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A THERMOGRAVIMETRIC STUDY OF POLYVINYLIDENE CHLORIDE IN POLYMERS

BY

CHARLES EDWARD SINGLETON

A THESIS
SUBMITTED TO THE GRADUATE FACULTY
OF THE UNIVERSITY OF RICHMOND
IN CANDIDACY
FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

APPROVED:

W. Allan Powell
J. Stanton Pierce
R. Dean Decker

JULY, 1969

DEDICATION

Dedicated to my wife whose patience, self-sacrifice and encouragement have enabled me to complete this work.

ACKNOWLEDGMENT

On completion of this project I wish to express my sincerest thanks to Dr. W. A. Powell. His personal guidance and interest in supervising this work have made a solution to this problem possible.

I am grateful to Dr. S. A. G. Singer, Research Director at E. I. du Pont de Nemours & Co., Inc., for his contribution to and support of this project.

The author wishes to express his gratitude to E. I. du Pont de Nemours & Co., Inc. for allowing the use of their laboratory facilities to carry out this project.

Finally I wish to express my thanks to Mrs. Jean F. Bates who so kindly consented to type this thesis.

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INTRODUCTION

In the manufacturing of thin films such as cellophane, polymers employed as coatings greatly improve film functionality. Polymers such as polyvinylidene chloride, polyvinyl chloride, polyvinyl acetate and many others are used as coatings or components of coatings designed to improve the functionality of a film. Selection of polymers with properties that will meet the requirements of the finished film product is a continuing process of film manufacturers. Physical and chemical characterization of the polymer along with coating functionality are the factors involved in the selection. Chemical composition is the most important factor affecting polymer characteristics and must be known if one expects to relate properties to polymers. Composition analysis of macromolecules is a very tedious and time consuming task, usually requiring fractionation or other means of obtaining low molecular weight polymers. Low molecular weight polymers are usually soluble in common solvents and therefore more easily analyzed. The number of polymers available for coatings is quite large; therefore, to facilitate selection of coating polymers, there is a great need for a rapid technique of chemical analysis.

The object of this project was to develop the technique of thermogravimetric analysis as a rapid method for quantitative composition analysis of polymers. A homopolymer and copolymer of vinylidene chloride were used in this study.

Previous studies of vinylidene chloride have been carried out by reaction flask decomposition, requiring capture of the volatile material and removal of the residue, followed by quantitative analysis; however, this has not been done using a thermogravimetric analysis method. Data from the conventional method were used to determine reaction kinetics, and the data were compared in this study with values obtained by the thermogravimetric method.

HISTORICAL

I. Thermogravimetric Analysis

The technique of following the gain or loss in weight of a heated body as a function of the temperature and of the time is extremely old. Early researchers studied the change in weight with respect to temperature by placing a weighed substance in an oven for a prescribed time. The sample was then removed, cooled, and reweighed. There are a number of obvious difficulties involved, making this procedure less than desirable. Honda (23) in 1915 improved the procedure for thermal weight change studies by the introduction of a thermobalance. This method of investigation developed by Honda and improved by Guichard (18) and Chevenard (14) gave birth to an analytical method known today as "thermogravimetric analysis". Considerable impetus was given to thermogravimetric analysis by the construction of an automatic recording thermobalance by Chevenard in the early 1920's. It was used to study manganous sulphate, chromic anhydride and other inorganic substances by Honda (23). Guichard (19) studied the dehydration of phosphates.

The thermobalance evolved from the Honda balance beam type through the wire torque type to the null type, devised by Angstrom (3). This type is the basis for the modern thermogravimetric balances, including the Du Pont 950 used by the author which is shown in Figure 1.

Thermogravimetric analysis of polymeric substances utilizing a thermobalance was developed in the late 1940's by Jellinek (25, 26). This technique has been applied to studies involving polymer physical or chemical changes resulting in a gain or loss of weight as a result of vaporization, polymerization, degradation, absorption, and adsorption. However, it has been applied most often to degradation reactions.

Jellinek studied degradation reactions and determined pyrolysis products, reaction kinetics, and proposed degradation mechanisms for polystyrene and polyethylene. Polystyrene, polypropylene, and several other polymers were studied by Madorsky (30, 31, 32, 33). Decomposition reaction kinetics were determined from thermal data. Thermal stability of the polymers and pyrolysis products were also determined from either the thermogram or analysis of volatiles.

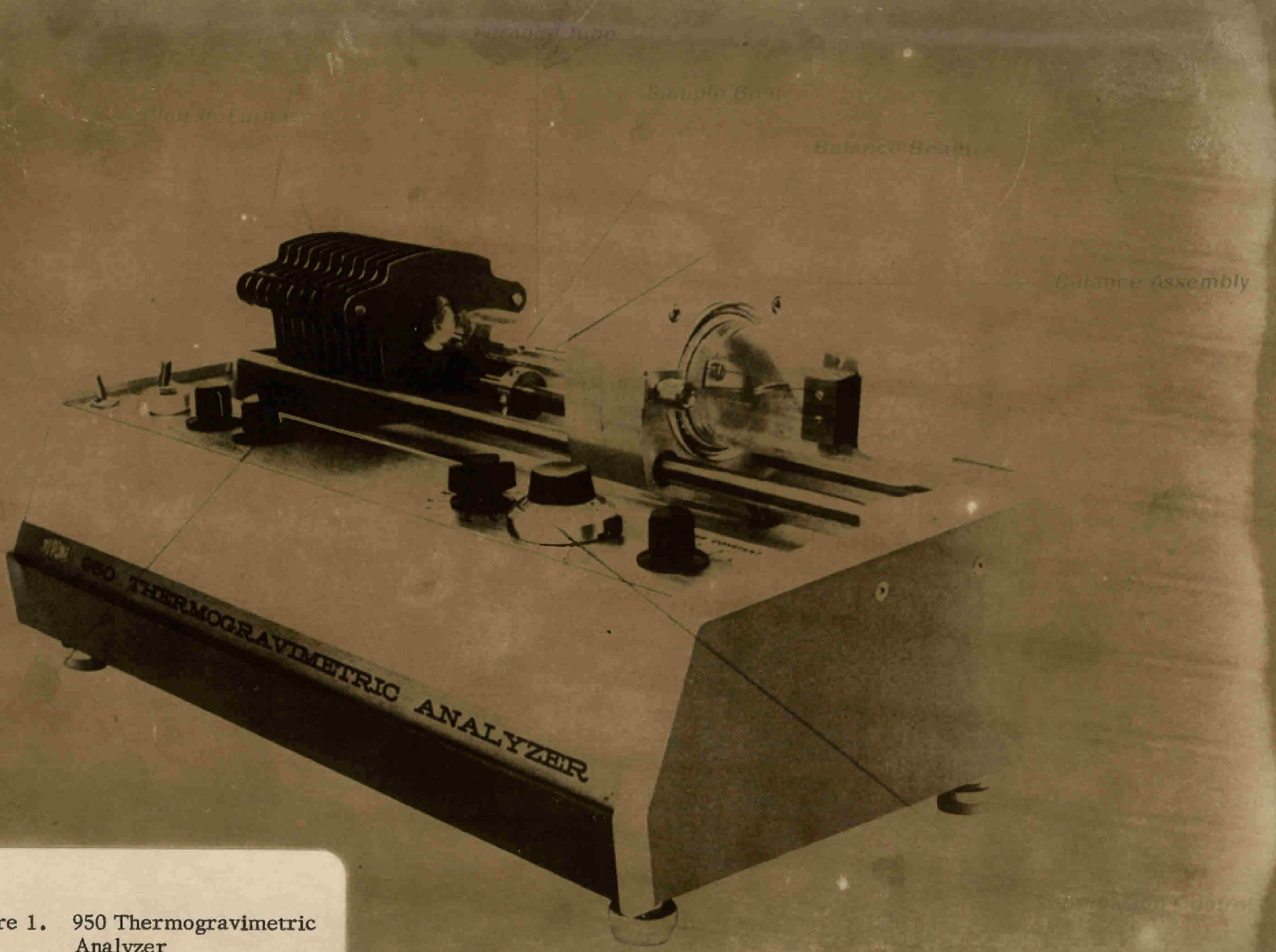


Figure 1. 950 Thermogravimetric Analyzer

Anderson and Freeman (1, 2) employed thermogravimetric analysis as a means of determining the kinetics of thermal degradation of styrenated polyester. Reaction kinetics under the experimental conditions were evaluated by the method of Freeman and Carroll (17). Decomposition of styrenated polyester in air and argon demonstrated the effect of oxygen on polymer degradation and its alteration of reaction kinetics. Data from thermograms and the resulting derivatives of thermograms substituted in the Carroll, Freeman equation (see page 43) produced a reaction order, energy of activation and frequency factor for each degradation reaction step.

Cameron and Fortune (7) evaluated data developed from thermogravimetric studies of polymers, compared it to theoretical data, and have shown that extreme importance must be placed on interpretation. Various integral methods for calculating kinetic parameters have been derived (11, 12, 13, 24, 36, 37) and, based upon Cameron's evaluation, the method of Coats and Redfern (11) is most generally useful.

II. Characterization of Polyvinylidene Chloride

Polyvinylidene chloride is a vinyl polymer produced by the Dow Chemical Company, introduced in 1940 as a clear wrapping film of 85% vinylidene chloride - 15% vinyl chloride called saran. Copolymers of varying composition have been introduced since that time with properties tailored to the end-use. The homopolymer of vinylidene chloride is of limited commercial importance due to its essentially infusible and intractable nature. Copolymers, however, are of great importance as film formers or as a coating for films such as cellophane, polyolefin, or polyester.

Vinylidene chloride is formed by the pyrolytic elimination of HCl from 1,1,2-trichloroethane. This monomer is catalytically converted to the polymer by a batch emulsion polymerization reaction, briefly described in the Appendix (page 52). Copolymers are prepared by the same procedure with the monomer ratio selected to obtain the desired copolymer properties.

Thermal decomposition of polymers of vinylidene chloride has been investigated by Burnett, Haldon, and Hay (5, 6, 22, 23). In their studies, finely divided powdered polymer samples were decomposed in an all-glass apparatus under high vacuum; the volatile products were collected in liquid nitrogen traps and quantitatively determined at room temperature with a calibrated manometer. Qualitative analysis was accomplished by pumping the vapors from the manometer to collection traps; for example, auramine adsorption traps (page 40) and infrared gas analysis cell. In this four-part dehydrochlorination study by Burnett, Haldon and Hay, Parts I and IV (5,6) and by Haldon and Hay, Parts II and III (21,22), it was shown that: (1) only HCl is evolved at temperatures up to 220° C; (2) the reaction is first order with respect to loss of HCl with an activation energy of 30 ± 1.5 kcal mole^{-1}; (3) the reaction is initiated at "weak links" in the polymer chain which may be chain ends, unsaturated groups, or branch points; (4) further elimination of hydrogen chloride proceeds by a "zipper" process along a main chain, the length of the "zip" is reduced for copolymers; (5) the mechanism is apparently a free radical process; (6) acrylonitrile comonomer did not participate in neighboring group activation during the decomposition reaction although the rate did increase. The increased rate is due to increased collision number as a result of increased chain mobility, rather than change in activation energy. The activation energy is greater with the copolymers rather than homopolymers by about 6 kcal mole^{-1}. It is about 37.0 ± 1.5 kcal mole^{-1}. This series of investigations assisted the author as a general and specific reference for both the quantitative and kinetic parameters.

Conventional isothermal methods such as that described above, although quite accurate, require measurement of rate changes over a series of constant temperatures. Two disadvantages of this method are: (1) that a collection and identification at each temperature is required, and (2) a certain amount of decomposition occurs in reaching that temperature. Although the technique of thermogravimetric analysis (TGA) has been proven to be extremely valuable in polymer characterization studies, it has not been applied to the quantitative analysis of polymers of vinylidene chloride.

EXPERIMENTAL

I. Reagents

Polymer A, Dow Chemical Co.

Polymer F-220, Dow Chemical Co.

Auramine-O, C.P. or equivalent, Pfaltz & Bauer, Inc.

Calcium Oxalate Monohydrate, Reagent Grade or equivalent

All other reagents were C.P. or equivalent

II. Apparatus

Thermogravimetric Analyzer, Model 950, Du Pont Co., Cat. No. 950000

Differential Thermal Analyzer, Model 900, Du Pont Co., Cat. No. 900001

Glass trapping system

Micro-buret, 10 ml

Gas Filter Traps

Gas Flow Meter, Brooks-Mite, Model 2001-V, with Flo-Mite needle valve, Brooks Instrument Co.

III. Development of Method

The object of this section was to develop a quantitative thermogravimetric method for the determination of polyvinylidene chloride present in polymers. This method was based on two basic assumptions: (1) that only one mole of hydrogen chloride is evolved per monomer unit of vinylidene chloride between the temperatures of 150° C and 250° C (5, 20), and (2) that comonomers do not interfere with hydrogen chloride evolution (21). In developing this method two control polymers were selected. A homopolymer of vinylidene chloride and a two-component copolymer of vinylidene chloride and acrylonitrile 80/20% were examined. The polymer samples are commercially available from the Dow Chemical Company as Saran A (homopolymer) and F-220 (copolymer). Physical and chemical properties determined by the author are shown in Table I.

