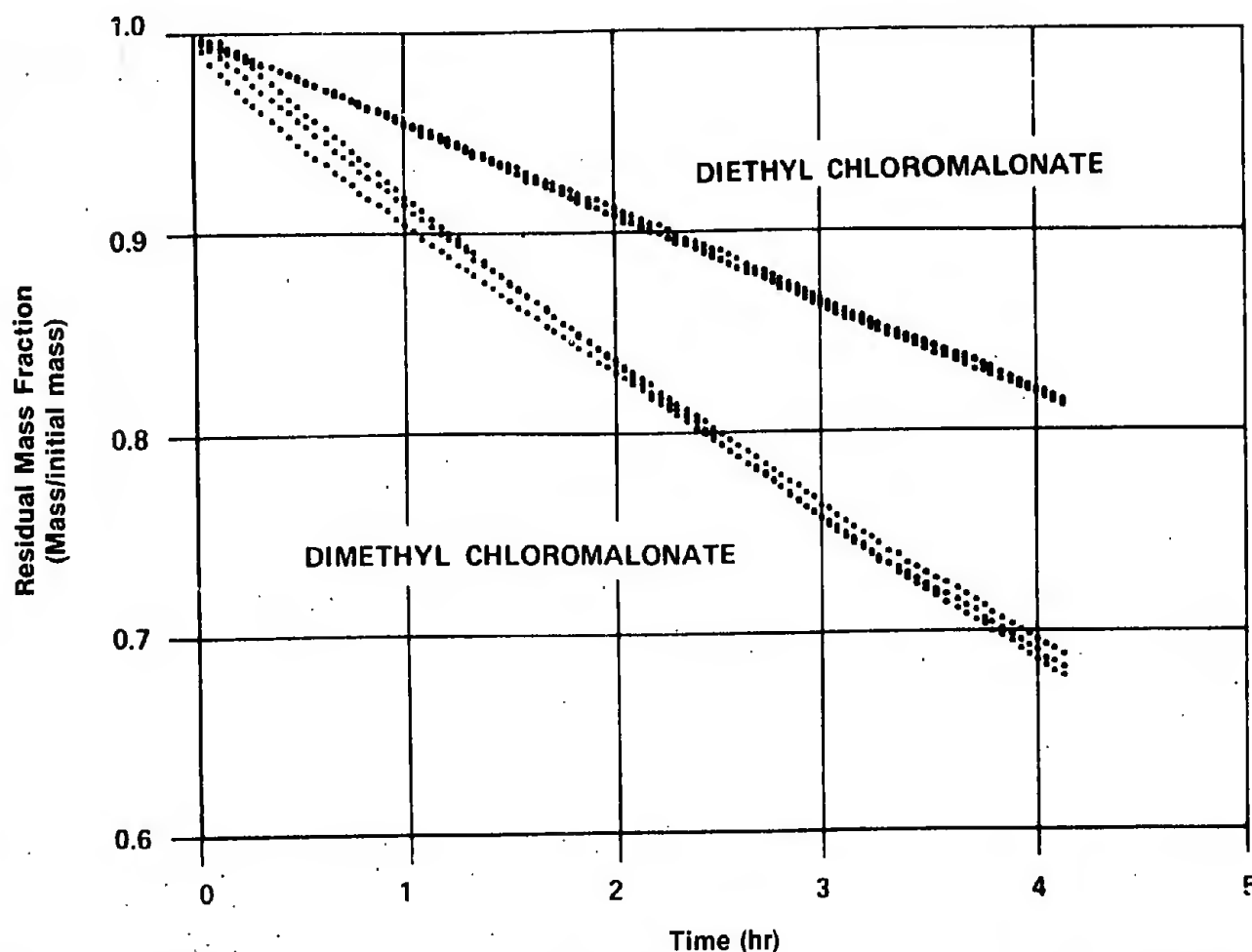


Figure 8. Comparison of Three Repetitions of an Environmental Evaporation Experiment from a Polyurethane Substrate for Two Liquids as Sessile Drops of a Polymer Solution: POLY(MMA/EA/BA) in Diethyl Chloromalonate and Dimethyl Chloromalonate

Figures 10 and 11 present examples of both the time-temperature profile imposed on the sample and the resultant weight-loss versus time profile. Figure 10 shows an exponential time-temperature profile relevant to many processes; the temperature rises to about 165 °C and immediately cools to ambient temperature. The weight decreases from 7.7 to 5.2 mg during this single thermal event; the influence of several sequential profiles can also be measured by successive sweeps, and the number of profiles required to desorb a specific fraction of liquid can be obtained. The time-temperature profile is obtained by moving a preheated furnace tube back and forth around the sample with a precalibrated technique. Figure 11 presents an exponential temperature profile to a plateau at about 85 °C on the right axis. The resultant decrease in liquid mass on or in the polymer is shown on the left axis.

