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FINAL REPORT

CONTAMINANT REMOVAL FROM ENCLOSED ATMOSPHERES BY REGENERABLE ADSORBENTS

Contract NAS2-7896

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Ames Research Center
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MAR 1975

May 15, 1974

toward a better environment . . .

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES
(continued)

LIST OF TABLES

I. SUMMARY

The long-range goal of this research is the development of a regenerable activated carbon system for removal of contaminants from spacecraft atmospheres on missions of extended duration. This program phase examined the use of catalyst-impregnated activated carbon for contaminant adsorption, followed by in-situ regeneration by low-temperature catalytic oxidation of adsorbed contaminants.

Seven different spacecraft contaminants were selected for testing. A platinum catalyst was selected based on prior research which showed it to be the most efficient of several oxidation catalysts investigated. Platinum was deposited on activated carbon by liquid phase impregnation with chloroplatinic acid, followed by drying and high-temperature reduction.

Results were obtained from three different experimental test systems:

- --A thermal gravimetric analysis (TGA) apparatus was used to determine the weight loss of a contaminated carbon granule as its temperature was increased in the presence of air.
- --A differential scanning calorimeter (DSC) apparatus was used to follow the endothermic and exothermic processes occurring for a contaminated carbon granule as its temperature was increased in the presence of air.
- --A one-inch diameter granular carbon column was used to study the regeneration of a fixed carbon bed . Repetitive contamination/regeneration cycles were conducted to determine regeneration losses and to define potential problems in oxidative regeneration.

The DSC and TGA results showed that oxidation occurred for three of the selected contaminants, caprylic acid, diisobutyl ketone (DIBK), and acrolein, but no appreciable oxidation was detected for the remaining four contaminants, tetrachloroethane, freon 114, vinyl chloride, and thiophene. The contaminants which oxidized were all oxygenated hydrocarbons (C-H-O); whereas the contaminants that were not oxidized were halogenated or sulfur containing hydrocarbons.

The contaminants which were not oxidized were completely removed from the carbon by thermal desorption. When a carbon granule was heated at a rate of 10-15°C/min while flushing with air, these contaminants were completely removed below a temperature of 350°C. Since the carbon did not become pyrophoric until about 400°C, no significant loss in adsorptive capacity would be anticipated during repetitive cycling with these contaminants.

For two of the three contaminants which oxidized, caprylic acid and DIBK, oxidation occurred both with and without the catalyst. For non-catalytic carbon, two DSC peaks were observed for contaminant oxidation. For the platinum-impregnated carbon, the same two peaks were observed for oxidation on the carbon support, plus a large additional peak for oxidation on the platinum catalyst.

Neither caprylic acid nor DIBK was completely removed following low-temperature oxidation even with the catalyst present. At a programmed heating rate of 15°C/min caprylic acid was removed from non-catalytic carbon at 375°C but was not completely removed from platinum-impregnated carbon until 450°C. For DIBK at the same heating rate, removal was complete at 400°C for both platinum-impregnated and non-catalytic carbon. In single-cycle regeneration with caprylic acid and DIBK, therefore, the platinum-impregnated carbon did not exhibit any advantage over non-catalytic carbon.

Repetitive contamination/regeneration cycles were conducted with the DIBK contaminant using the TGA apparatus. Regeneration was achieved by heating at 15°C/min in air to 400°C. In repetitive cycling platinum-impregnated carbon was clearly superior to non-catalytic carbon in the amount of contaminant removed at low temperatures.

The losses in adsorptive capacity during repetitive TGA cycling with DIBK as contaminant were quite small. Over eight cycles the average loss in adsorptive capacity was 0.5% per cycle for the platinum-impregnated carbon, and over the final 5 cycles the loss was only 0.13% per cycle. Four contamination/oxidation cycles were conducted with non-catalytic carbon and the average loss in adsorptive capacity was only 0.025% per cycle.

These results clearly indicate that the contaminants investigated can be removed by oxidation with very little loss in adsorptive capacity. This is very encouraging when compared to the much higher losses for thermal desorption of caprylic acid and DIBK at 200-300°C. Depending on the exact desorption temperature and time, the loss in adsorptive capacity can range upward from several percent per cycle for these contaminants. (The effect of higher desorption temperatures and longer desorption times has not, however, been investigated.) It may be concluded that oxidation is clearly superior to thermal desorption at temperature levels of 200-300°C.

While oxidative regneration is clearly superior to thermal desorption under the conditions investigated, the advantages of platinum-impregnated carbon over non-catalytic carbon for oxidative regeneration are not as pronounced as originally anticipated. However, two advantages for platinum-impregnated carbon are:

1) the superior performance in repetitive cycling with DIBK, and
2) promotion of the oxidation of acrolein which was not oxidized by other catalytic carbons. (It is reasonable to suppose that other spacecraft contaminants may behave similarly to acrolein and would require the presence of a catalyst for oxidation.)

