DIFFERENTIAL THERMAL ANALYSIS
OF ORGANIC WASTE

By

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CHAPTER I

INTRODUCTION

The formulation of efficient waste treatment processes, design of waste treatment facilities and development of waste treatment methods, requires comprehensive knowledge of the waste composition. Within recent times the amounts and varieties of organic waste, both municipal and industrial, have increased. To a large extent, this increase has followed the increase in population and continued expansion of industrial development. The problems of waste disposal and water pollution control have stimulated interest in the revision of established analytical methods used in sanitary chemistry and fostered the development of new methods.

Presently, three basic analytical tests, chemical oxygen demand, COD, biochemical oxygen demand, BOD, and thermogravimetric solids are the principle sanitary engineering tests used to measure the nature of organic wastes. The first two tests, COD and BOD, provide a "yardstick" measure of the amount and nature of the carbonaceous material in a waste stream by measuring the amount of oxygen required to react with the organic material. The thermogravimetric tests are used to determine water content and amount of carbonaceous material by weight loss during heating. Experience and study have shown that these tests provide a reliable index to the organic loading and nature of the organic matter in waste materials; however, this index is empirical and has been established by experience and correlation rather than by strict application of stoichometric chemical relationships. In a general sense, all of these tests are based on mass balance hypothesis. Obviously, a complete analysis of the waste material coupled with quantitative knowledge of the chemical, physical, and biological reactions would be of great value in designing and operating waste treatment facilities. The large variation in organic waste composition, as well as the continued increased diversity of these materials, does not permit such an analysis. The above features, together with the significant influence of small quantities of some organic materials on waste treatment processes require the development of rapid and accurate analytical methods.

Recent developments in analytical chemistry instrumental methods have shown that physical methods are often applicable for "on stream" or continuous monitoring and in many cases are able to measure materials beyond the sensitivity limit of wet chemistry methods. Instrumental analytical methods have demonstrated that often a chemical species or material may be determined qualitatively and/or quantitatively by relating the specific energy absorption or emission to the material. This relationship suggests a possible basis for determining the nature and amount of carbonaceous material in organic waste materials.

Organic chemistry has established that carbon is most unique; it is capable of reacting with itself and practically all other chemical elements to form a large variety of compounds. The chemical characteristics of carbon compounds are very dissimiliar and make for a difficult problem in analysis. One common feature of practically all carbon compounds is their ability to react with oxygen under proper conditions and produce heat. The reacting rate and threshold temperature, as well as the amounts of heat produced by specific reactions are well established for many pure organic compounds and show considerable variation. In consideration of the proposed analytical technique, using heat of combustion to indicate quantity and nature of the organic material in organic waste samples; thermal measuring methods, techniques, and apparatus employed in metallurgy, agriculture, and clay mineralogy were examined and reviewed. The basic thermal measuring method in these disciplines is calorimetry; however, there has been increased interest and development work in differential thermal analysis, DTA.

The features of DTA analytical method which are desirable for sanitary engineering application are: (a) provides a rapid method for measuring the nature and quantity of carbonaceous materials in organic waste samples, (b) provides a method for measuring thermal energy changes in organic waste treatment systems, and (c) suggests a basis for development of a semiautomatic analytical system.

Statement of the Problem

The purpose of this study was to determine the feasibility of using differential thermal analysis techniques to measure the degradation of organic materials in a laboratory simulated organic waste treatment process.

CHAPTER II

SUMMARY OF THE LITERATURE

The basic concept of differential thermal analysis as well as the basic requirements were detailed by Le Chatelier (4) in his early work. Differential thermal analysis, DTA, differs from conventional methods of thermal analysis in that temperature changes accompanying thermal energy reactions are measured rather than changes in dimension or mass.

In general, two types of thermal reactions, exothermic and endothermic, occur during heating of a material. Differential thermal analysis functions by measuring the differential temperature generated by a sample and a standard material exposed to a high temperature environment.

Generally, the standard and the sample are heated at the same rate or exposed to the same temperature environment. During the heating process the sample material may undergo a series or sequence of thermal reactions such as melting, boiling, combustion, or isothermal phase changes. In each of these reactions, energy is either absorbed or evolved by the sample. The thermal energy change accompanying each reaction is reflected in the differential temperature generated by the sample and the standard.

The differential temperature plotted against the temperature of the standard material constitutes a thermal energy profile or thermogram of the sample material. Excursions or peaks to one side of the base line represent exothermic reactions, whereas similar peaks on the other side of the base line represent endothermic reactions. The base line is the line of zero differential or some other experimentally established reference point. The location of peak temperatures are characteristic for each material or reaction and some function of the thermal curve (usually area) is proportional to the amount of reactant material. Thus, the DTA is, in general terms, a thermal spectrometer.

The three basic or elemental components of the DTA system are a controlled heat source, sample holder, and a differential temperature measuring device. The type and construction of each of these units and the integration of the units is variable. Moreover, the development of DTA has often been carried out for specific industrial applications, thus making many modifications of the original equipment. A typical basic DTA component system is shown in Fig. 1.

Other investigators have stated the general requirements of the heat source and have described this portion of the apparatus as being the most important (5). The heating rate available for conventional DTA furnaces is limited by the power supply and materials of construction. With rare exception, electric resistance heaters are used for heating the furnace. The attractive features of electric powered heating systems are their ease of control, measurement of input power, low maintenance requirements and economy of manufacture. The less attractive features of electrical powered furnances are their non-linear heating rates and interference sometimes produced by the large electrical currents induced on the temperature measuring systems.

Design of the DTA heat source or furnace is usually determined by the application. In the case of ceramic, mineralogical, or metallurgical

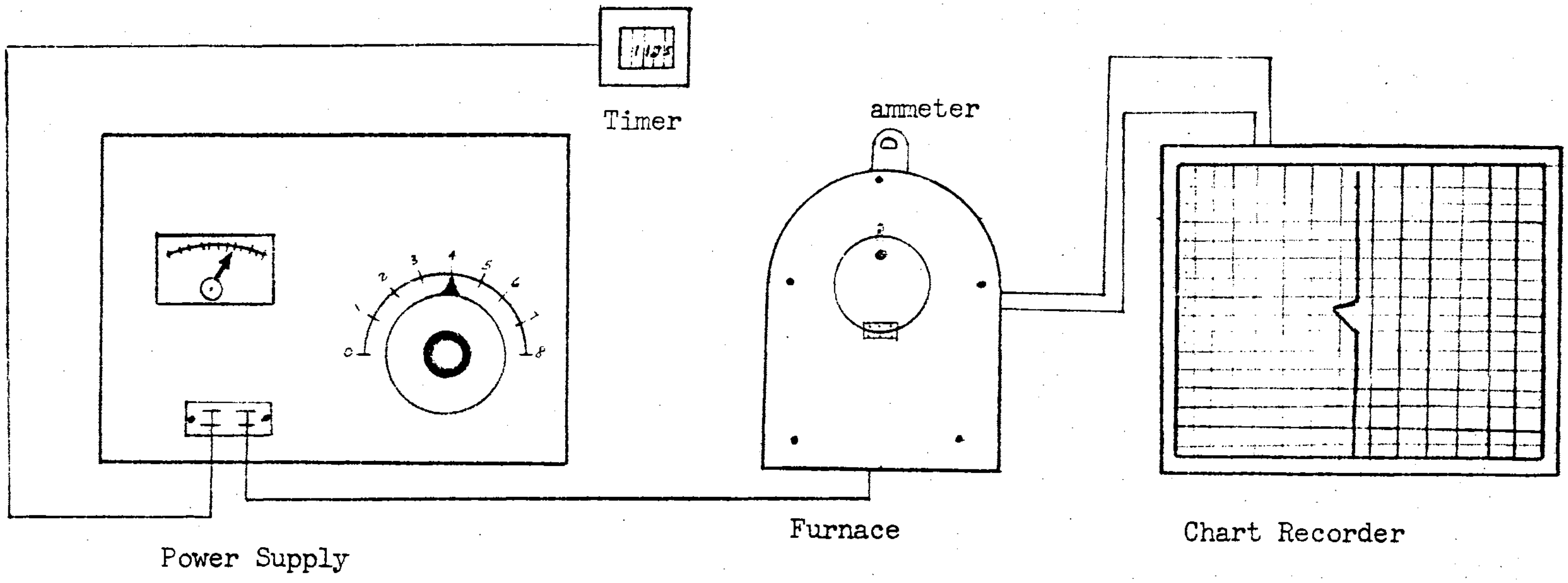


Fig. 1. Block Diagram of Apparatus

applications, the furnace is usually designed to have small dimensions, low heat loss characteristics, and large power requirements (5). This design is based on using a very small sample together with a large rate of heating to facilitate measuring small energy changes. Aside from the specific application features of the DTA heat source, there is unanimous agreement among investigators on the necessity of heating rate control, durability, and reproducibility of heating rate (5, 12, 13). The high temperature requirements - often as high as 1200°C - as well as the rapid heating rate - 5 to 20°C per minute - require high quality special materials. Ceramic materials are often used and are highly recommended for the furnace body. High quality platinum, nickel, and nickel-chromium, nichrome, wire are recommended for the electric resistance heating elements (5).