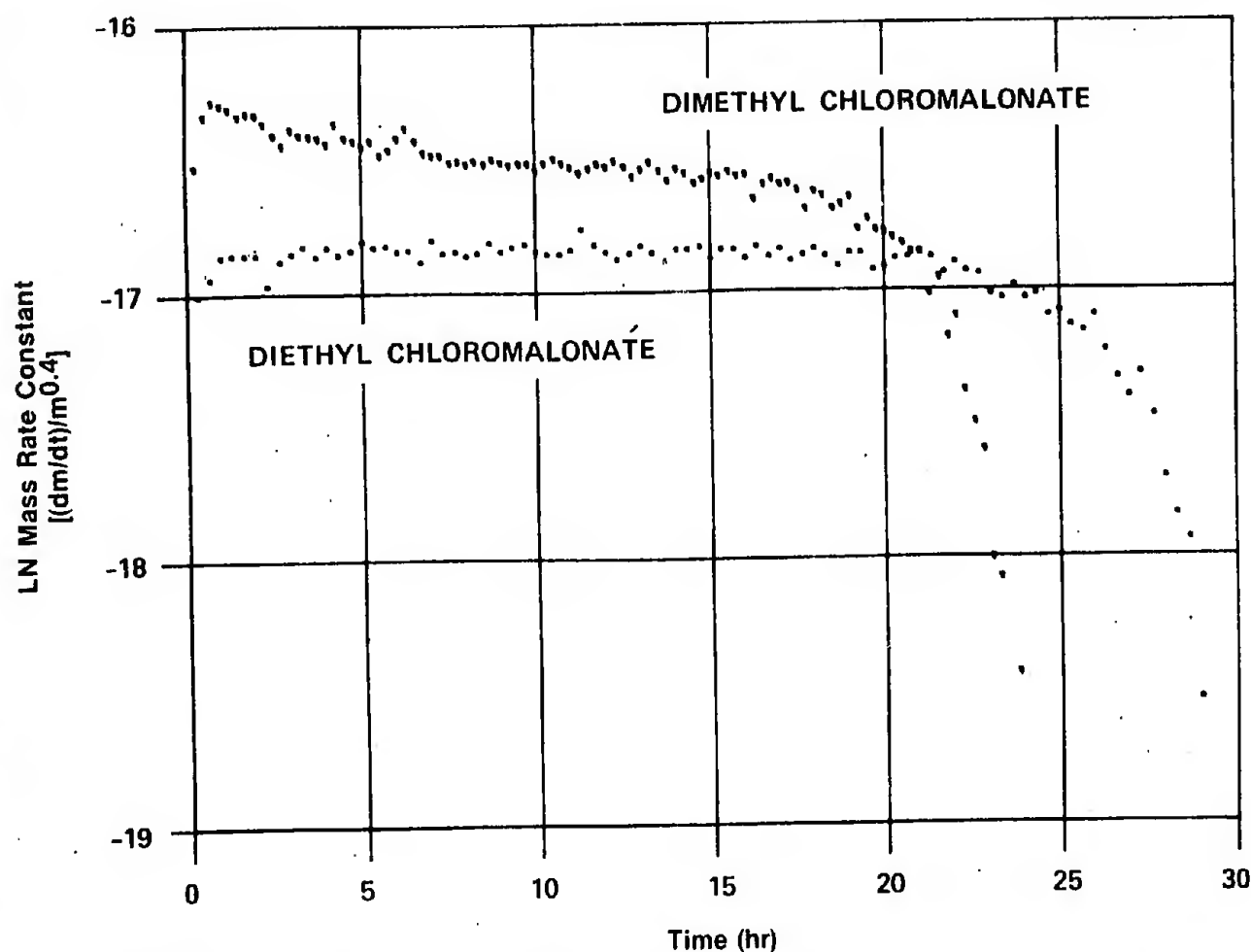


Figure 9. Comparison of Rate Constants as a Function of Time During Environmental Evaporation from a Polyurethane Substrate for Two Liquids as Sessile Drops of a Polymer Solution: POLY(MMA/EA/BA) in Diethyl Chloromalonate and Dimethyl Chloromalonate

Evaluation of results suggests that a transient thermal event can cause transport and redistribution of the remaining liquid within the polymer. Immediate environmental evaporation measurements sometimes reflect this change in a rate effect. In general, measurements under environmental conditions can both precede and follow dynamic or transient thermal exposures. Because data-sampling parameters are quite different for experiments lasting a few seconds versus a few days, storage on different data files is used. Additional software was developed for these thermal desorption experiments; for example, calculation of 1-5 time constants for the exponential profiles.