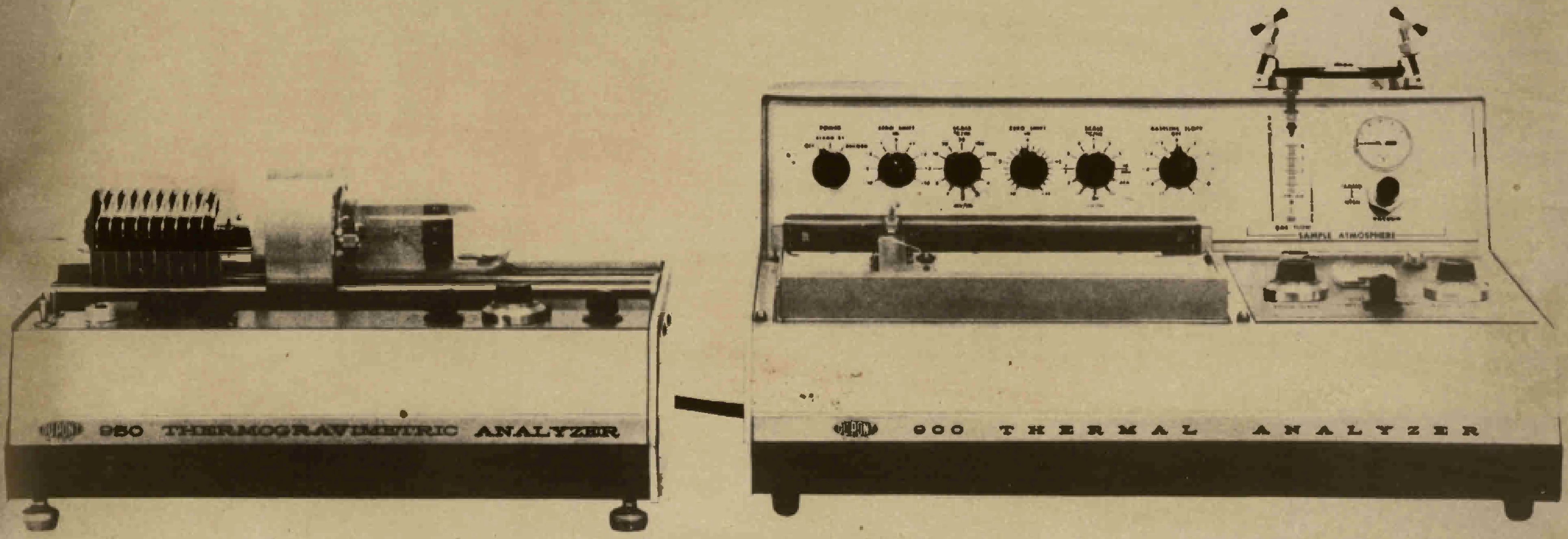
Table I. Physical and Chemical Properties

	Polymer A		F-220	
	Charged	Found	Charged	Found
Composition by %				
Vinylidene Chloride	100	98.11	80	77.99
Acrylonitrile	0.0	0.0	20	19.69
Chlorine	73.20	71.82	58.56	57.09
Nitrogen	0.0	0.01	5.28	5.20
Crystalline M.P. (DTA)	178-183° C		None	
Decomposition Temp. (DSA)	208		202° C	
(TGA)	201		197° C	
Number Av. M.W. ± 5% (Os)	41,000		42,000	

The chemical composition values for the polymers are based on the quantity of chloride and nitrogen as determined from elementary analysis. Theoretically, 73.2% of the vinylidene chloride homopolymer is chloride and for an 80/20% vinylidene chloride/acrylonitrile copolymer the theoretical nitrogen content is 5.28%. The crystalline melting point was determined by differential thermal analysis while other thermal equipment was used for decomposition temperatures. The differential scanning calorimeter cell (DSC) gives a higher temperature for rapid decomposition than the thermogravimetric analyzer (TGA). The number average molecular weight is the same for both polymers, within the limits of the osmometric pressure method.

A. Instrument Operation

The Du Pont 950 Thermogravimetric Analyzer is a plug-in module for the 900 Thermal Analyzer shown in Figure 2 and utilizes the temperature programmer-controller and X-Y plotter of the 900 console. The 900 Thermal Analyzer is the basic console and is a solid-state electronic temperature programmer-controller which permits a wide range of temperature scanning conditions from -190° C to 1600° C. It can be programmed to heat, cool, hold at a given temperature (for short time periods only), cycle and operate isothermally depending on individual needs. The heating and cooling rates and the starting



950 TGA module plugged into 900 Thermal Analyzer

Figure 2. 900 Thermal Analyzer

temperature of the experiment can be selected by program mode switches. The X-Y recorder conveniently plots chemical, physical, or mechanical properties as a function of temperature or time. The specifications of the 900 console unit have been tabulated and are shown in Table II.

Table II. 900 Thermal Analyzer Specifications

Temperature Range	Depends on module
Operating Mode	Heat, Cool, Hold, Isothermal, Cyclic
Sample Size	Depends on module
Program Heating Rate	0.5 to 30° C/min
Heating Rate Accuracy	± 5% or 0.1° C/min
Heating Rate Precision	0.1° C/min
Heating Rate Linearity	± 1% or 0.01° C/min
Heating Rate Stability	Less than 5% change in heating rate for a 20 volt line change
Drift in Isothermal Position	Less than 1° C/hr
Drift in Hold Position	Less than 3° C/hr
Program Starting Temperature	Continuously Variable
Sample Atmosphere	Static or Purge
Y Axis Scale	0.004 0.008 0.02 0.04 0.08 0.2 0.4 mv/in
X Axis	0.4, 0.8, 2, 4, 8 mv/in
Chart Speed	0.05 to 10 in/min

The 950 module is an easy to operate thermal balance made functional through its attachment to the 900 console. Specifications of the 950 module are shown in Table III.

Table III. 950 Thermogravimetric Analyzer Specifications

Capacity	300 mg including sample pan
Weight Ranges	1, 2, 5, 10, 20, 50, 100 mg (full 5-inch scale)
Temperature Range	To 1200° C
Suppression	110.00 mg
Suppression Accuracy	± 0.04% of suppression
Sensitivity of Weight Measurement	0.2% of full 5-inch scale
Precision of Weight Measurement	0.4% of full 5-inch scale
Accuracy of Weight Measurement	± 1.0% of full 5-inch scale
Isothermal Temperature Stability	1° C/hr
Time Constant	0 Direct 1, 2, 5 seconds
Heating Rate	0.5 to 30° C/min
Pressure	Atmospheric to 1 Torr
Purge Rate	Up to 1 liter/min

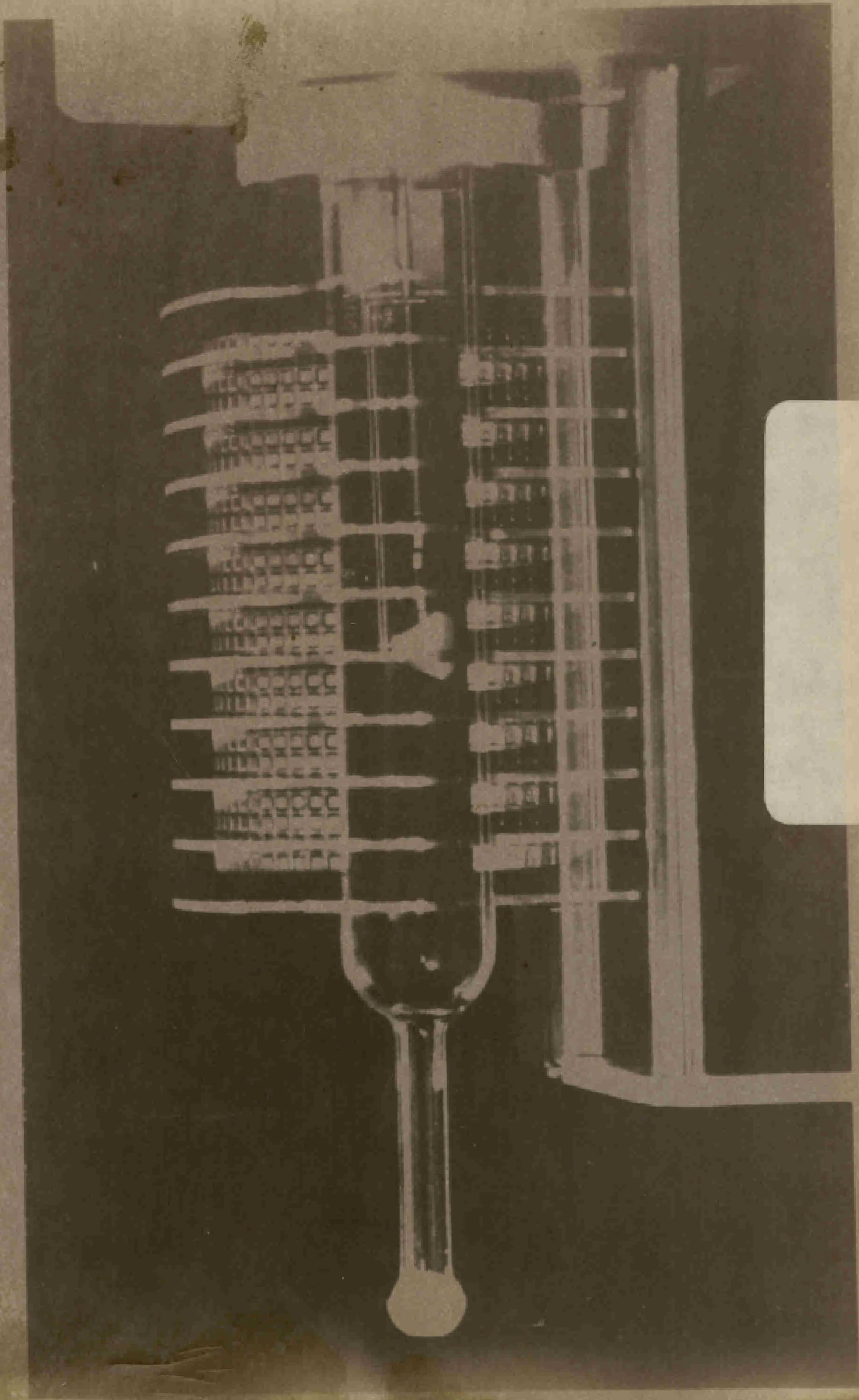


Figure 3. TGA Furnace

and water of hydration can be accurately measured for a wide variety of substances (9). Calcium oxalate monohydrate is one such substance which lends itself to accurate and theoretical weight losses at given temperatures. It was therefore used to determine the accuracy and sensitivity of this instrument and to standardize operating procedure. Standardization of operating procedures began with instrument calibration followed by a measure of its sensitivity and accuracy. Instrument calibration was conducted as described in the TGA manual, while instrument sensitivity and accuracy were determined for this instrument from data developed from decomposition studies of a standard sample of calcium oxalate monohydrate.

According to the calibration procedure described in the TGA manual, the pen position is first adjusted to represent a convenient recorder zero point. This is followed by taring the quartz balance beam rod by placing counterbalance weights on the counterweight arm. Counter weights are adjusted until a pen deflection of less than ± one-half inch from zero is obtained. The quartz rod is now balanced to within 10 mg of its weight, the remaining weight is counterbalanced with the balance control knob. The recorder pen is adjusted to the previously established zero for each sensitivity setting with the balance control knob. This completes the counterbalance steps for the quartz balance beam. Zeroing the recorder and balance with the chart zero is the next step and is accomplished in two operations. First, the recorder pen is adjusted to the chart zero by depressing the balance recorder zero button (this electronically removes the balance from the system), followed by shifting the recorder pen to the chart zero with the recorder shift control. Release of the balance recorder zero button will reconnect the balance. The second operation is to adjust the pen to the chart zero with the balance control knob. Now the balance and recorder are zeroed on the chart zero. The balance sensitivity is then evaluated by placing a standard 50 mg weight in the slot on the balance beam and determining the weight deviation at each sensitivity setting. The TGA span calibration control knob is adjusted until the recorder pen indicates 50 mg on the chart at each sensitivity setting. The instrument is then ready for operation with an accuracy of ± 1.0%.

Calibration of the instrument was followed by determination of its actual sensitivity and accuracy by decomposition studies of a standard sample. Comparison of its theoretical vs actual weight loss values permitted calculation of instrument accuracy and also assisted in establishing operating parameters. Calcium oxalate monohydrate was used as the standard allowing an accuracy check at three temperature ranges.

Decomposition of calcium oxalate monohydrate when heated in a nitrogen atmosphere occurs in three steps, loss of water of hydration, followed by carbon monoxide and finally carbon dioxide. Theoretical quantities are lost within the approximate ranges of 125-200, 425-540, and 615-785° C, respectively. Calibration of the 950 TGA was effected by comparison of each weight loss step, as observed, to theoretical values. These values are: for water, 12.32%; for carbon monoxide, 19.18%; and for carbon dioxide, 30.11%. From this comparison, operating procedures were established and parameters most conducive to quantitative analysis were determined. Operation of the instrument was perfected by performing trial runs with this standard.

A powdered sample of the C.P. grade standard was transferred from a storage vial to the platinum sample pan of the instrument. The amount of sample was determined by the instrument settings which are adjusted according to the nature of the study. For example, a substance that loses a great deal of weight over the temperature range should have a low scale setting so that the entire weight loss is recorded. A general guide is to adjust the sensitivity so that the sample weight would place the needle at the top of the chart and so that sample weight loss would cause complete transverse of the recording needle to the bottom of the chart. Therefore, a sensitivity setting that will allow full scale deflection for the total weight loss within the temperature range will be the most accurate setting. A sample weight of approximately 20 mg of calcium oxalate monohydrate satisfies this requirement.

Having adjusted the instrument settings to obtain an approximate weight and after loading the pan, the thermocouple was positioned just above the sample insuring that it was not in direct contact. Care must be exercised that sample swelling on heating will not cause contact with the thermocouple. The furnace tube was replaced and a nitrogen flow established. Nitrogen serves two purposes; it provides an inert atmosphere and it removes volatile substances as they evolve, thus reducing the possibility of interaction with the sample. An accurate sample weight was recorded. The entire balance assembly was moved into position, with the sample shielded by the furnace tube, in the center of the furnace. The furnace was activated and heated at a predetermined rate to approximately 900° C. Heating rates are continuously variable from 0.5 to 30° C per minute with a range of ambient to 1200° C. The temperature range is selected simply by selecting temperatures that will encompass those where weight loss occurs. Selection of a heating rate is more dependent upon the nature of the study. For example, glass transition studies or melting point studies are improved by rapid heating rates 15 to 30° C per minute. Decomposition studies, especially of polymers, are improved by slower heating rates. A rate of 5° C per minute is almost standard for decomposition studies. After heating the calcium oxalate monohydrate sample to approximately 900° C, the furnace was deactivated and the instrument switched to a stand-by mode. The thermogram was removed from the X-Y recorder and examined to determine the actual weight loss for each phase. These values were converted to percentages and compared with theoretical values, as shown in Table IV.

Table IV. Calcium Oxalate Monohydrate Decomposition

No.	Sample Wt. mg	% Weight Lost 125-200° C (H_2O)	425-450° C (CO)	615-785° C (CO_2)	Total
Theoretical		12.32	19.18	30.11	61.61
1	22.38	12.20	16.09	29.71	58.00
2	23.38	12.10	18.18	30.88	61.16
3	22.88	12.46	18.36	30.29	61.11
4	36.91	11.51	17.61	30.48	59.60
5	27.23	12.12	18.36	29.38	59.86
6	35.34	12.17	17.26	29.71	59.14
7	23.00	11.30	17.39	30.43	59.12
8	22.70	11.72	17.89	29.34	58.95
9	34.60	12.43	17.92	30.35	60.70
Average		12.00	17.66	30.06	59.74
Standard Dev.		0.40	0.74	0.54	1.07
Relative Stand. Dev.		0.034	0.042	0.018	0.018
% Relative Stand. Dev.		3.4	4.2	1.8	1.8

Deviations of the observed weight losses from theoretical weight losses were noted with respect to temperature range, sensitivity settings, heating rate, and purge rate. This instrument sensitivity is such that an accuracy of 3.0% of the true value was obtained with a precision of 2.0%.