Control of the heating rate of a DTA furnance requires careful consideration of the thermal system and the control mechanism. With respect to electrical resistance heaters, simple variable resistance or rheostat control has been used. This control is sufficient for vernier or secondary control but is insufficient for large electrical current requirements.

The power requirements of electrical heating elements usually demand a high amperage, low voltage power source. A variable voltage transformer with adequate current rating can be used to generate a smooth reproducible heating rate. The high efficiency and predictable characteristics of transformer control makes possible linear operation of the furnace by means of automatic program control or by fully floating program control (5). Regardless of what method is used to control heating rate, the heating rate must be reproducible, since the shape of the DTA curve and the peak temperature are affected by the heating rate (11).

The base line and peak area of the DTA thermogram are influenced by the sample holder and block; location and type of temperature measuring device; size, geometry, and location of sample; and the thermal characteristics of the sample and standard. The material chosen for the sample holder, block, thermocouples, and standard must be inert and stable with regard to the sample and reaction products (5). The sample holder, block, and standard are generally selected on the basis of their thermal properties.

The ideal geometry for the sample holder and sample is one which has a minimum surface area to volume ratio together with minimum dimensions; hence, a small sphere. These geometric characteristics make for maximum response per unit of differential temperature. These ideal conditions, though hypothetical with regard to direct application, do suggest a design basis. A right cylinder with a diameter to depth ratio of one and with dimensions of less than one centimeter are a close approximation of the ideal conditions for geometry and size. Most apparatuses use sample holders that will contain a 0.2 to 0.5 gram sample (5).

The temperature measuring and recording device is dependent upon the temperature range involved. With low temperatures, a thermistor may be feasible or a mercury thermometer could be used. A mercury thermometer could not be used efficiently with minute samples because of the heat loss that would be involved. A pyrometer could be used but in most cases it would not be sensitive enough. Thermocouples connected to a galvonometer circuit have been used effectively to measure temperature and temperature difference. The electromotive force, e.m.f., produced when two dissimilar metals are heated or cooled is indicative of the temperature.

Selection of the thermocouple materials is based upon the operating temperature range, amplification factor of the recording device, and the sample material. The thermocouples must be capable of producing a measurable e.m.f. for a small temperature change. Rare-metal thermocouples are expensive and produce a small e.m.f. but they are generally more durable than base-metal thermocouples. For maximum sensitivity, base-metal thermocouples are used. The less attractive features of base-metal thermocouples, shorter life and limited temperature range, are offset by the more attractive features; easily constructed, inexpensive, and a large e.m.f. is generated. Base-metal thermocouples produce a large e.m.f. and in some applications the differential e.m.f. is sufficient to drive a sensitive recorder. The temperature of the reference material and the differential temperature are usually measured by placing thermocouples in or near the sample and reference materials.

Recent literature shows that differential thermal analysis is used extensively in ceramics, geology, chemistry, mineralogy, and metallurgy. One of the major interests in these fields is measuring small energy changes which accompany structural changes.

Differential thermal analysis has been used to "fingerprint" pure organics by Morita and Rice (7). They showed that the thermogram of specific organic molecules was unique and could be used to identify the organic species. In another study Rice (8) used DTA to characterize starches.

The application of DTA to problems in organic waste analysis is not revealed in the literature. Probably the closest approach to this application was the study and correlation of DTA thermograms together with gas-liquid chromotography of copolymers by Bombaugh, Cook, and Clampitt (1).

CHAPTER III

METHODS AND MATERIALS

The development of an analytical method and associated apparatus requires evaluation of all contributing factors and rational compromises in the design of the apparatus. The central problem in this study was development of a functional experimental apparatus compatible with the aims and objectives of the study. In order to accomplish this objective, the findings of other investigators together with knowledge of the thermal and chemical nature of organic waste materials were used to design a preliminary experimental study.

The first phase of the preliminary experimental study involved selecting materials and components for construction of the apparatus. Several furnace designs were considered and an adiabatic type furnace using two heaters was constructed. This design used an external cylindrical heater as a heat barrier and an internal cylindrical heater for the primary heat source. This design, although capable of rapid heating and negligible heat loss, presented a complicated heat rate control problem and was not compatible with the sample holders developed later in the investigation.

Experience gained in the first furnace design study showed that a strict utilitarian design was necessary; hence a simple cylindrical furnace geometry was selected with provision for easy access to the sample holder. The major features of this furnace, which was used with minor modification for the duration of the study, are shown in Fig. 2 and 3. The electric heating elements used in the furnace were half cylinders, six inches in diameter and twelve inches long. Each half cylinder consisted of a coiled length of nichrome wire embedded in a three-fourths inch thick ceramic matrix. The body or supporting structure of the furnace was constructed of "transite."

The experimental furnace was assembled by locating the cylindrical heaters in the center of the end blocks, then fastening the compression bolts to the end blocks. Following assembly of the heater and end blocks, the outer metal shell was positioned about the heater and the entire assembly aligned and locked into position. The annular space between the heater and outer metal shell was packed with magnesia insulation.

The electric power supply and control for the furnace was constructed using a 0-130 volt, 20 amp variable voltage transformer. A schematic diagram of the power supply and control circuit are shown in Fig. 4. In practice, the furnace power level was established by calculating the voltage and amperage required to produce a desired wattage. Preliminary study of the power supply system which included measurement of the electrical resistance of the heater at room temperature and advanced temperatures showed that the calculation method was adequate for predicting power levels. An a.c. voltmeter attached to the secondary of the variable voltage transformer, monitored the output voltage, and a second a.c. voltmeter attached to the furnace windings monitored the voltage applied to the heaters.

The relationship between heating rate and power input to the furnace was developed by measuring the temperature produced at various