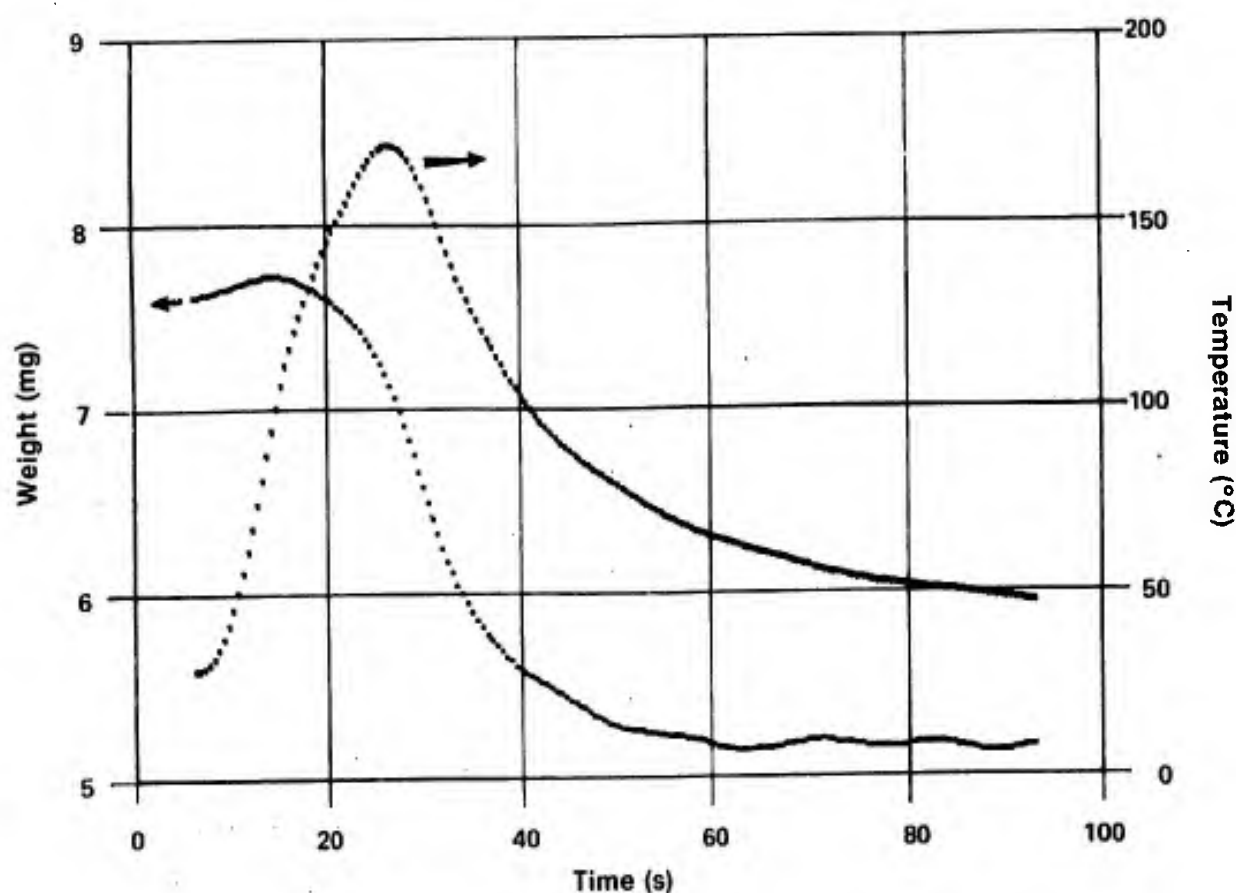


Figure 10. Weight-Loss and Temperature Versus Time During a Flash Thermal Desorption Experiment from a Polyurethane Substrate for a Sessile Drop of a Polymer Solution: POLY(MMA/FA/BA) in Dimethyl Adipate

3.5 Transport Variables and Computerized Instrumentation.

The table contains a number of transport variables and variable properties. The computer microbalance system capabilities are listed in the columns in terms of the range, typical values, precision, accuracy and signal processing (data offset, scaling, or nulling operations, etc.). Those capabilities that are made possible by, or enhanced by, the computer interface are underlined; these capabilities are numerous and critical to the success of this experimentation.