B. Polymer Degradation Procedures

Polymer quantitative analysis utilizing a thermogravimetric analyzer has been limited mainly to determination of additives that are physically mixed with polymers (9) and for kinetic studies (7). These studies have been conducted with a variety of polymers and types of TGA instruments, consequently the experimental parameters varied widely. The particular instruments used, polymers studied, and purpose of the study in most cases dictate the experimental parameters. Therefore, a generally recommended procedure for a thermogravimetric quantitative study of polymers is not available and instrument settings, polymer weight, and purge gas flow rate had to be established for this study.

As a point of reference, initial decompositions of the polymers were conducted using the procedure established with calcium oxalate monohydrate. This procedure was then modified by evaluating the effect of instrument dial settings, purge gas flow rate, and sample weight on the pattern and consistency of polymer weight loss. After development of a procedure that gave reproducible weight loss curves, a method was developed for the quantitative determination of evolved hydrogen chloride gas. The quantity of hydrogen chloride determined was then correlated with the quantity of weight lost to verify the thermogravimetric procedure as a method for quantitative analysis of polyvinylidene chloride in polymers.

Using the same procedure as that for calcium oxalate monohydrate, it was found that the majority of polymer weight loss occurred over the first one-third of the Y axis scale and that a sample weight of approximately 20 mg was necessary to give a full scale Y axis deflection. The heating rate of 15°/min was found to be too rapid to allow accurate correlation of temperature of occurrence with the weight lost. From these facts, it was found that instrumental parameters had to be selected based on the information sought and the instrument limitation. It was decided by the author to select a sensitivity based on the sample weight, expected weight loss, and temperature of occurrence that would produce a full scale thermogram. A full scale thermogram will result when the instrument is set so that the X and Y scale of the recorder will record a complete response to minimum temperature and weight changes, respectively. The sensitivity setting was established experimentally by first decomposing a polymer with a low instrument sensitivity and a high temperature scale. This produced a thermogram that included each change in weight for the full temperature scale and a measure of its magnitude. The Y axis, weight change axis, was then expanded by increasing the sensitivity through a reduction of the number of milligrams per inch of chart scale; the magnitude to which this can be done is limited by the sample weight.

Having determined that the X and Y axis sensitivities are established from arbitrary sample weights, the magnitude of the weight loss deflection, and the temperature range in which the deflection occurs, the only remaining instrument variable is the heating rate.

A study was conducted to establish the optimum heating rate for the decomposition of vinylidene chloride polymers. The objective was to determine the fastest heating rate possible for quick analysis, and at the same time produce a maximum and accurate weight loss for a given polymer within a given temperature range. Heating rates of 5, 10, 15, and 20° C/min were used to decompose a vinylidene chloride polymer. The percent weight loss for several temperatures were determined and compared for the different rates, as shown in Table V. The quantity of weight lost was determined directly from the thermograms at the specific temperature indicated.

Table V. % Weight Loss vs Heating Rate

Point Measured °C	Heating Rate, °C/min 5	10	15	20
200	1.57	0.79	0.40	0.31
225	11.95	6.19	4.31	3.30
250	37.50	26.01	20.59	17.37
275	46.23	45.12	43.18	41.59
300	50.31	50.12	49.32	48.90
350	55.19	55.59	55.23	54.87
400	58.18	58.76	58.42	58.25
450	60.46	61.14	60.73	60.61
500	62.97	63.52	62.65	62.97

It was found that the slowest heating rate produced the greatest weight loss for the initial decomposition reaction, and at lower temperatures. This is shown in Figure 4. The overall weight loss was about the same. Based on this, a heating rate of about 5° C/min should produce a maximum weight loss within the temperature range studied. C.J. Keattch (28) and A. Reisman (35) conclude that there is neither an optimum nor a standard heating rate, but that a heating rate of 3 to 5° C/min was suitable for most studies.

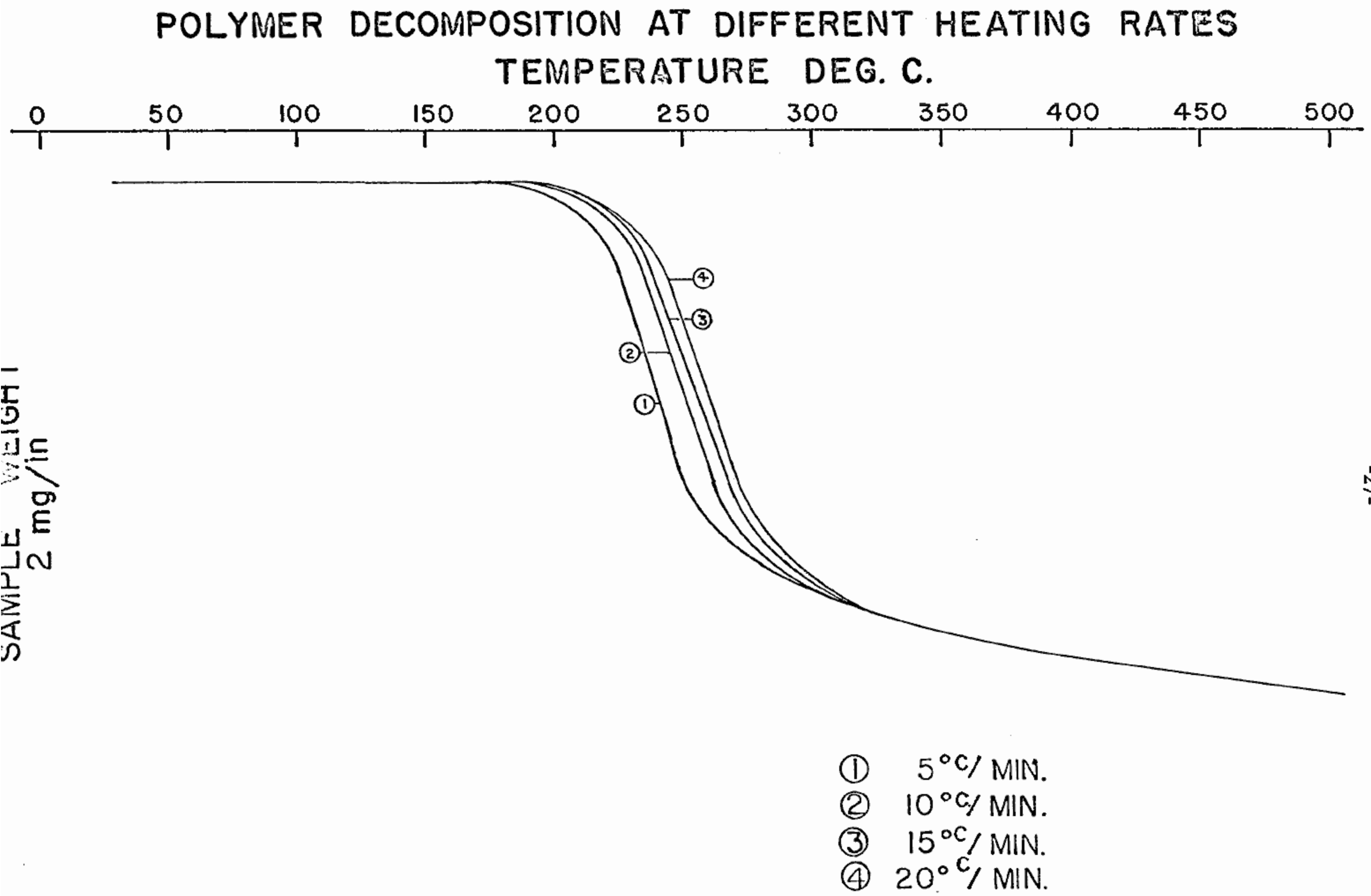


Figure 4. Polymer Decomposition at Different Heating Rates

The experiments were studied in an inert atmosphere (20, 28) of nitrogen gas controlled at a constant flow rate. The inert gas served two functions: (1) to maintain a constant unreactive atmosphere during polymer decomposition (20) by removing the volatile substances as they evolve, and (2) to act as a carrier to transfer the volatile material from the furnace to collection traps (28). Unlike the heating rate and sample weight, the gas rate of flow did not show a detectable effect on the decomposition pattern when controlled at any rate between 0.1 and 2.0 cfh. The rate was therefore varied between these values from one series of experiments to the next depending on the experimental design. For example, if the experiment was designed to obtain a decomposition pattern, then a flow rate between 0.5 and 2.0 cfh was established. However, when collection traps were attached, the flow rate was controlled on the low side to produce a slow flow through the traps, allowing maximum trapping exposure time. The rate of flow was controlled with a Brooks Model 2001V gas flow meter. Nitrogen from a commercial gas cylinder was passed through several filter traps prior to passing through the flow meter and decombustion chamber. Filter traps of glass tubes, two containing ascarite and one containing an indicator, trapping material, drierite, and glass wool. Moisture and minute particles are thus removed from the gas.

A guideline for instrumental parameters, sample weight and flow rate is listed in Table XIII in the Appendix. Polymer decomposition thermograms and the resulting quantitative calculations are included in the Appendix, pages (54, 55, 56).

Data of the average weight lost for both polymers at several temperatures are shown in Table VII. Ten polymer samples of each were decomposed.

Table VII. Average Percent Weight Loss from Thermograms

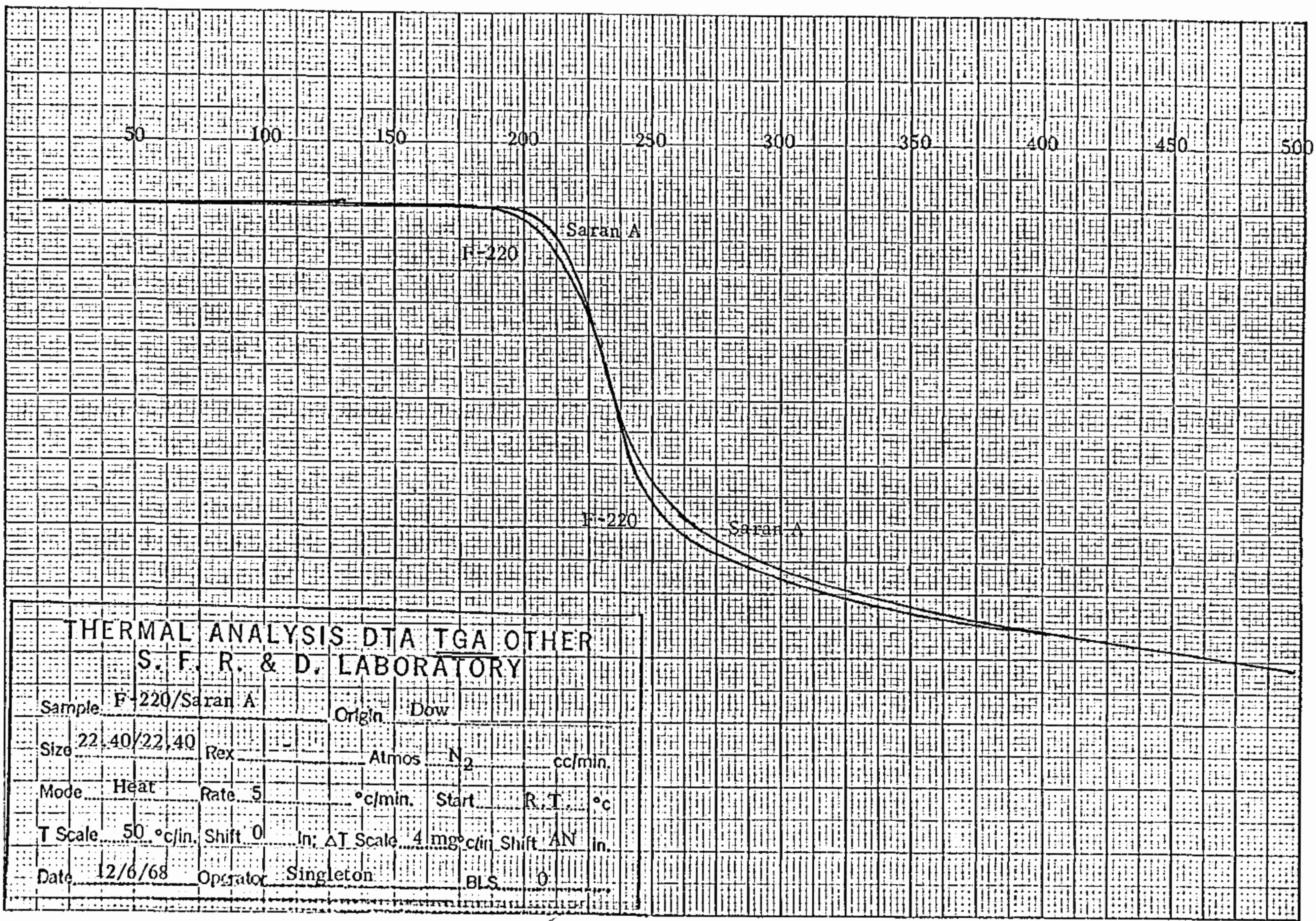
Temperature °C	Polymer A	Polymer F-220
200	0.67 ± 0.58	2.71 ± 1.68
225	10.65 ± 5.77	15.61 ± 6.88
250	36.22 ± 5.03	37.24 ± 8.38
275	45.93 ± 2.05	46.64 ± 3.28
300	49.86 ± 1.96	50.63 ± 2.16
325	52.97 ± 1.85	52.97 ± 1.89
350	55.30 ± 1.99	54.76 ± 1.68
375	57.31 ± 1.99	56.19 ± 1.54
400	59.23 ± 1.83	57.50 ± 1.69
425	60.61 ± 1.97	58.86 ± 1.51
450	61.97 ± 1.80	60.27 ± 1.54
475	63.51 ± 1.91	61.39 ± 1.54
500	65.11 ± 1.75	62.54 ± 1.63
Theoretical(a)	37.65	30.15

(a) Theoretical values are based on the loss of one mole of hydrogen chloride per monomer unit of vinylidene chloride when decomposed below 250° C.