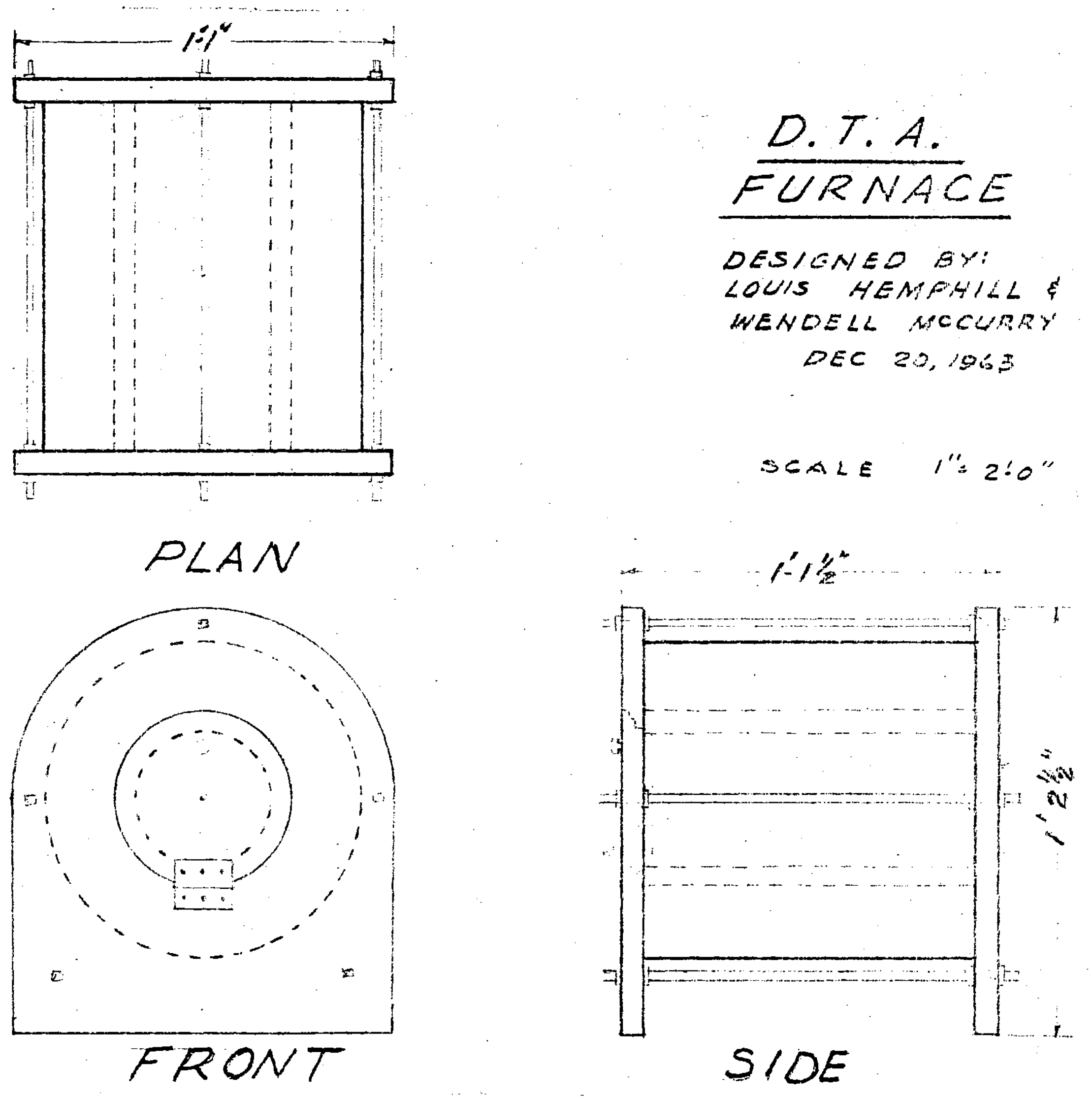


Fig. 2. Furnace

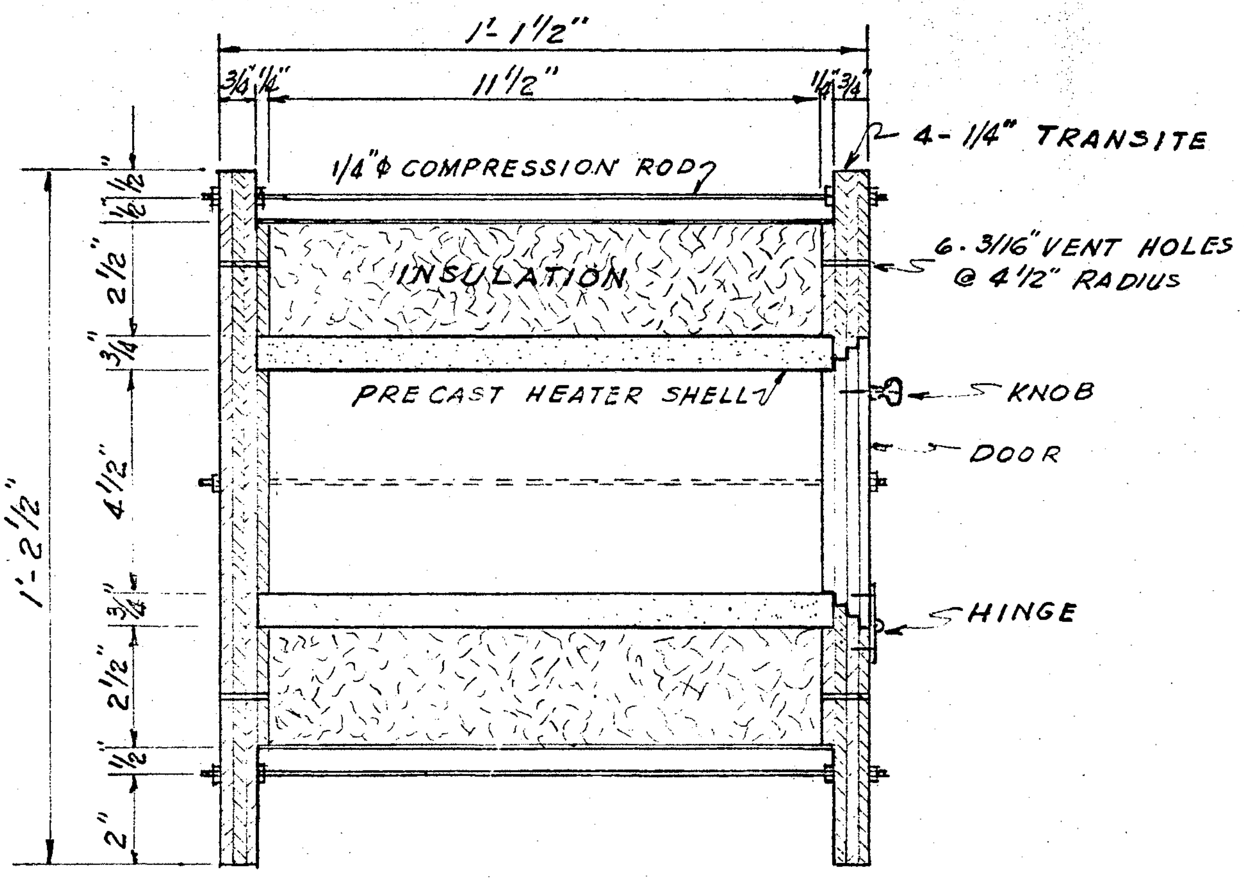


Fig. 3. Sectional Elevation of Furnace

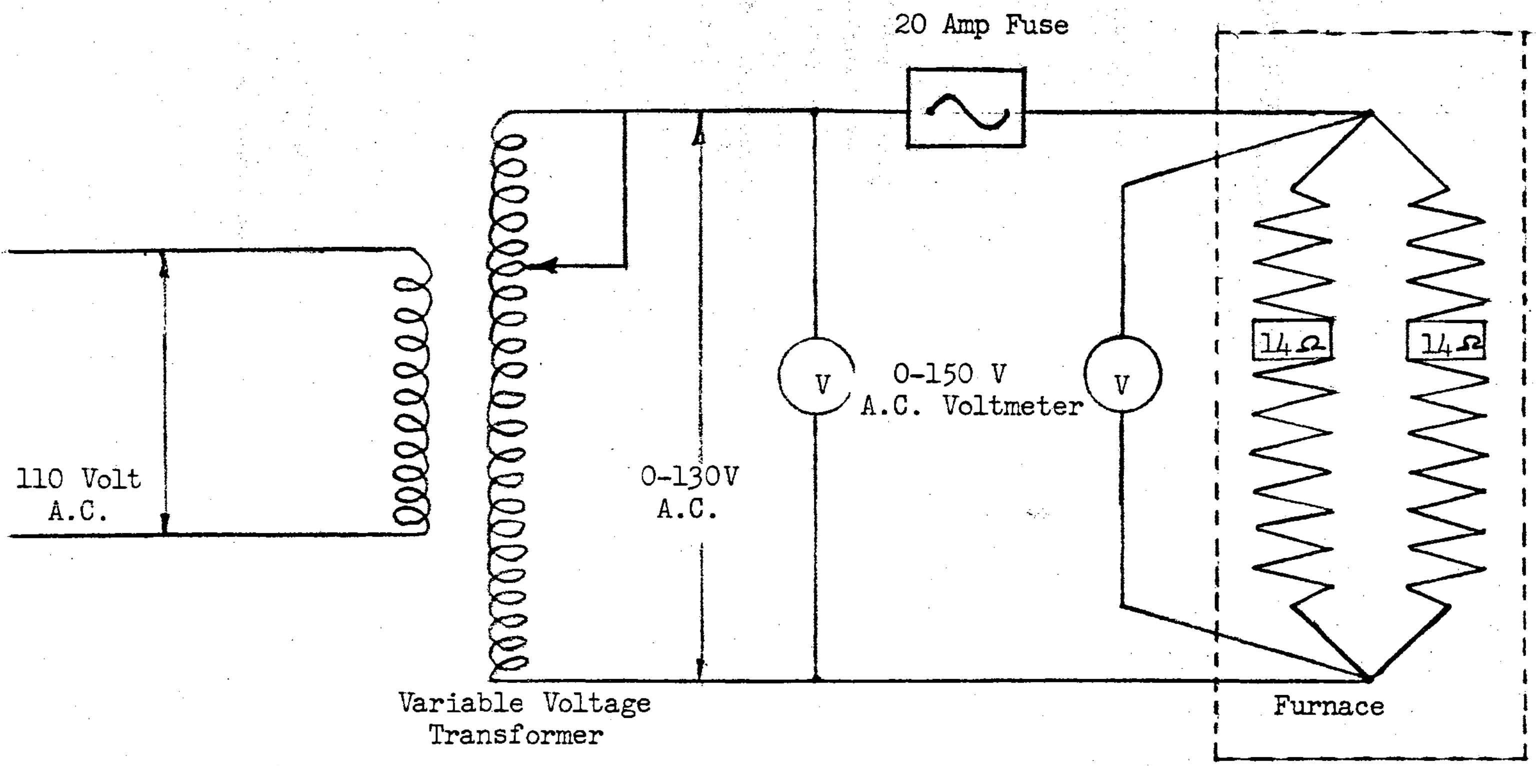


Fig. 4. Power Supply and Control Circuit

power settings. Replicate determinations were used to establish the reproducibility of the system. The heating rates developed for several power levels are shown diagramatically in Fig. 5. It is interesting to note that the temperature increase per unit time is linear over a large portion of the curve. In fact, the heat loss, evidenced by a decrease in heating rate, is generally not apparent until about 500°C.

In order to facilitate measurement of the furnace temperature, a microammeter iron-constantan thermocouple indicator was constructed. This temperature measuring apparatus was calibrated by comparing the microammeter deflections with measured temperatures. A schematic diagram of this device is shown in Fig. 6. The response of this device to temperature changes permitted use of a linear conversion factor. This factor, slope of the calibration curve in Fig. 7, was 56°C per microamp.