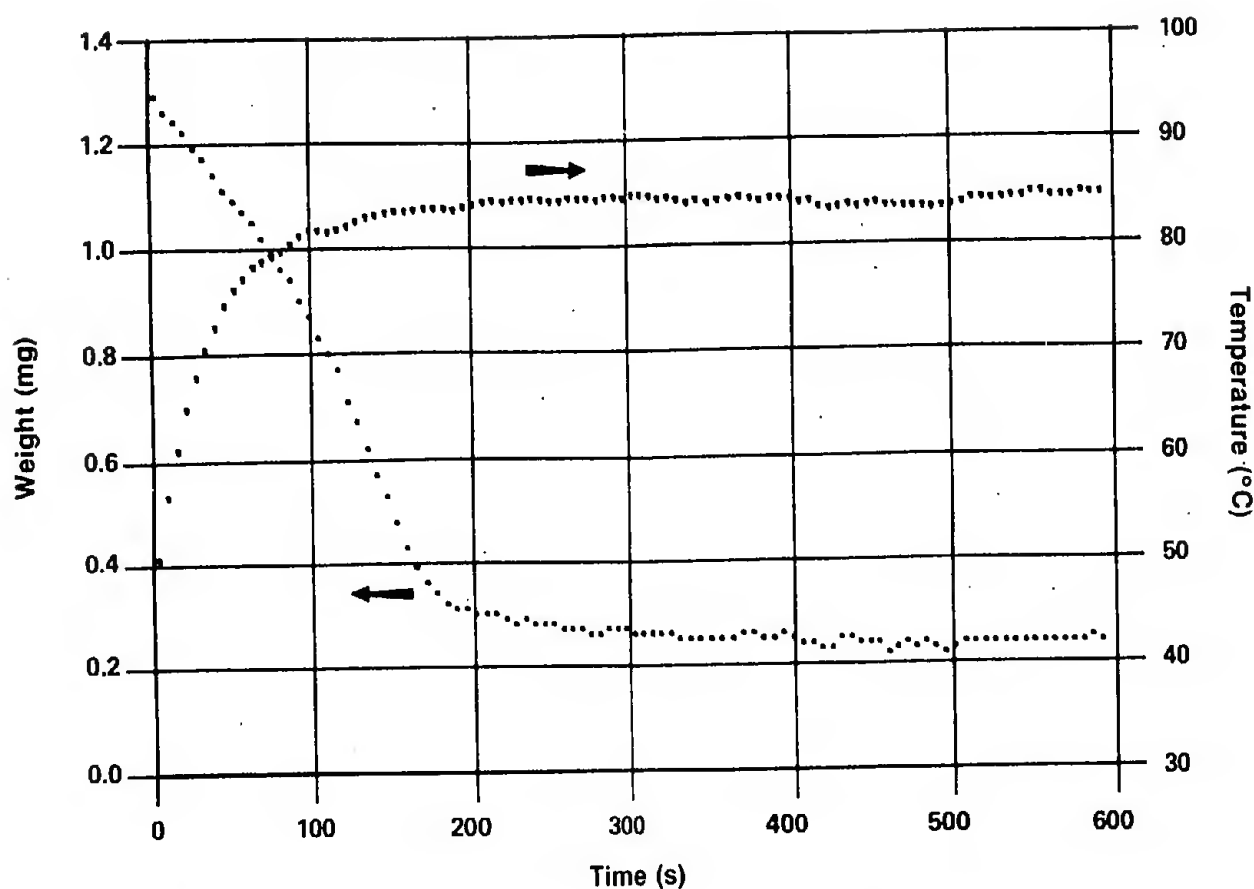


Figure 11. Weight-Loss and Temperature Versus Time During a Flash Thermal Desorption to a Plateau for a Liquid Drop on a Polyester Substrate: Ethylene Glycol

Table. Transport Values and Their Measurement Characteristics Improved by Computer Interfacing of a Microbalance Assembly

Transport Variable	Range	Typical Values	Precision	Accuracy	Signal Processing
Time					
Environmental	>100 yr	4-64 hr	<1 μ s	1 μ s	NA
Thermal	>0.2 ms	10-30 s	<1 μ s	1 μ s	NA
Temperature					
Environmental	20-30 °C	24-26 °C	+0.3 °C, 95% CI	+1%	Scaling, thermocouple calibration, corrections
Thermal	25-1000 °C	25-125 °C	+1 °C		
Mass	1-200 mg	2-10 mg	<+0.4%, FS >+0.07%	+1% FS	Polymer suppression, scaling

4. CONCLUSIONS

The application of a versatile research-oriented computer system has converted a conventional TGA system into an instrument capable of high quality measurements of transport processes under conditions ranging from environmental experiments lasting days to flash desorption experiments lasting seconds.

In addition to the experimentation quality that can be attained, the quantity of experimentation is also an advantage of computer-interfaced instruments. Over 250 experiments were completed during a 10-month period; about 200 of these were of significant interest and were retained as stored computer data files.

Most of the environmental experiments were performed overnight or over weekends allowing full use of the thermal analysis system for other research. Less than one-half hour is required to convert to the conventional mode. Therefore, both the quantity and quality of the experimentation recommend the conversion of thermal instrumentation and the application of computer interfacing to transport rate measurements.

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