The above data and typical thermograms as reproduced in Figure 5 show that the polymers decomposed with about the same pattern. Polymer F-220, the copolymer, being less stable than the homopolymer, began to lose weight around 190° C while the homopolymer began to lose weight around 197° C. The copolymer was also found to lose more weight than the homopolymer during the reaction, with the maximum difference occurring at approximately 262° C. The temperature range of 212° C to 250° C is the area in which the most rapid loss of weight occurs and is about the same for both polymers. The total weight loss is also approximately the same for both polymers indicating that the weight lost is not theoretically related to the quantity of polyvinylidene chloride present.

C. Collection of Gaseous Products

A procedure to quantitatively collect the gaseous product(s), predominately HCl (5,6 , 20), evolved during polymer decomposition was developed. The already established inert gas flow, through the reaction chamber, facilitates this collection by acting as non-reactive carrier. Utilizing nitrogen as the transfer system, it was necessary to construct a collection apparatus to serve as a trap and titration flask, and also to select an efficient trapping solution. A solution of sodium hydroxide or silver nitrate can be used to efficiently collect the hydrogen chloride gas evolved. A dry trapping system of auramine powder, that



THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY

Sample F-220/Saran A Origin Dow
Size 22.40/22.40 Rex - Atmos N_2 cc/min.
Mode Heat Rate 5 °c/min. Start R.T. °c
T Scale 50 °c/in. Shift 0 In; ΔT Scale 4 mg°c/in Shift AN in.
Date 12/6/68 Operator Singleton BLS 0

Figure 5

is basic in nature, was also used in this study. The media utilized were sodium hydroxide, silver nitrate, and auramine, and the advantages and disadvantages of each will be discussed below.

The collection solutions were also used to assist in the construction of an efficient trapping system. The first system was an Erlenmeyer flask containing a sodium hydroxide solution and was connected to the reaction chamber outlet with a glass tube. A series of polymer samples were decomposed while the evolved gases bubbled through the sodium hydroxide solution. The excess sodium hydroxide was titrated with a standard hydrogen chloride solution. Using phenolphthalein or a pH meter, erratic results were obtained. This was attributable to inefficient trapping of evolved HCl due to insufficient gas exposure to the collection medium. This was verified by connecting the sodium hydroxide containing Erlenmeyer to one containing a silver nitrate solution; by passing the decomposition gases through both traps, the development of a cloudy appearance in the silver nitrate trap verified the escape of hydrogen chloride from the sodium hydroxide trap.

Another disadvantage of the Erlenmeyer system was the increased carrier gas pressure required to force the liquid out of the inlet tube. As the bubble was released, the pressure was reduced and the solution refilled the tube. This phenomena repeats continuously during the reaction and a regular pulsing action is established. Pulsation of the flow rate causes the sample pan to oscillate which transferred to the balance as a vibration which is recorded on the thermogram as erratic deflections.

The efficiency of the Erlenmeyer trap can be improved by increasing the volume of the solution. However, this would also increase the magnitude of the vibration. To increase the solution depth, thus the efficiency, without increasing the volume of solution, the Erlenmeyer flask was replaced with a test tube, shown in Figure 6. A series of polymers were decomposed and the volatiles trapped with the test tube system. Titration of the excess sodium hydroxide was still erratic and a cloudiness appeared in the silver nitrate trap when attached. To improve the efficiency of this trapping system, glass beads were placed in the sodium hydroxide trap. A third set of polymers were thermally decomposed and the evolved gases passed through the trap. A silver nitrate trap was attached to test the glass bead, sodium hydroxide trap efficiency, indicated by the dotted lines in Figure 6. The silver nitrate solution remained clear indicating that the sodium hydroxide, glass bead trap was removing all of the hydrogen chloride vapors. However, the bulkiness of the glass beads would not allow "in tube" titration and quantitative transfer of glass beads and collection solution was very inconsistent.

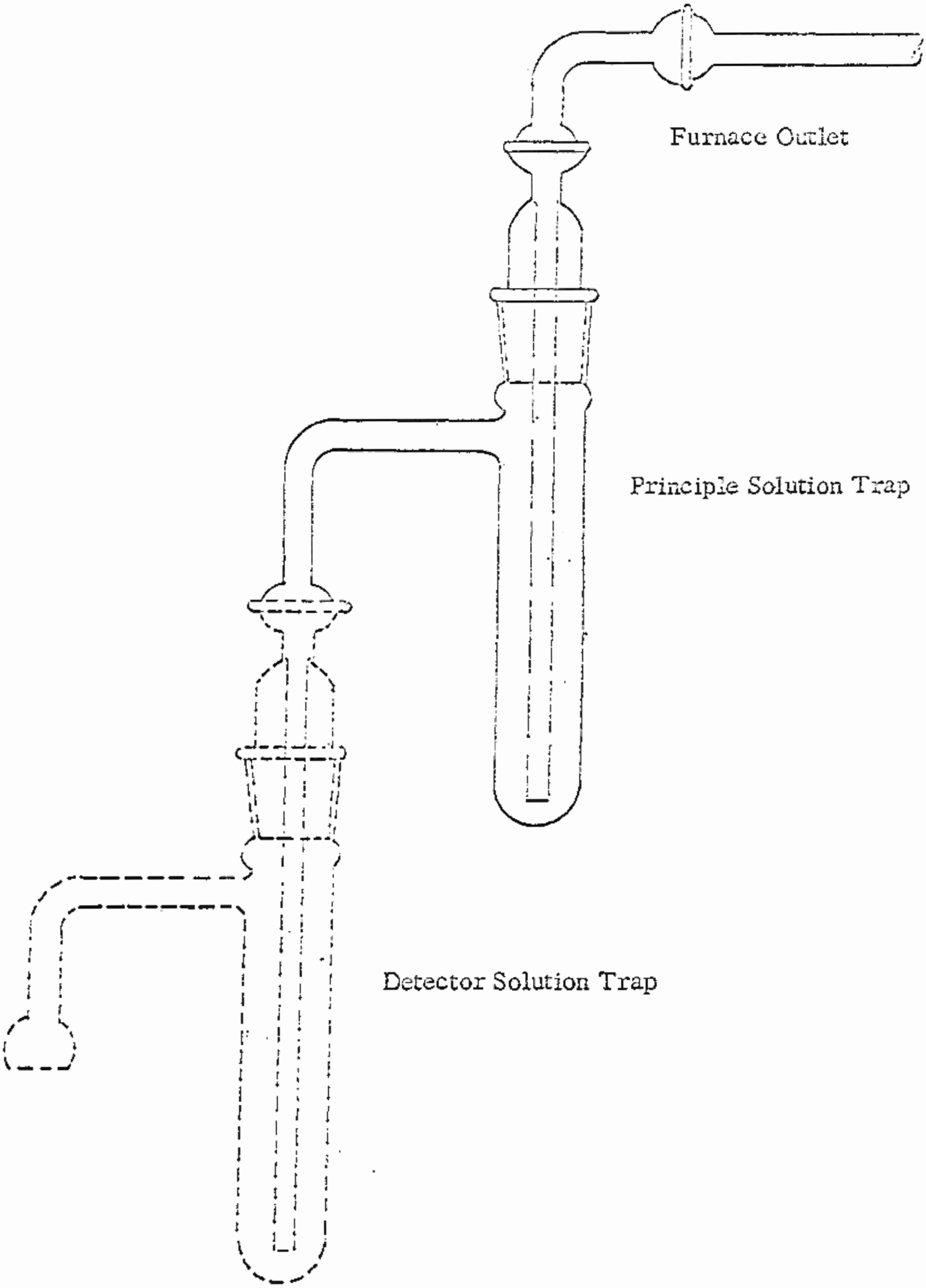


Figure 6. Solution Absorption Traps for Hydrogen Chloride

This system was modified by exchanging the glass beads and glass in-let tube with a gas dispersion tube. The gas dispersion tube, in the test tube trap, with a solution of sodium hydroxide, proved to be an efficient trapping system which also allowed direct titration of the excess sodium hydroxide. Figure 7 represents the complete unit.

During the development of an efficient trapping system, both sodium hydroxide and silver nitrate were used as the principle trapping media. Using a second or detector trap containing a silver nitrate solution, either medium in the principal trap proved efficient. However, it was found that the formation of silver chloride in the gas dispersion tube reduced the nitrogen flow rate causing an increase in the sample chamber pressure. This change was not transmitted to the recorder but detected by a drop of the flow meter indicator. Since the decomposition reaction involves gaseous product evolution, an increase in surrounding pressure could reduce the rate of reaction and thus create an error in the kinetic results. Thermograms from polymer decomposition with silver nitrate in the principal trap did not indicate a change in the reaction rate. However, to eliminate the possibility of interference, the author decided not to use silver nitrate except as an indicator. Data from the sodium hydroxide system using the test tube-gas dispersion tube trap were collected to evaluate this procedure as a means of quantitatively collecting the decomposition gaseous products. The results are shown in Table VIII for gases trapped to a temperature of 250° C.

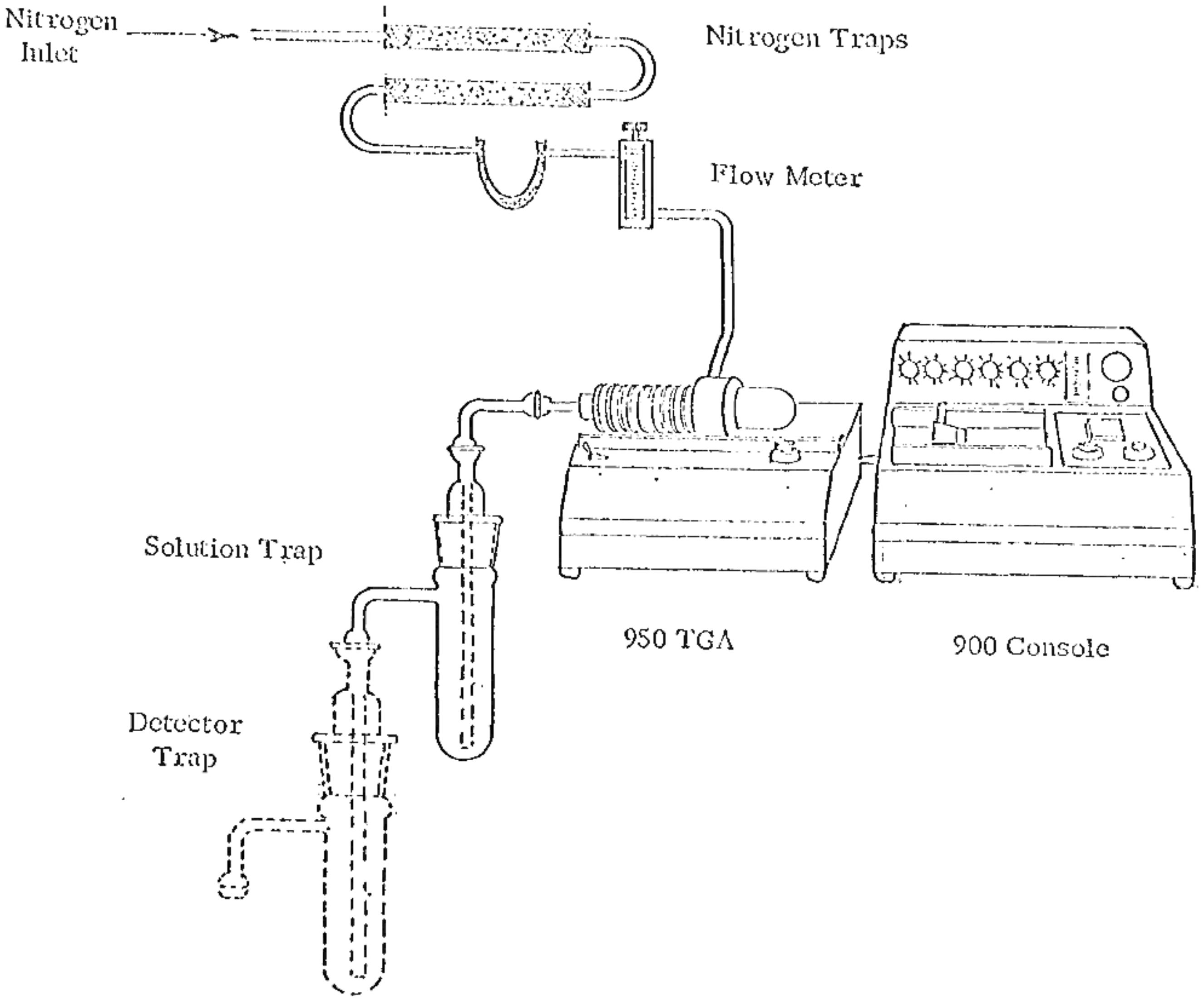


Figure 7 - Schematic of Assembled Apparatus

Table VIII. Sodium Hydroxide Collection of Hydrogen Chloride

Sample	Weight mg	NaOH ml	HCl ml	HCl %
		Homopolymer		
1	22.12	40	17.26	56.35
2	19.92	40	17.99	53.84
3	21.59	40	17.26	57.74
4	21.48	20	5.61	66.80
5	22.19	20	6.52	54.89
6	22.20	20	6.59	54.11
7	22.12	20	8.57	32.97
8	21.18	20	6.12	62.00
9	21.60	20	6.05	61.57
10	21.28	15	3.32	57.23
11	22.38	15	3.38	53.78
12	23.25	15	2.77	58.02
13	22.30	15	5.64	29.82
		Copolymer		
1	21.52	15	5.08	37.10
2	21.30	15	4.35	45.66
3	21.84	20	6.12	60.13
4	20.95	20	6.59	57.34
5	20.90	20	7.35	48.81

Table VIII
(Continued)

Sample	Weight mg	NaOH ml	HCl ml	HCl %
6	21.99	20	6.59	54.63
7	23.19	20	5.79	60.02
8	21.19	20	6.65	56.02
9	22.40	20	6.15	58.31
10	21.16	20	6.78	54.63
11	22.00	20	9.75	20.37
12	21.11	20	8.70	33.08
		Blank		
1		40	22.49	
2		20	11.63	
3		15	8.43	

As can be seen, the quantity of HCl trapped is not consistent; therefore, a correlation of the hydrogen chloride trapped and the weight lost cannot be made.