The measurement and recording of differential temperatures between standard and sample requires evaluation of; thermal reactions, applicable detectors, resolution, sensitivity, and stability. There are numerous temperature sensitive detectors which might find application to DTA systems; however, thermocouples and thermistors are generally used. The popularity of these devices and their increasing use is due to the development of high sensitivity, integral amplifier-recorder devices.

Consideration of construction methods and designs reported by others showed that thermocouples are most often used for differential thermal measurements (5, 9). The availability and dependability of high quality thermocouple material probably accounts in large measure for the popularity of these devices. Basically, the thermocouple, junction of two dissimilar metals, develops an electrical potential difference which is proportional to the temperature. The amount of potential difference,

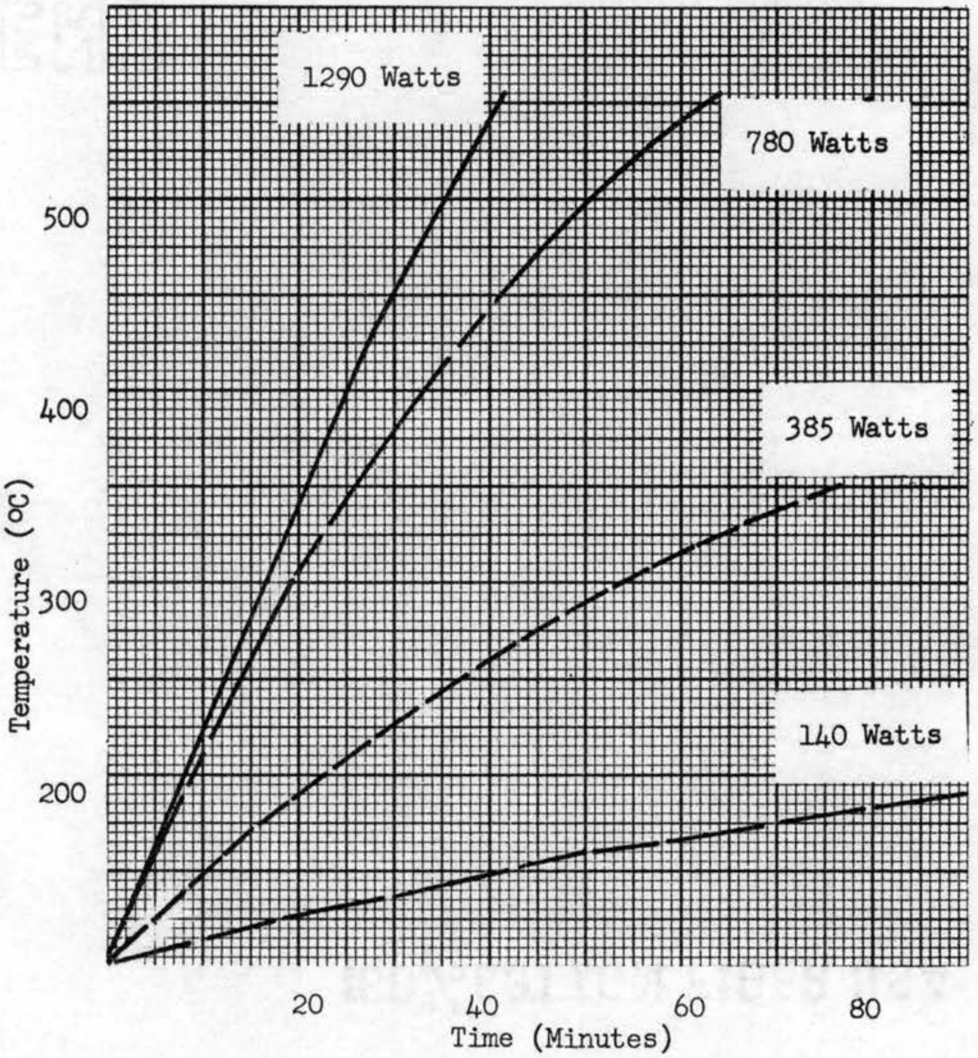
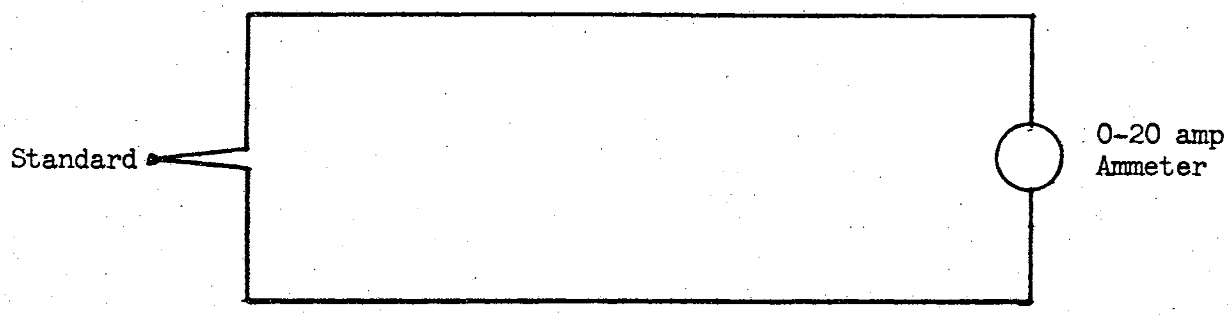


Fig. 5. Heating Rates for Different Power Levels

Differential Temperature
Measuring Circuit



Temperature Measuring Circuit

Fig. 6. Temperature Measuring Circuits

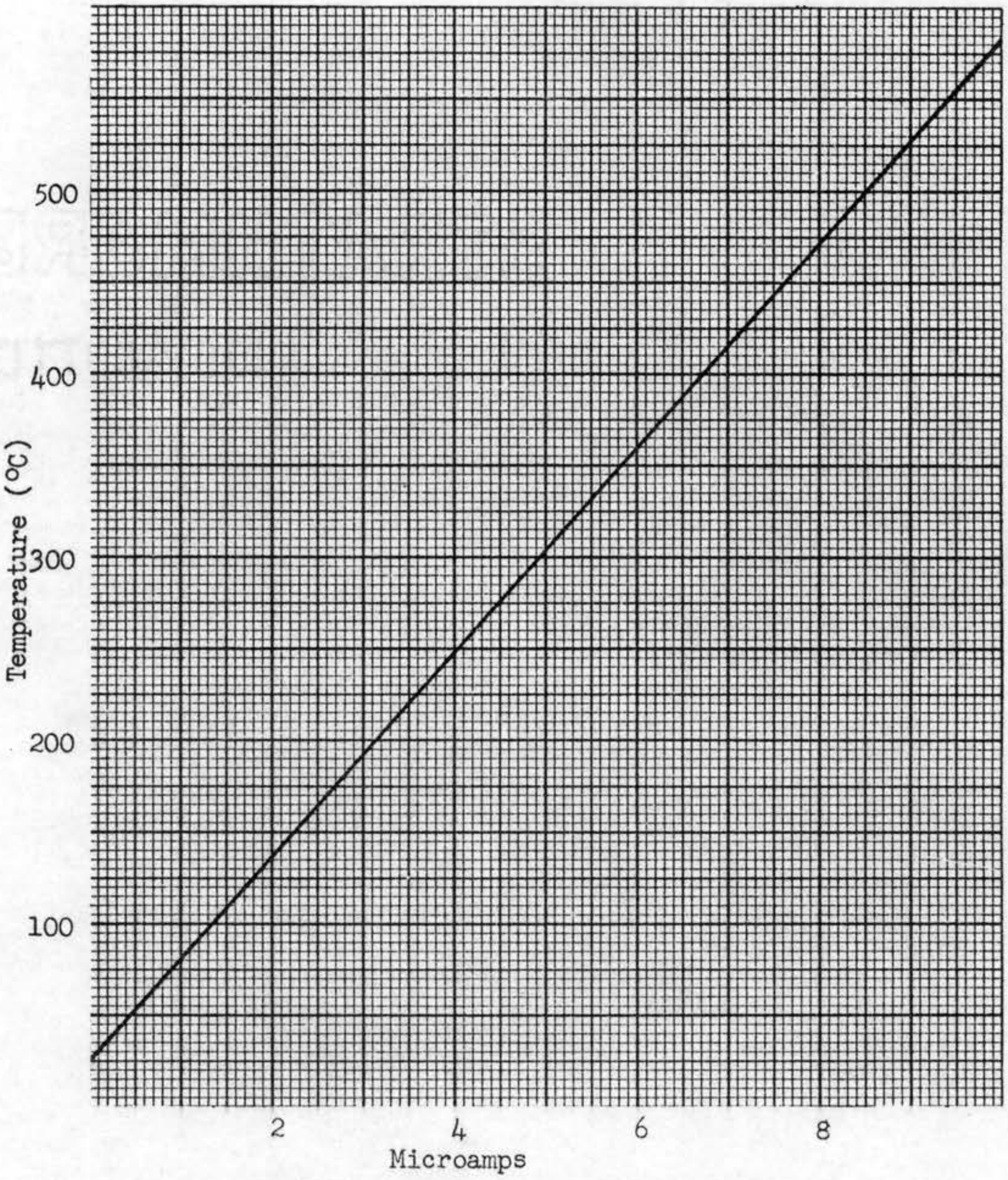


Fig. 7. Temperature Calibration Curve

voltage, developed per degree temperature depends on the composition of the thermocouple. Noble metal thermocouples, such as platinum-platinum rhodium, have very stable characteristics and are reserved for reference. In many applications, other materials, principally alloys, such as iron-constantan, copper-constantan, and chromel-alumel are used. These latter materials, not as reliable or well standardized as platinum-platinum rhodium materials, produce more voltage per degree temperature and are less expensive. A list of alloy type thermocouples, together with the e.m.f., produced by each thermocouple are presented in Table I.

The application of a thermocouple temperature measurement system requires a voltage measurement device. The constant measurement or monitoring of temperature is most conveniently handled by combining the thermocouple with a self balancing potentiometer or strip chart recorder. The range of voltage generated by the thermocouple is small, usually in the order of millivolts, and thus requires a very sensitive meter for measurement. In many applications, it is necessary to use a linear amplifier in conjunction with the thermocouple to discern small temperature changes. The sensitivity and resolution limit of the thermocouple is dependent on the resolution and sensitivity of the measurement meter.

Recently, there have been developed small resistance thermal elements, thermistors, which are excellent temperature measuring devices. The detection system in these devices consists of a metal or semiconductor material in which the conductivity or resistance changes in an established pattern with temperature. Two groups of thermistors are available which have positive temperature coefficients and negative temperature coefficients. The positive group increase in resistance

TABLE I

RELATIONSHIP OF THERMOCOUPLE MATERIAL TO E.M.F. PRODUCED

Temperature Above Cold Junction Temperature	Iron-Constantan Millivolts	Chromel-Alumel Millivolts	Platinum 10% Rhodium Millivolts
75 - 600°C	4.4 to 33.7	3.3 to 25.3	0.5 to 5.2

TABLE II

SAMPLE HOLDERS

No.	Material	Inside Diameter (inches)	Wall Thickness (inches)	Depth (inches)	Bottom Thickness (inches)	Thermal Conductivity BTU/hr./sq.ft./°F/ft.
1	Brass	0.360	0.010	0.604	0.020	58
2	Copper	0.375	0.010	0.604	0.010	222
3	Stainless Steel	0.360	0.010	0.604	0.010	9.4
4	Stainless Steel	0.390	Variable	0.604	0.010	9.4

with increase in temperature and the negative group decrease in resistance with temperature increase. The nature of the thermistor element, which permits temperature measurement by means of resistance, constitutes a more sensitive measuring element than the thermocouple; moreover, the measurement of resistance can be achieved without high-gain linear amplification. These features, sensitivity and direct measurement are advantageous in DTA and were considered in the initial conceptual design. The only limiting feature of the thermistor is the inherent instability of the element above 300°C.

The differential temperature measuring system which was used throughout the study consisted of iron-constantan thermocouples coupled to an integral amplifier strip chart recorder. Iron-constantan thermocouple material was selected on the basis of its high voltage output per degree centigrade (6). In order to maximize response and minimize the influence of the measuring system on the measurements, small gage thermocouple wire, B and S No. 30, was employed.

Direct measurement of differential temperature was provided by connecting the thermocouples in series opposition, as shown in Fig. 6.

The recording instrument used in this study was a Brown Electronik machine modified to accomodate direct recording of temperature. A scale from -100°C to +100°C was attached to the instrument to facilitate calibration. The sensitivity of this instrument after modification was 0.059 inches deflection per degree centigrade differential temperature. Chart speed of the instrument was regulated to 0.66 inches per minute which corresponded to a furnace temperature increase (in the linear heating rate region) of 11°C per minute.

Sample holders were positioned in the center of the furnace floor in a machined block. The block used for the major portion of the study was machined from mild steel stock to fit the curvature of the furnace floor. Preliminary study and experimentation showed that this apparatus provided rigid support for the sample holders and afforded ample heat transfer area.

The sample holders, due to small size and close location to thermocouples and sample, are capable of influencing the DTA response patterns to a high degree. In order to determine the effect of various materials on the DTA response patterns and optimize response three materials, brass, copper, and stainless steel, were selected for study as sample holder materials. Three pairs of sample holders, small cylinders, were machined from bar stock. The dimensions of the sample holders are listed in Table II. In addition to the above sample holders, an additional "distorted", variable thickness sidewall stainless steel cylinder was also studied.

Washed and acid leached Ottawa testing sand was selected for the standard reference material. A stock of this material was prepared for use by seiving and drying at 103° for 12 hours. During the latter portion of the study, another material, calcined ash, was investigated for application as a standard material. The preparation procedure for the calcined ash consisted of heating the dairy waste to 700°C, cooling the residue and grinding it to a fine powder consistency.

Following construction of the components and preliminary evaluation of the system, a standard furnace operation program was developed. The standard program consisted of adjusting the power supply to 55 volts until the furnace temperature reached 65°C, then increasing the voltage to 88 volts for the duration of the heating cycle. This program provided a reproducible average heating rate of 11°C per minute.

Calibration of the experimental apparatus was developed using pure organic reference materials. Benzoic acid was selected as the basic primary reference material since the thermal properties of this material are well established. Calibration of DTA instruments was achieved by correlating the DTA response area corresponding to the melting point pattern of benzoic acid. When pure benzoic acid is exposed to an increasing temperature, a series of response patterns are drawn. The first segment of the response pattern is a straight line which is followed by a sharp angular excursion to the left. This latter excursion continues for a short time, then describes a sharp peak and returns to the base line. This pattern of response is shown in Fig. 8 and is a differential temperature reflection of the heat of fusion of benzoic acid. Additional peaks are produced during the heating cycle which represent boiling and combustion. The distinctive feature of the heat of fusion peak is its iso-thermal nature and conservation of all material in the sample holder.