A second trapping system was designed for quantitative collection and to assist in identification of the gaseous reaction products. Auramine (5) base, a yellow powder, forms a deep red hydrogen chloride salt when exposed to HCl. The auramine powder was placed in a glass tube that could be attached directly to the outlet of the furnace tube, as shown in Figure 8. As the polymer decomposed, the nitrogen carrier gas transported the evolved gases through the auramine trap. Only hydrogen chloride or strongly acidic gases will be trapped by the auramine; other gases will pass through the trap. When used for quantitative data, the trap tube containing auramine should be dried for 1 hour at 105° C, cooled in a dessicator, weighed, and then attached to the furnace tube outlet. With this method the polymer is decomposed and the evolved gases passed through the auramine trap. A deep red coloration of the base indicates the formation of the hydrogen chloride salt. Color conversion of approximately half of the auramine indicates an excess base and complete extraction of the evolved HCl. The trap is disconnected and weighed. The increase in weight is equivalent to the quantity of HCl trapped. The results are shown in Table IX.

Table IX. Auramine Collection of Hydrogen Chloride

Sample	Weight mg	Trap Wt. mg	HCl %
1	22.20	7.0	31.53
2	22.89	11.2	48.93
3	21.46	5.40	25.16
4	21.19	9.15	43.18
5	21.22	15.0	70.69

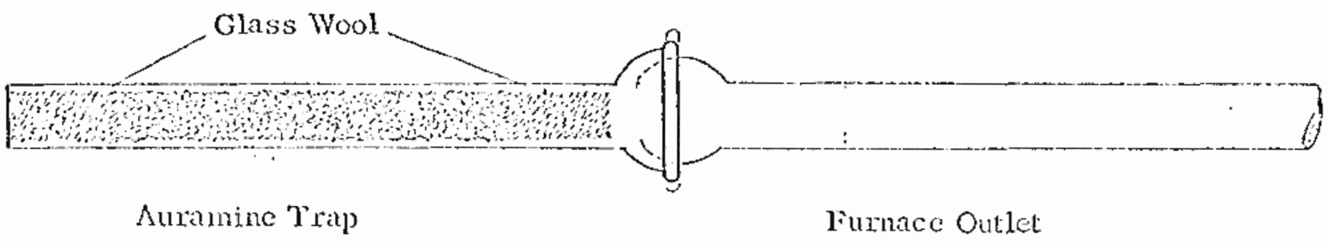


Figure 8 - Hydrogen Chloride Absorption Trap

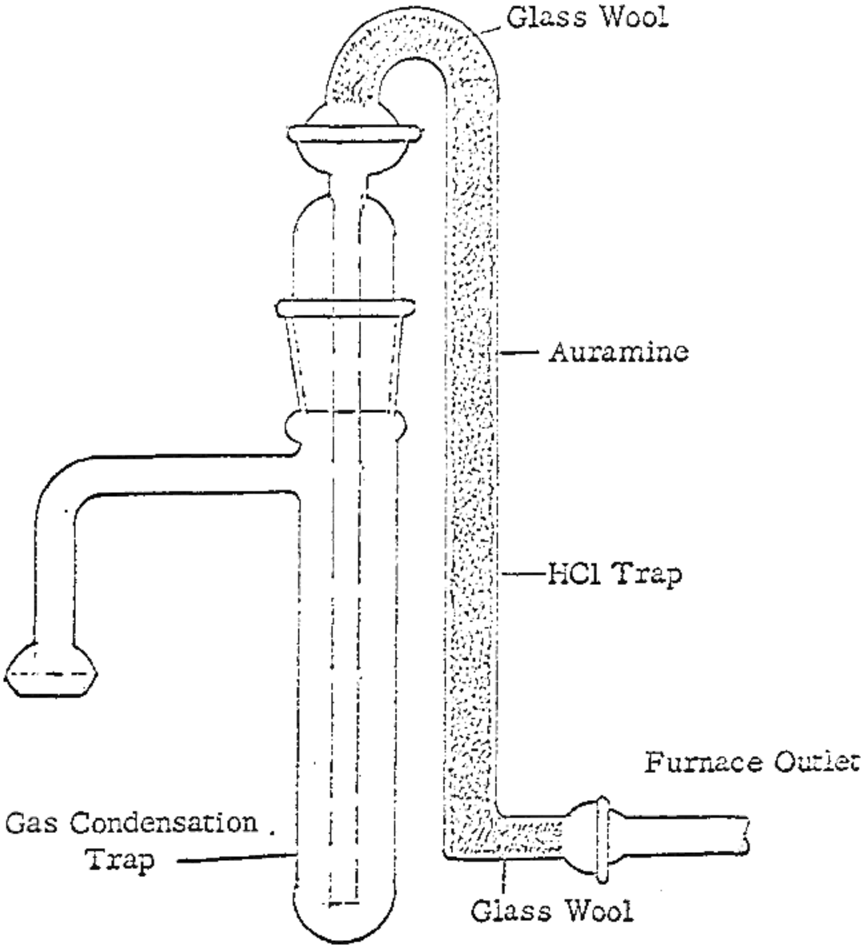
The above results show that the percent of hydrogen chloride evolved is not constant.

In order to determine if other volatile chloride compounds are being formed, the following experiment was carried out: dried auramine was placed in a goosenecked tube which was inserted between the furnace outlet and a liquid nitrogen trap, as shown in Figure 9. HCl was trapped, as before, allowing the other gaseous decomposition products to pass into the liquid nitrogen trap. The liquid nitrogen container was removed, allowing the condensed liquid in the trap to vaporize. Gas samples were extracted and analyzed by gas chromatography. Only trace quantities of methylenedichloride and another unidentified substance were detected.

Data from these gas collection experiments show that: (1) hydrogen chloride is the major gas evolved during the decomposition of polymers of vinylidene chloride, and (2) the ratio of hydrogen chloride to the other gases evolved varies from one experiment to the next.

IV. Kinetics of Reaction

Methods of differential thermal analysis are being employed increasingly in the investigation of pyrolytic reactions. Recently, various methods have been reported (7, 17) for the estimation of overall kinetic parameters from thermogravimetric analysis, of which



Liquid N_2 Dewar Flask Surrounds Gas Condensation Trap

Figure 9 - Trap for Volatiles other than HCl

Freeman and Carroll's method (17) has been most widely applied. They derived equations for non-reversible reactions so that rate-dependent parameters such as energy of activation and order of reaction may be calculated from a single experimental thermogravimetric curve. The method is suitable for determining order and energy of activation of simple reactions. The expression

$$\Delta \log (dw/dt) = X \Delta \log W_r - (\Delta E/2.3R) \Delta(1/T)$$

where dw/dt is the rate of reaction, X is the order of reaction, ΔE is the energy of activation, R is the gas constant, T is the absolute temperature, and where $W_r = \Delta W_c - \Delta W$ (proportional to amount of reactant), ΔW being the weight loss at the point where dw/dt is taken, and ΔW_c being the total weight loss associated with a given reaction. Anderson and Freeman (1, 2) used this expression to evaluate the kinetics of degradation for several polymers. It was used by the author for kinetic evaluation of the thermograms resulting from the dehydrochlorination of polyvinylidene chloride.

Kinetic values obtained by this and other means (5, 6, 21, 22) are discussed and compared on page 48 and a brief outline of the calculations and necessary graphs are shown in the Appendix, pages 63-71.

V. Discussion

A series of experiments was first carried out, using the operating procedure established, in which the polyvinylidene chloride polymers were degraded over a temperature range of ambient to 500° C. Thermograms produced from this study were examined and the resulting data analyzed for the purposes of (1) characterizing the polymers studied, (2) obtaining kinetic parameters, and (3) quantitative correlation of weight loss to polymer composition.

Figures 10 and 11 in the Appendix are examples of the type of thermograms produced. The thermograms are very similar in pattern; however, the copolymer is less stable as can be seen by the more rapid drop-off at a lower temperature. Tables XIVand XV in the Appendix and Table VII, page 29, also show that the copolymer begins to lose weight at a lower temperature than the homopolymer. This is logical since the homopolymer is more crystalline and thus more stable. This confirms the results reported by Burnett and co-workers (6) who also found that the acrylonitrile copolymer was less stable and that the rate of loss was greater than for the homopolymer. The instability and thus the increase in rate is due to the increased chain mobility resulting from the presence of acrylonitrile in the polymer.

Burnett and co-workers reported that the dehydrochlorination of one mole of HCl per monomer unit is the only reaction in the temperature range of 120 to 220° C when decomposed isothermally. This study demonstrated that HCl was the major component evolved up to a temperature of 225° C when the polymer was decomposed isothermally, as shown in Table XVI in the Appendix, but other reactions and thus other components were evolved under isothermal degradation at 245° C. Analysis of the gases evolved during dynamic thermogravimetric decomposition were also found to be composed of predominately hydrogen chloride, as shown in Table X.

Table X. Percent Hydrogen Chloride in Evolved Gases
TGA

Temperature °C	Percent Wt. Loss	Percent HCl[a]
250	36	103
275	46	81
300	50	74

[a] Determined from the auramine trap value.

The temperature recorded by the thermogravimetric method for the evolution of hydrogen chloride is higher than that for the isothermal method. This is due to the design and nature of thermogravimetry and the instrument as well as the polymer decomposed. This instrument measures the temperature near the sample and therefore the results are somewhat higher than expected. This is shown in Table XI, and in Figure 12 in the Appendix, for calcium oxalate monohydrate.

Table XI. Decomposition of $CaC_2O_4H_2O$

Reaction	Duval (14)	Thermogram
- H_2O	100-240° C	125-200° C
- CO	400-500	425-540
- CO_2	660-830	615-785[a]

[a] Lower value may be related to purge rate.

The error is caused by using the "increasing heat" method with the result that reaction temperatures so determined are usually higher than those determined by the isothermal method. Part of this is merely thermal lag and part is due to the finite time required to cause a detectable weight change. An excellent example of this thermal lag was demonstrated by decomposing the sample at different heating rates, as shown in Figure 4. The apparent change in decomposition temperature as the heating rate is increased is demonstrated by the change in the temperature of the first detectable weight loss. Therefore, going from isothermal to 5°/min also results in an apparent change in the decomposition temperature. The thermal lag and time required for detection of a weight change allows the recorder to record a temperature above that of the polymer and that required for dehydrochlorination. This thermal lag is also demonstrated in the temperature determined as the point of onset of additional decomposition reactions. Isothermally, complex reactions were detected at 245° C while by thermogravimetric methods a temperature of approximately 260° C was determined, as shown in Figure 13 and Table XII in the Appendix.

To further characterize these polymers, experiments were conducted to determine the effect of oxygen in air on the rate of degradation at ambient and elevated temperatures. Figure 14 shows that two rapid decomposition steps occur, the dehydrochlorination at approximately 200° C and total polymer destruction at approximately 525° C. The homopolymer is more stable than the copolymer in air as well as nitrogen for the dehydrochlorination reaction; however, both polymers are entirely vaporized at approximately 600° C. Air has no apparent catalytic effect on the dehydrochlorination of either polymer in the temperature range utilized for polymer coating of films.

As previously reported (5, 6) the rate of decomposition is proportional to the molecular concentration and several hypotheses have been proposed to relate the molecular concentration to the mechanism of decomposition. Burnett and workers demonstrated an agreement with the end-group initiation mechanism which proposes that the decomposition is initiated at unsaturated end-groups (6). Based on this, the reaction rate would be directly proportional to the number average molecular weight. It has been found that the polymers studied have a number average molecular weight of 42,000 by the osmotic pressure method, and therefore an equivalent number of end groups. Consequently, they would have approximately an equivalent decomposition reaction rate.

The increasing heat method does not allow complete expulsion of HCl at low temperatures, due to the short time period at any one temperature and since the approximate equal decomposition rates will not allow a distinction at any temperature, it must be concluded that this thermogravimetric procedure cannot be used for the quantitative determination of polyvinylidene chloride present in polymers.

The Anderson and Freeman (2) method was utilized to determine the kinetic parameters for the decomposition reaction of the polymers studied. The calculations are shown in the Appendix, pages 63-71. The resulting activation energy of 71 kcal/mole is not in agreement with that reported in the literature. The activation energy E of 30 kcal/mole as reported by Burnett and coworkers was determined from a completely different experimental design. In their work the polymers were decomposed isothermally at temperatures below 220° C. As shown by the author, discussed on page 45, isothermal degradation at a temperature of 225° C demonstrated that nearly theoretical quantities of hydrogen chloride are evolved. Therefore, Burnett and coworkers limited their study to a temperature range that did not activate complex interfereing reactions. The high activation energy and an unusual reaction order of 4.4 from this study are consistent with the fact that the decomposition reaction is not a simple first order reaction throughout the temperature range studied. This was also indicated by the inconsistent quantity of hydrogen chloride determined in the evolved gas. Since hydrogen chloride was the only gaseous substance evolved, one reaches the conclusion that a complex dehydrochlorination reaction is initiated as the temperature approaches 250° C, the upper temperature limit for this study, producing erratic evolution of a second mole of hydrogen chloride from the monomer units. The resulting thermogram is a summation of the primary dehydrochlorination reaction and the secondary dehydrochlorination reaction(s). The Anderson and Freeman method was derived from the relationship $dw/dt = k\,w^x$ where dw/dt is the rate of reaction, k is the rate constant, w is proportional to the concentration, and x is the order. This relationship is for simple reactions where x is usually 1 and the rate is the result of the reactant A going to product B only. In this study the degradation of the polymer is complicated by side reactions or autocatalysis and will not fit this equation. A complete study of the mechanism of degradation of polyvinylidene chloride would be required to determine its kinetic parameters from thermogravimetric data.

VI. Summary

This is a study of the technique of thermogravimetry as a method for the quantitative analysis of polymers of vinylidene chloride. The kinetic parameters of the decomposition reaction were calculated and discussed.

APPENDIX

Polymerization Procedure

Solution 1	Solution 2	Solution 3
Reaction Flask	Catalyst	Monomer

1. Vinylidene chloride is washed with 5% caustic in water to remove the inhibitor. Remove the caustic with water.
2. Bring Solution 1 to 36° C in a water bath and add Solution 2. Allow the solutions to mix thoroughly.
3. Start the addition of Solution 3 at a slow rate and stir the mixture for approximately one and one-half hours. The end of the reaction is indicated by a decrease in the reflux rate.
4. Filter the polymer through a cheesecloth, place in a plastic container and freeze. Freezing coagulates the polymer particles.
5. Wash the polymer with water to remove the excess catalyst and allow to dry.