Realistic organic waste materials available for study were numerous; however, the study of a new analytical method by means of a recently constructed instrument requires a supply of consistent samples. Several organic waste sources and samples were considered prior to selection of dairy waste. The major feature of this material, which was the basis for selection, was its mode of production. The dairy waste was collected from a controlled dairy herd which was fed a specific diet. Preparation of the dairy waste samples was accomplished by laboratory scale aeration. Small samples of the aerated sludge were removed from the aerater at frequent intervals and reserved for study. Prior to DTA

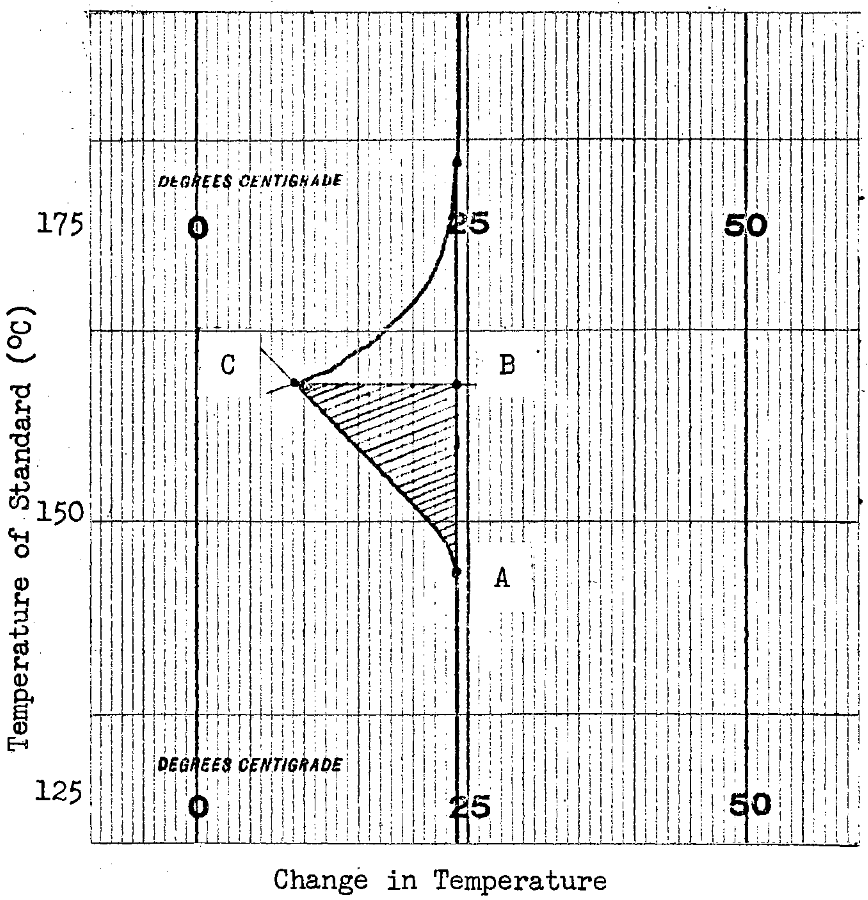


Fig. 8. Typical Endothermic Reaction Curve

thermal study the sludge samples were dried in 103°C oven.

Major characteristics of the organic dairy waste material are listed in Table III.

Analysis of DTA Thermograms

The response of the DTA apparatus was provided by means of the strip-chart recorder described above. In order to establish a basis of reference and comparison for the calibration and experimental study, it was necessary to formulate an analysis procedure and method for the DTA thermograms. Three methods of area determinations, total area, right triangle area, and product area were applied to the thermogram recordings. These methods were selected to represent two extremes, total pattern area and proportional areas. It was assumed that the total area values would be the most distinctive and realistic reflections of the sample materials; whereas, the proportional area methods, approximations, might form the basis for rapid routine analysis procedures. Total area of the DTA thermograms were determined by plaimeter. Triangle area was determined in accordance with the procedure described by Dean (2). Product area was determined by multiplying the height of the response curve times the base. The latter method was reserved for application to the organic waste thermograms.

In the experimental study, it was noted that the base line was displaced to the right during the combustion of the organic waste samples. This displacement was determined to be typical of the instrument design and nature of the sample. Additional study showed that this displacement did not alter the precision or operational nature of the apparatus.

TABLE III

CHARACTERISTICS OF WASTE MATERIAL

Sample Number	Strength mg COD/gm	Volatile Solids %	Total Solids %
1	827	61.4	2.3
2	874	62.2	3.6
3	949	70.0	7.5
4	951	70.0	7.5
5	1080	65.5	13.7
6	1140	74.4	14.1

The chemical oxygen demand, COD, of the organic waste samples was determined in accordance with the procedures listed in *Standard Methods for the Examination of Water and Waste Water*, 10th edition (14).

CHAPTER IV

RESULTS AND CONCLUSIONS

Results

The apparatus described in the method and materials section proved to be functional and durable. Following standardization of the furnace design and fabrication, a total of 101 experimental runs, including 60 calibration experiments and 41 organic waste sample DTA determinations, were completed.

Response of the instrument system in terms of calories per square inch showed the influence of sample holder, fabrication precision, and materials. It is interesting to note that each sample holder material produced a characteristic response pattern and that stainless steel favored the largest response followed by brass and copper. The order of increased response was in inverse order of the thermal conductivity of the sample holders. In addition, the distorted stainless steel sample holder (non-uniform side wall thickness) produced highly variable responses. These studies showed that reliable reproducible response is a function of the sample holder material and fabrication precision. The sample size, mass and preparation also influenced the response pattern and precision.

Early in the investigation, it was noted that small samples of benzoic acid, less than 250 mg, produced atypical response pattern with high variability. A sample of the response values produced by the small samples are listed in Table IV.

The influence on the response patterns of the DTA standard reference materials, sand and calcined waste, showed small differences. Calcined ash assisted in producing slightly larger response, and permitted recovery of the instrument to the initial base line.

Sample preparation studies showed that a consistent preparation procedure is required. The bulk density of the sample influenced the response to a high degree. Sample packing by means described in the methods and materials section made consistent response and aided sensitivity. Preliminary study and experimentation indicated that sample stratification, non-uniform settlement of sample, during the heating cycle produced extreme variation and random response of the instrument.

In addition to the operation and design factors incorporated in the apparatus, a method was developed for evaluating the system for spurious deflections or noise. This evaluation procedure consisted of recording the response of the instrument when both sample and standard were loaded with sand during a heating cycle. This procedure permitted separate evaluation of instrument noise, electrical line supply noise, and erratic behavior of the strip chart recorder. This method proved very valuable in locating small difficulties and improper alignment of the apparatus.

Analysis of the benzoic acid response curves by three methods, total area, right triangle area, and product area showed that the right triangle and product area methods are both sufficient for rapid determination of response area. In addition, both the right triangle and product area values provide a more consistent evaluation of the response area. The right triangle and product area methods were also used to

TABLE IV

COMPARISON OF RESPONSES USING BENZOIC ACID, BRASS SAMPLE HOLDERS, AND ASH CONTROL

Sample Weight	Heat of Fusion	Total Area Response		Right Triangle Response		Product Area Response	
(mg)	(cal)	in.^{2}	(cal/in.^{2})	in.^{2}	(cal/in.^{2})	in.^{2}	(cal/in.^{2})
197	6.68	0.183	36.5	0.125	53.4		
197	6.68	0.210	31.8	0.180	37.1		
236	8.00	0.455	17.6	0.359	22.3		
254	8.61	0.410	21.0	0.320	26.9	0.95	9.1
258	8.75	0.400	21.9	0.290	30.2	0.81	10.8
258	8.75	0.411	21.3	0.318	27.5	0.73	12.0
268	9.09	0.350	26.0	0.292	31.1	.63	14.3
Average based on all samples over 250 mg			22.6		28.9		11.6
Standard Deviation			5.3		2.0		2.2

analyze the organic waste material responses. Inspection of the values in Tables IV, V, and VI shows that there is only slight differences in the right triangle and product area values, whereas, the total area values show larger deviations. It is also interesting to note that the variation between standard runs decreased as experience in operation increased.

The response pattern produced by benzoic acid was similar for all DTA determinations. The changes in amptitude reflect changes in sample size, sample preparation or sample holder and are described in the previous section.

The instrument response pattern provided by digested and undigested samples of dairy waste was very similar. Typical DTA response patterns for the digested sludge and undigested sludge are shown in Fig. 9 and 10. Inspection of the DTA thermograms in Fig. 9 and 10 shows that the response pattern for both samples follow the same general shape. The raw dairy waste samples produced excursion to the right and a broad crested peak pattern. Digested sample materials produced a deviation from the base line at a higher temperature and a smaller differential temperature per unit mass of sample material.

An additional feature of these thermograms was noted. Samples of undigested and digested waste material selected on the basis of detention time to insure that the same material was sampled provided more consistent response patterns. These samples are listed in Table VI.

Using the right triangle area method and the average value from organic waste material number one (Table I and III), a relationship of COD to calories was found to be 0.34 mg COD per calorie. This result compares to a value for activated sludge stated by Goldstein and Lokatz

TABLE V

INSTRUMENT RESPONSE USING BENZOIC ACID, COPPER SAMPLE HOLDERS, STAINLESS STEEL SAMPLE HOLDERS, ASH CONTROL, AND SAND CONTROL

Condition	Sample Weight (mg)	Heat of Fusion (cal.)	Right Triangle Response (in.^{2})	Right Triangle Response (cal/in.^{2})
Copper Holder				
Ash	257	8.71	0.230	37.9
Ash	319	10.8	0.287	37.7
Sand	294	9.97	0.260	38.3
Sand	295	10.0	0.250	40.0
Steel Holder				
Ash	231	7.83	0.440	17.8
Ash	233	7.90	0.360	21.9
Ash	227	7.70	0.530	14.5
Ash	243	8.24	0.430	19.2
Sand	240	8.14	0.340	23.9
Sand	274	9.28	0.430	21.6
Sand	262	8.87	0.370	24.0
Sand	258	8.57	0.300	29.2
Sand	285	9.65	0.390	24.7
Sand	262	8.90	0.360	24.7
Steel Holder Variable Wall Thickness				
Ash	293	9.93	0.180	55.2
Ash	322	10.9	0.220	49.6
Ash	282	9.56	0.690	13.9
Ash	246	8.34	0.200	41.7
Sand	293	9.93	0.540	18.4
Sand	274	9.29	0.120	77.4
Sand	276	9.36	0.100	93.6
Sand	315	10.7	0.325	32.9
Sand	256	8.68	0.130	66.8
Sand	262	8.88	0.060	148.0
Sand	255	8.64	0.204	42.4
Sand	269	9.12	0.450	20.3

TABLE VI

RESPONSE USING ORGANIC WASTE MATERIAL, BRASS SAMPLE HOLDERS, AND ASH CONTROL

Sample Strength (mg COD/gm)	Sample Weight (mg)	COD (mg)	Right Triangle (in.^{2})	Right Triangle Response (mg COD/in.^{2})	Product Area (in.^{2})	Product Area Response (mg COD/in.^{2})
874	417	364	26.0	14.0	49.2	7.40
874	430	376	27.6	13.6	46.9	8.02
874	410	358	28.1	12.7	51.0	7.02
1080	362	391	32.1	12.2	56.8	6.88
1080	365	394	23.6	16.7	42.9	9.19
1080	329	355	30.9	11.5	55.2	6.44
949	362	344	23.2	14.8	42.5	8.08
949	381	362	22.8	15.9	40.9	8.84
949	412	391	23.7	16.5	45.4	8.61
827	396	327	34.2	9.56	56.0	5.85
827	429	355	36.2	9.80	63.9	5.55
827	433	358	35.2	10.2	60.9	5.88
951	424	402	25.7	15.7	47.6	8.47
951	405	385	27.2	14.2	29.9	7.72
951	323	307	28.7	10.7	52.9	5.81
1140	352	401	33.1	12.1	65.9	6.09
Average				13.1		7.24
Standard Deviation				2.48		1.37