Table XII

Percent Hydrogen Chloride from Isothermal Decomposition

Polymer A

	TGA[a]	Combustion Tube[b]	
	245°C	225°C	245°C
1.	39.24	33.77	35.26
2.	43.71	37.10	44.04
3.	43.00	24.93	35.33
4.	54.61[c]	36.79	40.99
5.	43.47	35.57	41.11
6.	40.72		
Average	42.03 ± 1.96	35.81 ± 1.51	39.35 ± 3.89

Theoretical 37.63

a - Determined from weight loss
b - Determined from titration

Table XIII

Instrument Parameters

Function	Setting for	
	Calcium Oxalate	Polymer
T Scale (Temperature)	100°/inch	50°/inch
Δ T Weight Scale	4 mg/inch	Optional
Heating Rate	15°C/min	5°C/min
Program Mode	Increasing Heat	Increasing Heat Isothermal
Sample Weight	20 mg	Optional
Flow Rate	Moderate	Low to Moderate
Sensitivity	4 mg/inch	Most Sensitive

Table XIV

Percent Polymer Weight Loss from Thermograms

Sample Wt., mg.	Temperature, °C 200	225	250	275	300	325	350	375	400	425	450	475	500
						Polymer A							
21.48	0.7	6.05	32.59	44.69	49.12	51.91	54.70	57.03	58.89	60.06	61.45	62.62	64.24
22.19	0.90	15.32	40.12	47.32	51.15	54.08	56.56	58.58	60.39	61.74	62.87	64.22	65.80
22.30	0.0	9.42	36.77	43.05	46.64	50.45	52.91	54.93	56.95	58.52	59.64	60.99	62.78
21.28	1.17	17.62	40.88	47.23	50.99	53.81	58.39	55.22	58.27	59.92	61.33	62.50	65.08
22.40	0.22	14.51	39.29	46.21	49.78	52.68	55.36	57.14	58.71	60.04	61.16	62.50	63.84
20.19	1.73	18.33	43.09	49.78	53.49	56.71	59.44	61.17	62.90	64.14	65.38	66.86	68.35
24.35	0.20	3.69	29.77	46.41	50.31	53.59	56.26	58.73	60.78	62.62	63.86	65.70	66.74
20.28	0.23	6.72	34.28	44.47	48.17	51.18	53.73	55.58	57.43	57.82	60.21	61.83	63.46
21.60	0.23	4.16	29.17	44.21	49.07	52.31	55.32	57.41	59.26	60.65	61.81	64.35	65.74

Table XV

Percent Polymer Weight Loss from Thermograms

Sample Wt., mg.	Temperature, °C 200	225	250	275	300	325	350	375	400	425	450	475	500
F-220													
21.30	4.46	24.88	44.60	49.53	52.58	54.69	56.10	57.51	58.92	60.09	61.27	62.67	63.62
20.95	0.47	3.34	21.00	42.24	47.97	50.60	52.98	54.65	55.85	57.27	58.95	60.14	61.34
20.90	2.87	16.27	41.15	48.09	51.44	53.54	55.26	56.70	57.85	59.57	61.00	61.72	62.92
23.19	3.44	17.25	41.40	48.30	51.74	53.69	55.19	56.71	58.00	59.51	60.59	61.88	62.96
21.19	3.54	19.82	33.97	40.35	46.24	49.08	51.20	52.86	53.80	55.45	56.63	57.81	58.75
22.40	1.79	14.50	40.63	48.66	52.01	54.46	56.03	57.37	59.15	60.04	61.61	62.72	63.62
21.16	3.07	17.49	41.58	48.44	51.98	54.34	56.47	57.42	58.60	60.26	61.20	62.38	64.27
22.00	3.18	17.27	40.91	47.50	50.68	52.73	54.32	55.68	57.05	58.41	59.77	60.91	62.05
21.11	3.79	21.32	43.58	49.50	52.58	54.48	56.13	57.56	58.98	59.45	61.58	62.79	63.95
22.89	0.44	3.93	23.59	43.69	49.15	51.99	53.95	55.48	56.79	58.54	60.07	60.94	62.04

Table XVI

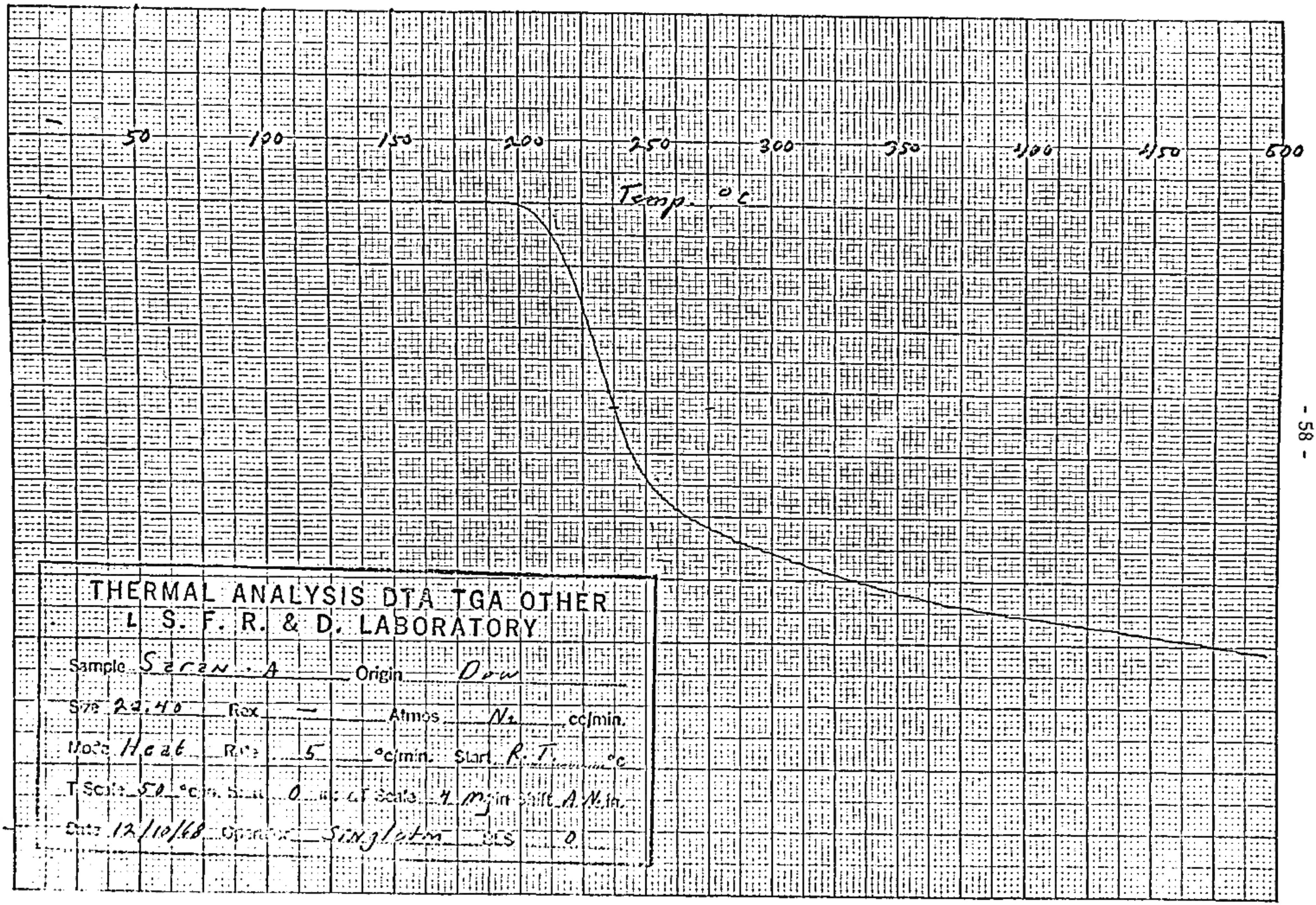
Percent Hydrogen Chloride from Isothermal Decomposition

Polymer A-Conventional Method

225°C	245°C
33.77	35.26
37.10	44.04
24.93	35.33
36.79	40.99
35.57	41.11

Theoretical 37.63

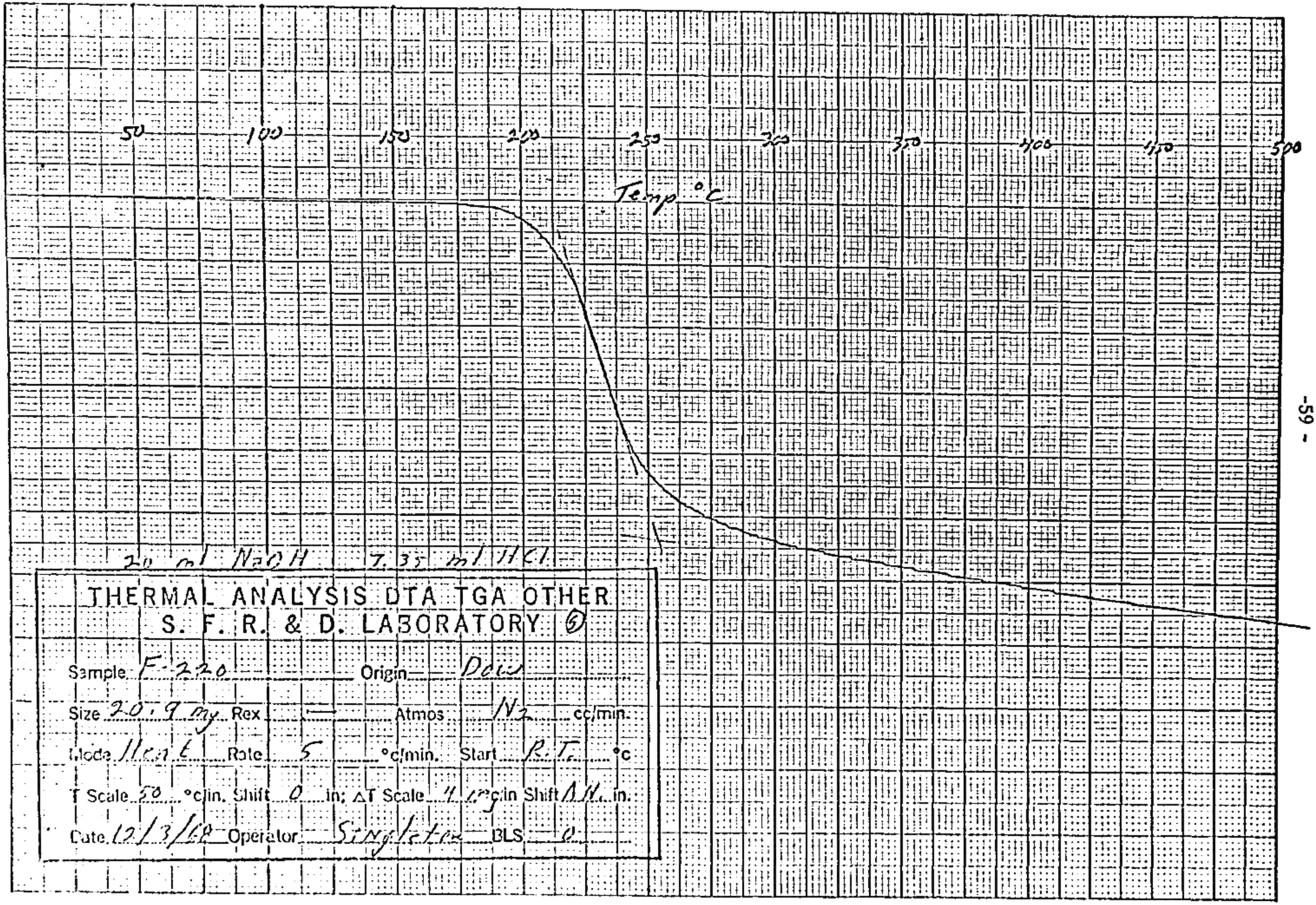
Determined from titration



THERMAL ANALYSIS DTA TGA OTHER
L. S. F. R. & D. LABORATORY

Sample Saran A Origin Dow
Size 22.40 Rex — Atmos N₂ cc/min.
Mode Heat Rate 5 °c/min. Start R.T. °c
T Scale 50 °c/in. Shift 0 in. ΔT Scale 4 mg/in Shift A.N. in.
Date 12/10/68 Operator Singletm DLS 0

Figure 10

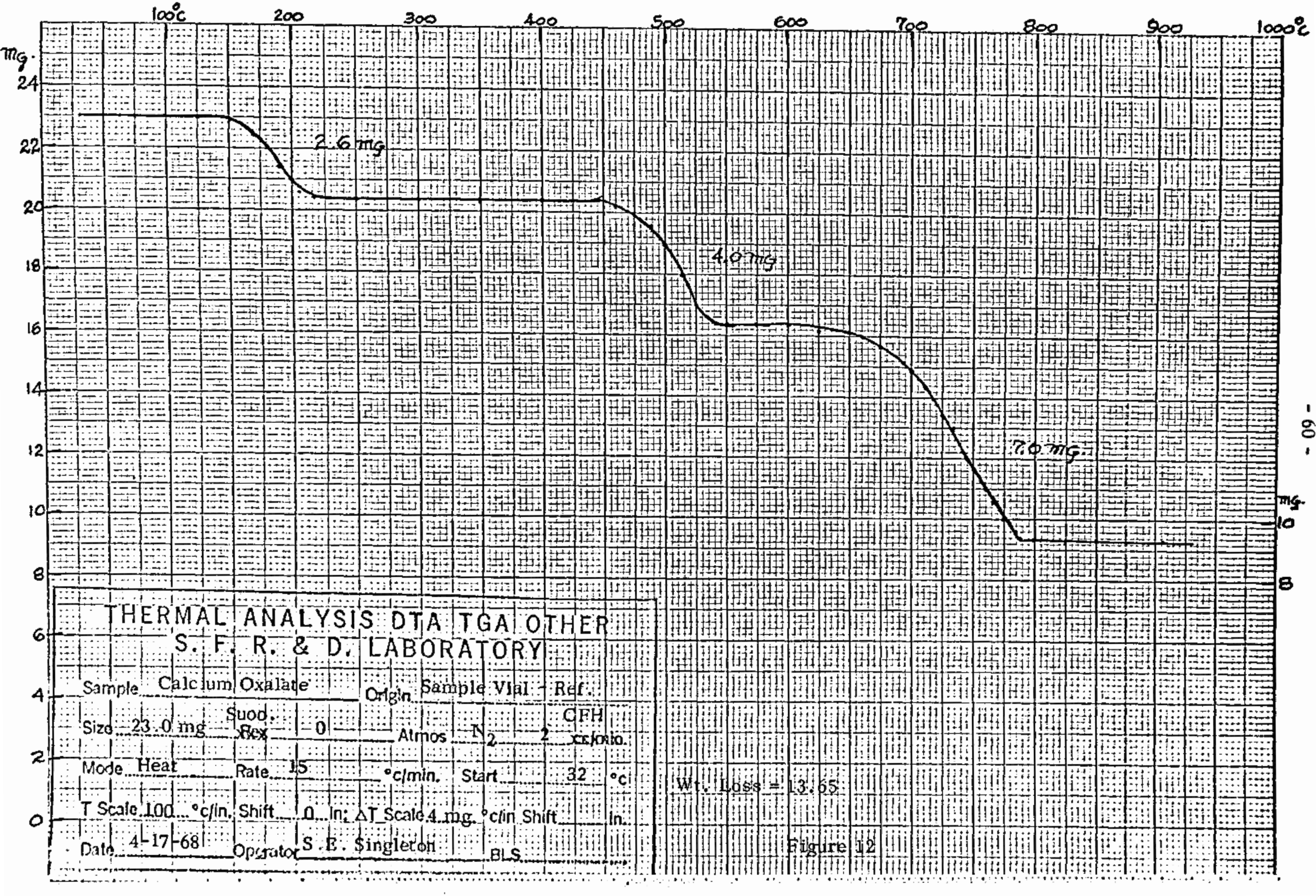


20 ml NaOH 7.35 ml HCl

THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY ⑤

Sample F-220 Origin Dow
Size 20.9 mg Rex — Atmos N2 cc/min.
Mode Heat Rate 5 °c/min. Start R.T. °c
T Scale 50 °c/in. Shift 0 in; ΔT Scale 4 mg/in Shift AH. in.
Date 12/3/68 Operator Singleton BLS 0

Figure 11.