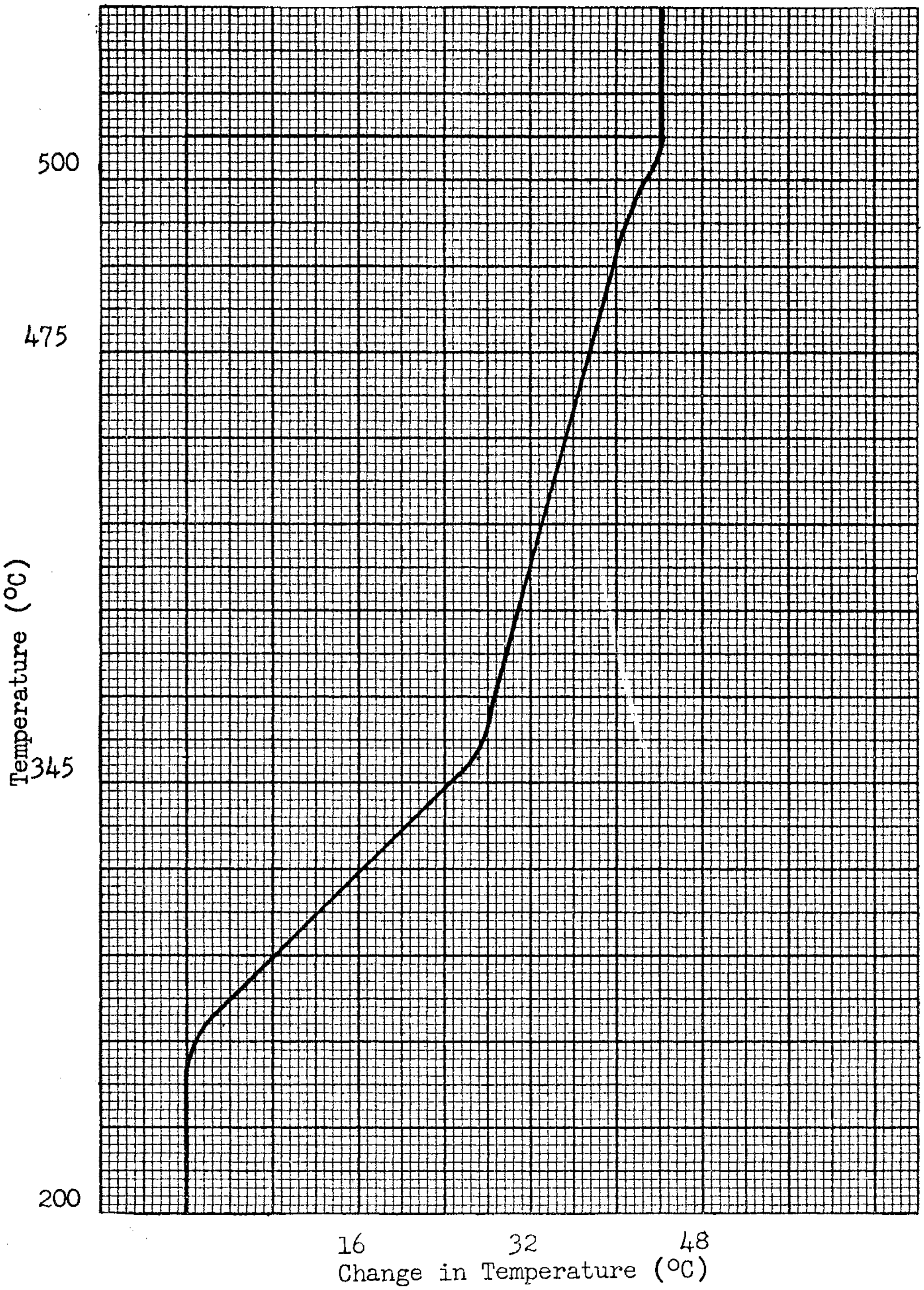


Fig. 9. Typical Digested Material Response

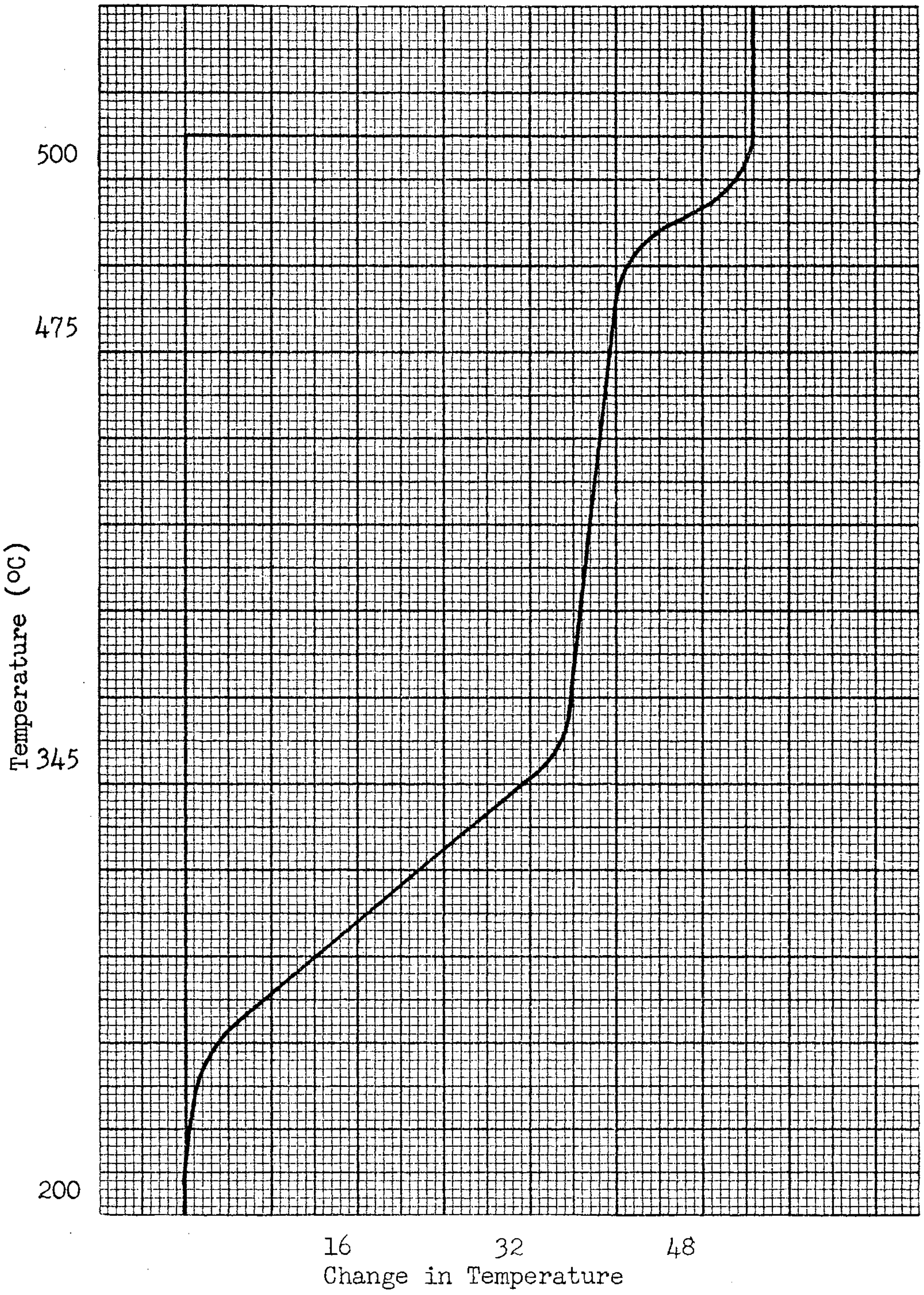


Fig. 10. Typical Undigested Material Response

TABLE VII

RESPONSE USING ORGANIC WASTE MATERIAL, COPPER SAMPLE HOLDERS, STAINLESS STEEL SAMPLE HOLDERS, AND SAND CONTROL

Sample Strength (mg COD/gm)	Sample Weight (mg)	COD (mg)	Right Triangle Response (in.^{2})	Right Triangle Response (mg COD/in.^{2})	Product Area Response (in.^{2})	Product Area Response (mg COD/in.^{2})
Copper						
827	457	378	37.2	10.2	62.6	6.04
827	440	364	36.5	9.97	62.7	5.81
827	388	321	33.7	9.52	52.6	7.38
1140	387	441	35.3	12.5	63.2	6.98
1140	314	358	29.2	12.3	48.7	7.35
Stainless Steel						
827	362	300	25.1	11.9	38.2	7.84
827	416	345	27.4	12.6	43.0	8.00
827	372	308	27.8	11.1	42.2	7.28

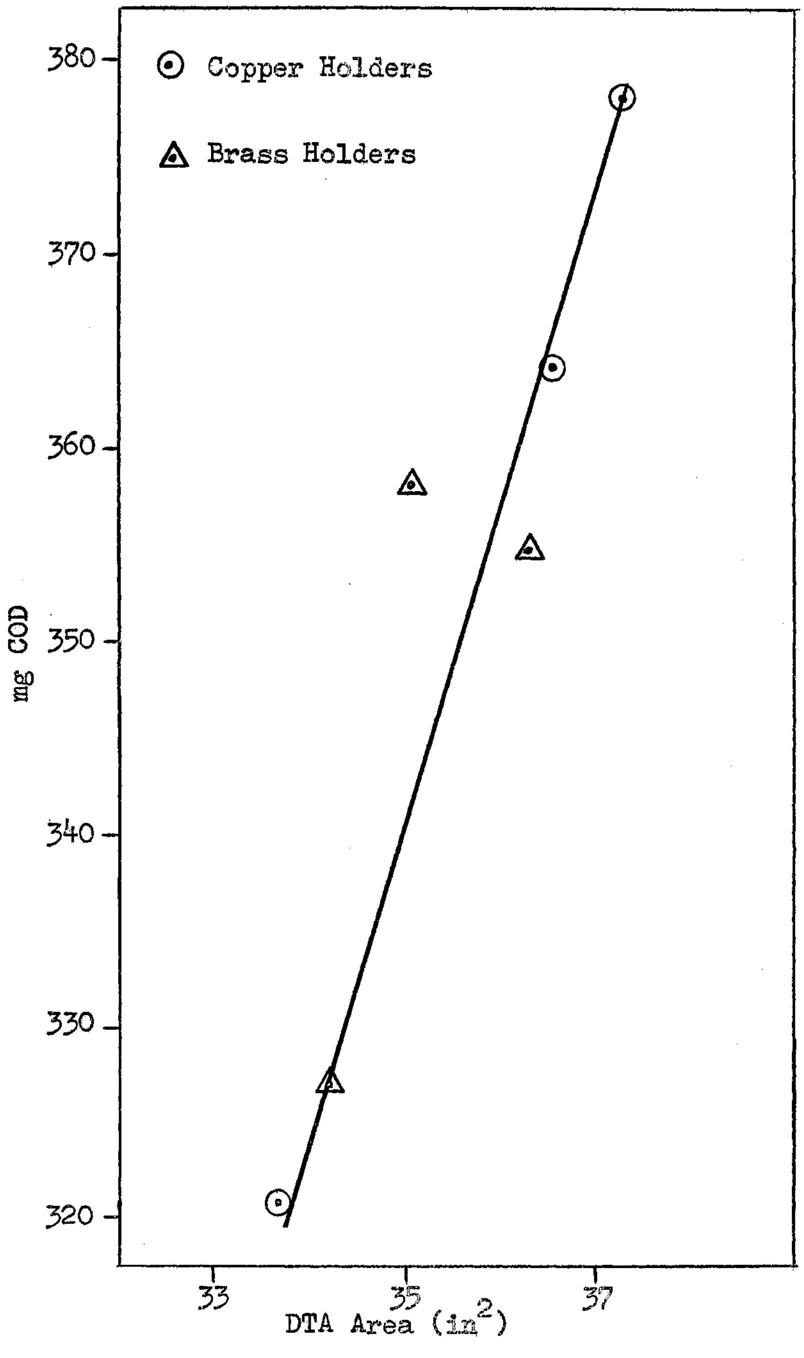


Fig. 11. Response From Copper and Brass Holders and Sample No. 1

(3) of 500 BTU per gallon for every 10 grams per liter of COD, which reduces to 0.30 mg COD per calorie.

A definite relation between COD and area is shown in Fig. 11. A linear relationship between area and COD does exist and shows the relation between extent of degradation and instrument response.

Conclusions

The purpose of this study, to determine if differential thermal analysis techniques could be used to measure the degradation of organic materials in a laboratory simulated organic waste treatment process, was realized.

The method of DTA thermogram analysis that proved to be the best is the right triangle method, but the product area method is adequate for a quick method of analysis.

Equally reproducible results can be obtained by using brass, copper, or stainless steel sample holders that have uniform dimensions but the short life of the brass and copper holders makes the stainless steel holders more desirable. The sand and ash control standards gave about equal results.

The findings of this study show that a relationship between the extent of degradation and response of the apparatus does exist; therefore, differential thermal analysis techniques can be used to measure the degradation of an organic waste material and indicates that this method can be applied to waste treatment plant operation as a supplement to the thermogravimetric and COD tests methods presently employed in waste treatment analysis.

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