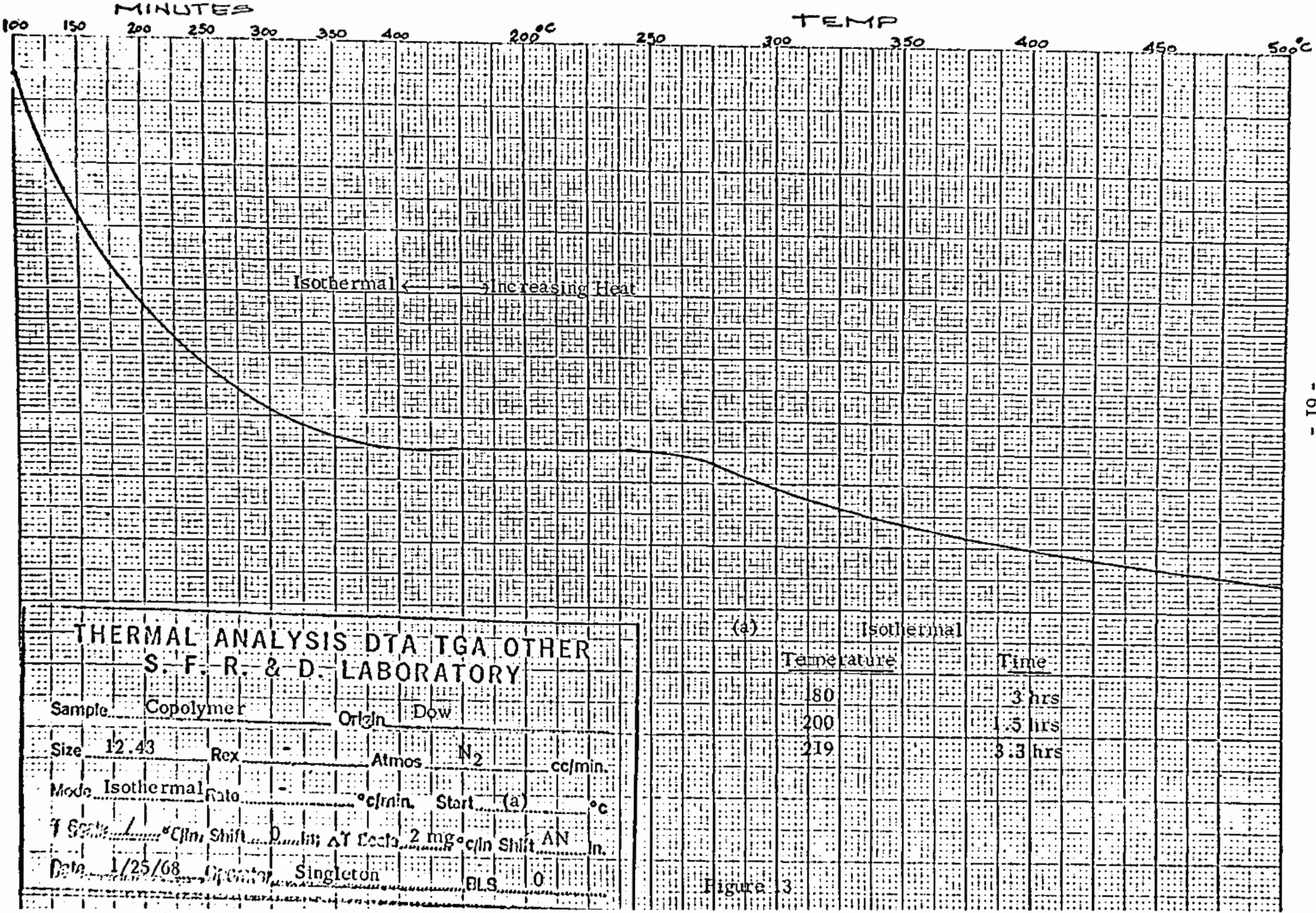


THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY

Sample Calcium Oxalate Origin Sample Vial - Ref.
Size 23.0 mg Susp. ~~Rex~~ 0 Atmos N_2 2 CFH ~~cc/min.~~
Mode Heat Rate 15 °c/min. Start 32 °c
T Scale 100 °c/in. Shift 0 In; ΔT Scale 4 mg. °c/in Shift In.
Date 4-17-68 Operator S. E. Singleton BLS

Wt. Loss = 13.65

Figure 12



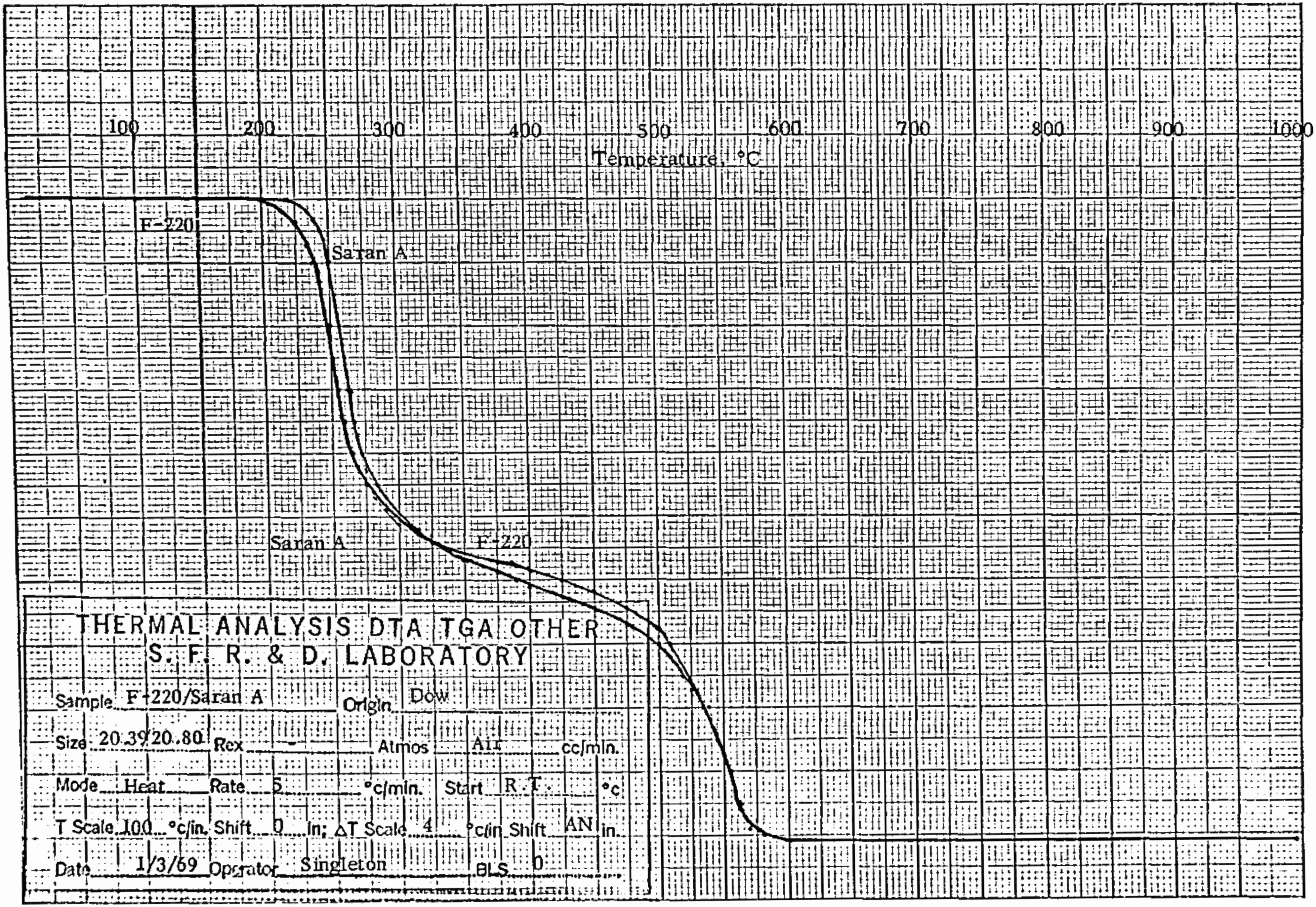
THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY

Sample Copolymer Origin Dow
Size 12.43 Rex - Atmos N_2 cc/min.
Mode Isothermal Rate - °c/min. Start (a) °c
T Scale 1 °C/in Shift 0 in; ΔT Scale 2 mg c/in Shift AN in.
Date 1/25/68 Operator Singleton BLS 0

(a) Isothermal

Temperature	Time
180	3 hrs
200	1.5 hrs
219	3.3 hrs

Figure 3



THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY

Sample F-220/Saran A Origin Dow
Size 20.39/20.80 Rex - Atmos Air cc/min.
Mode Heat Rate 5 °c/min. Start R.T. °c
T Scale 100 °c/in. Shift 0 in; ΔT Scale 4 °c/in Shift AN in.
Date 1/3/69 Operator Singleton BLS 0

Figure 14

CALCULATIONS

Derivation of Anderson-Freeman Equation

Where $(dw/v)/dt = k(w/v)^x$ (Rate for simple reactions)

$$dw/dt = k(w)^x$$

since $k = A e^{-E^*/RT}$

and $\ln k = \ln A - E^*/RT$

and by taking the ln of dw/dt we obtain

$$\ln dw/dt = \ln k + x \ln w$$

and substituting the value of k gives

$$\ln dw/dt = \ln A - (E^*/R)(1/T) + x \ln w$$

and for two points on the curve the equation would be

$$\ln (dw/dt)_2 = \ln A - (E^*/R)(1/T)_2 + x \ln w_2$$

and

$$\ln (dw/dt)_1 = \ln A - (E^*/R)(1/T) + \ln w_1$$

then the difference in rate between points T_2 and T_1 is given by

$$\Delta [\ln (dw/dt)] = -(E^*/R) [\Delta(1/T)] + x [\Delta \ln w]$$

the Anderson-Freeman equation.

Where dw/dt is the rate of reaction, x is the order of reaction, E* is the energy of activation, W is proportional to the amount of reactant and R and T are the gas constant and absolute temperature respectively.

The following calculation is an application of the above equation to the rate curve as shown in Figure 15.

Step 1. Determine the rate dw/dt for the time interval selected, within the limits of the temperature range studied, directly from the thermogram; Table XVIII

Step 2. Plot dw/dt and w_r vs 1/T Figure 16

Step 3. From the graph determine the values of dw/dt and w_r for a given 1/T Table XVIII

Step 4. Determine their logs and the Δ logs for a given Δ 1/T Table XVII

This will give values for the equation constants Δlog dw/dt and Δ log w_r for a given Δ 1/T and can be substituted in the Anderson-Freeman equation.

Step 5. This equation can be solved by plotting Δ log dw/dt vs Δ log w_r the slope of the resulting curve will give x the reaction order and the activation energy E* can be determined from the intercept. Figure 17

Step 6. The order and activation energy were determined from the slope and intercept as calculated by the method of least squares. Table XIX

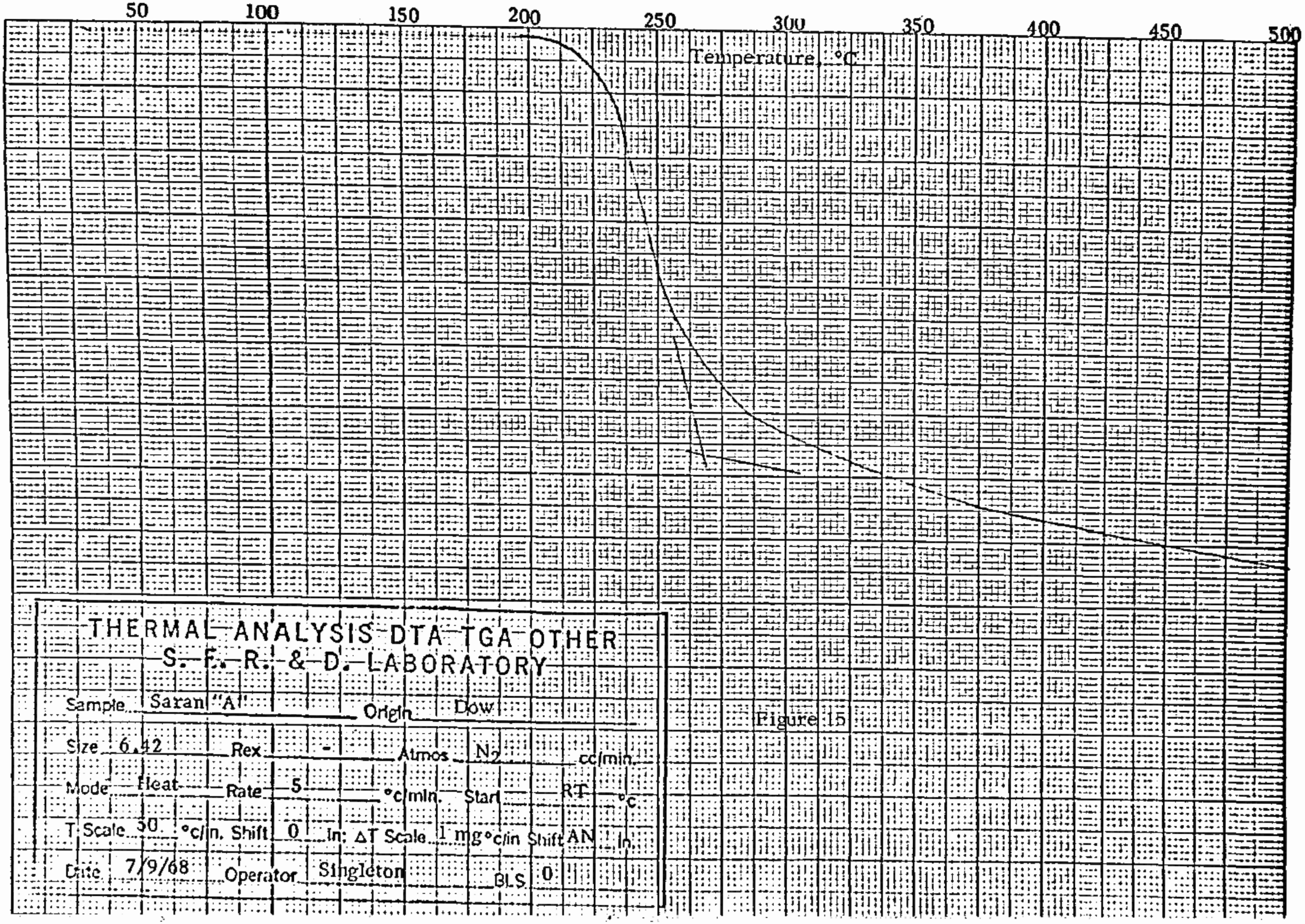


Figure 15

THERMAL ANALYSIS DTA TGA OTHER
S. F. R. & D. LABORATORY

Sample Saran "A" Origin Dow

Size 6.42 Rex - Atmos N2 cc/min.

Mode Heat Rate 5 °c/min. Start RT °c

T Scale 30 °c/in. Shift 0 In: ΔT Scale 1 mg°c/in Shift AN In.

Date 7/9/68 Operator Singleton BLS 0

Table XVII

Application to the Decomposition Thermogram for Polymer A

T, °C	$10^3/T$ K^{-1}	dw/dt x 10^2	Wr = $\frac{W}{74} - \frac{100}{74} \Delta W$ (1)
200	2.112	0.0	5.64
206.25	2.088	0.80	5.63
212.50	2.060	0.80	5.61
218.75	2.032	4.80	5.53
225.00	2.008	9.60	5.37
231.25	1.983	16.00	5.10
237.50	1.960	26.40	4.65
243.75	1.935	35.25	4.06
250.00	1.911	36.75	3.44
256.25	1.890	36.00	2.83
262.50	1.868	26.40	2.38
268.75	1.845	16.00	2.11
275.00	1.824	13.60	1.88
281.25	1.804	8.00	1.75
287.50	1.784	7.20	1.62

(1) W = 4.14 mg total weight lost
ΔW = weight lost at the point where dw/dt is taken

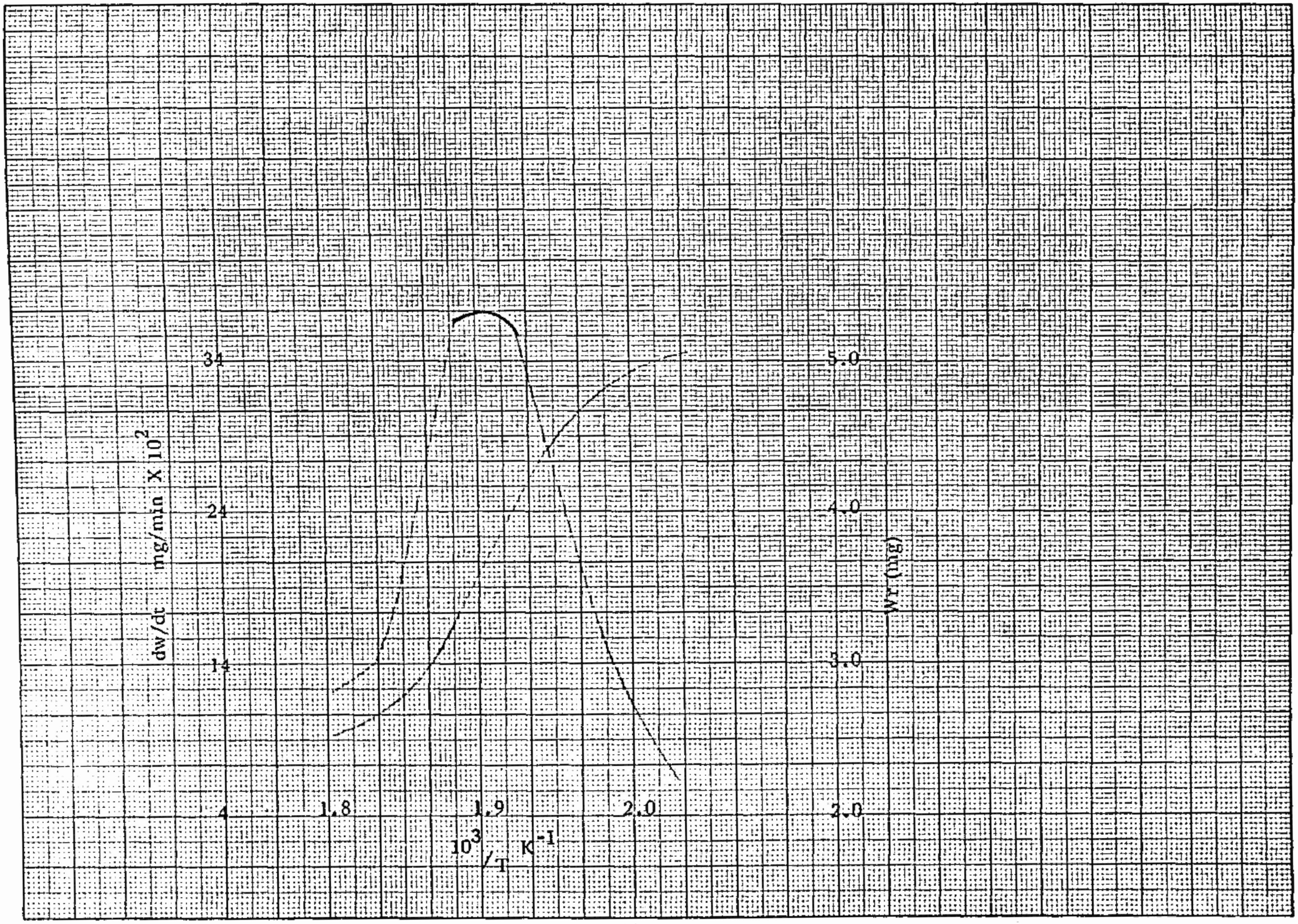


Figure 16

Table XVIII

Determination of Δ Log dw/dt and Δ Log Wr

10^2 dw/dt	Log dw/dt	Δ Log dw/dt	Wr	Log Wr	Δ Log Wr
.01	-2	-.845	5.63	.750	0.0
.07	-1.155	-1.456	5.63	.750	0.001
2.00	.3010	-.301	5.61	.749	0.005
4.0	.602	-.243	5.55	.744	0.007
7.0	.845	-.208	5.46	.737	0.012
11.3	1.053	-.183	5.31	.725	0.022
17.2	1.236	-.187	5.05	.703	0.037
26.5	1.423	-.114	4.64	.666	0.035
34.4	1.537	-.027	4.18	.621	0.056
36.6	1.564	-.001	3.67	.565	0.070
36.7	1.565	+.053	3.13	.495	0.075
32.5	1.512	+.160	2.63	.420	0.062
22.5	1.352	+.167	2.28	.358	0.051
15.3	1.185	+.074	2.03	.307	0.030
12.9	1.111	+.066	1.85	.277	0.042
8.8	.945		1.72	.235	

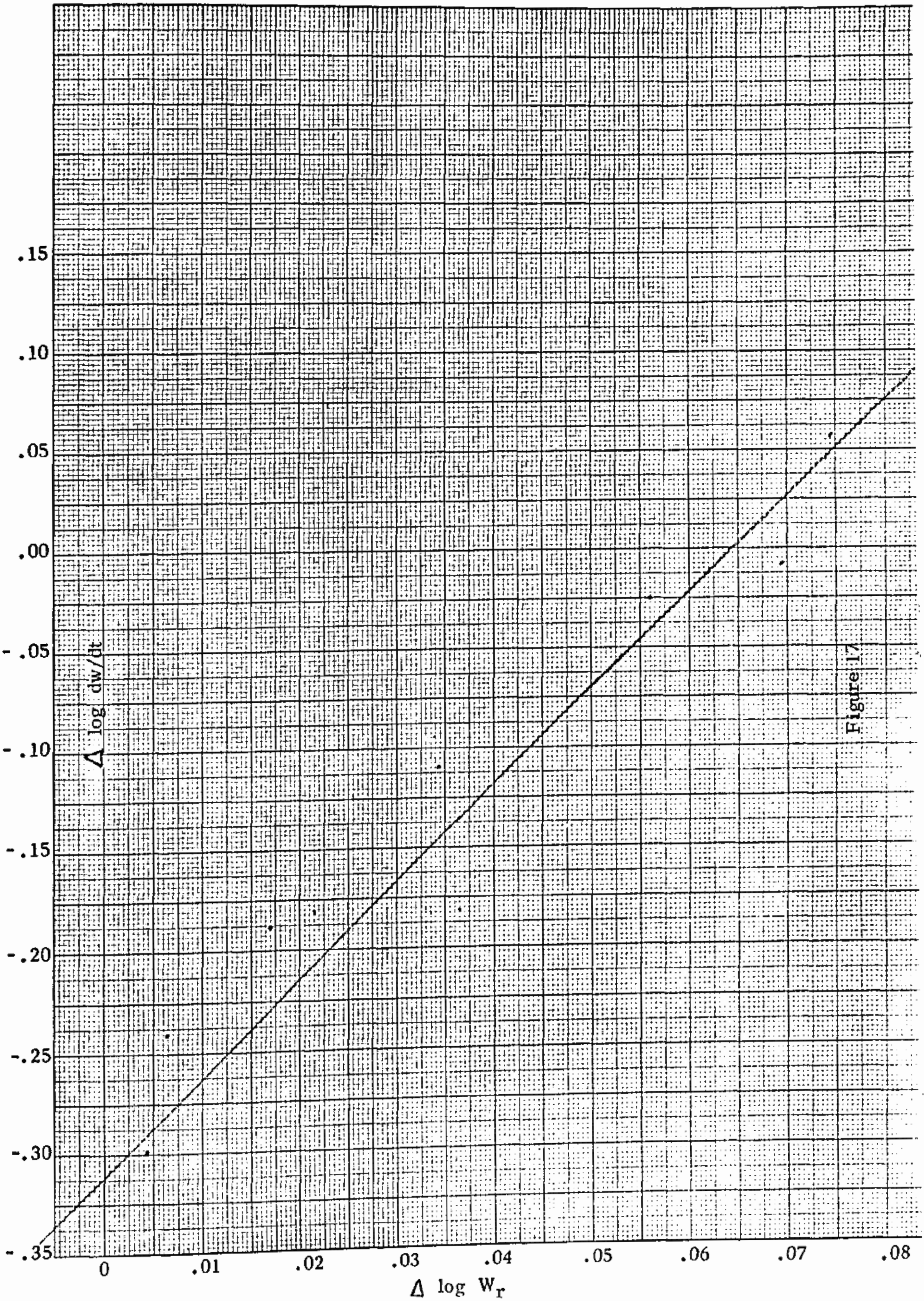

.15
.10
.05
.00
- .05
- .10
- .15
- .20
- .25
- .30
- .35
Δ log dw/dt
0
.01
.02
.03
.04
.05
.06
.07
.08
Δ log W_r

Figure 17

Table XIX

Least Squares Calculation

y	x	$x^2 \times 10^6$	$x.y.\ 10^3$
-.301	+.005	25	-1.505
-.243	.007	49	-1.701
-.208	.012	144	-2.496
-.183	.022	484	-4.026
-.187	.037	1365	-6.920
-.114	.035	1222	-3.990
-.027	.056	3120	-1.512
-.001	.070	4900	-0.070
.053	.075	5600	+3.925
$\Sigma y = -1.211$	$\Sigma x = .319$	$\Sigma x^2 = 16.909 \times 10^{-3}$	$\Sigma xy = -18.245 \times 10^{-3}$

$$D = 9 \times 16.909 \times 10^{-3} - (.319)^2 = .1522 - .1020 = \underline{.0502 = D}$$

$$\alpha_2 = \frac{1}{.0502}\left[- .016909 \times 1.211 + .319 \times .018245\right]$$

$$= \frac{1}{.0502}\left[- .02043 + .00582\right] = - \frac{.01561}{.0502} = -.311$$

$$\alpha_1 = \frac{1}{.0502}\left[- 9 \times 18.245 \times 10^{-3} + .319 \times 1.211\right]$$

$$\left[- .1641 + .386\right] / .0502 = .222 / .0502 = 4.42$$

$E^* = .311 \times 2.303 \times 1.987 \times .5 \times 10^5$

$E^* = 71$ K cal.

$M = 9$

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AUTOBIOGRAPHY

I, Charles Edward Singleton, was born on July 30, 1937 in Lebanon, Ohio, where I attended elementary school. I graduated from Lebanon High School in 1955 and enrolled in Central State College in Wilberforce, Ohio. I graduated with a B.S. degree in Chemistry in 1959 and entered the U.S. Army as a Second Lieutenant. After two years of active duty, I received an honorable discharge as a First Lieutenant in 1961 and entered Howard University Graduate School for one year. In 1962, I accepted a position as a chemist with the U.S. Government and in 1965 joined E.I. du Pont de Nemours & Co., Richmond, Virginia, as a chemist in the Research Division of the Film Department.