We conclude that these advantages are significant and the use of a catalyst-impregnated carbon for oxidative regeneration is to be recommended.

One potential limitation of a catalyst-impregnated carbon is the possibility of catalyst poisoning, particularly by sulfur-containing compounds. An adsorption-desorption cycle using thiophene as contaminant was observed to significantly decrease the activity of the platinum catalyst toward the oxidation of DIBK. The severity of this limitation will depend on the quantity of catalyst poisons to be removed by the activated carbon system and may be alleviated by the use of excess catalyst and/or a pre-sorber for poison removal.

Column tests were conducted with three of the selected contaminants: tetrachloroethane, DIBK, and caprylic acid. In agreement with the DSC and TGA results, no oxidation of tetrachloroethane was observed. Regeneration by thermal desorption was simple and efficient, but a portion of the tetrachloroethane decomposed to HCl during desorption.

While oxidation was observed for both DIBK and caprylic acid, both of these contaminants could be removed to an appreciable extent by thermal desorption. By heating the column under a nitrogen sweep and holding at a temperature of 250°C for 1 3/4 hr, 85% of the original DIBK was removed. For caprylic acid, 87% was removed by holding the column at 300°C for 1 hr.

Contaminant remaining after thermal desorption was removed by oxidation. Oxidation was initiated in this case by admitting a low flow of oxygen to the nitrogen stream flowing into the bottom of the heated column. Exothermic reaction occurred first at the bottom of the column and a narrow reaction zone moved up the column at a rate dependent on the rate of oxygen supply. The temperature within the reaction zone was also dependent on the rate of oxygen supply and on occasion exceeded 400°C (the carbon ignition temperature). The temperature at the center of the reaction zone was difficult to measure and control accurately. Since the reaction zone was so narrow (less than 2 cm), many thermocouples had to be placed along the length of the column for proper temperature monitoring. The oxidative regeneration was prone to instability: too much oxygen caused excessive temperatures within the reaction zone, and too little oxygen resulted in quenching of the reaction.

Oxidation could be initiated directly without prior thermal desorption by heating a small element at the bottom of the column to a temperature at which oxidation would occur and admitting oxygen. However, thermal desorption could not be avoided since heat was carried forward from the reaction zone and caused thermal desorption before oxidation. Thus a thermal desorption zone moved up the column ahead of the reaction zone.

Most of the losses incurred in repetitive cycling with the carbon column are attributable to problems associated with control of the oxidation. When a column was fabricated with a sufficient number of thermocouples for proper temperature measurement, no significant loss of carbon by oxidation was observed during adsorption/regeneration cycling.

Several models were considered for the regeneration of a carbon granule. The model most consistent with experimental data is the "external shell" model, in which reaction occurs at the exterior (superficial) surface of the carbon granule. The contaminant migrates from the interior to the exterior of the granule by surface diffusion and gaseous transport through the pores. Oxidation occurs on the particle exterior surface of the contaminant. The oxidation is rate limited by a surface reaction (with a substantial activation energy) rather than by a diffusional process.

The differential equations describing the regeneration of the column were derived but were greatly complicated by the dependence of the regeneration on the kinetic expressions for desorption and reaction. These expressions can only be determined experimentally, and preliminary attempts at fitting the reaction rate to a simple kinetic expression were unsuccessful. The difficulties associated with experimentally determining the kinetic expressions are probably prohibitive, and it may be more worthwhile to assume simple kinetic expressions and to determine the qualitative dependence of the regeneration on controllable variables.

A prototype system for spacecraft application is presently envisioned as two carbon columns alternating between adsorption and regeneration. Condensible products of thermal desorption and oxidation would be removed from spent regeneration air by cold-trapping.

Future work should be conducted at both the research and development levels. The research effort should examine other activated carbons, catalyst modifications (such as concentration of platinum), impregnation procedures, and catalyst additions. The selected catalytic carbons should be thoroughly compared to non-catalytic carbons, and thermal desorption should be extended to higher temperatures and longer times. Contaminants representative of all classes of spacecraft contaminants should be examined.

The development effort should be directed toward specifying an optimum system for oxidative carbon regeneration with or without the presence of an oxidation catalyst. Various methods of control should be devised and examined experimentally. Sufficient data should be generated to conduct a trade-off study between oxidative and desorptive regeneration. Details of the system design should be specified and a bench-scale model of the system should be constructed to demonstrate the feasibility of automatic operation.

II. INTRODUCTION

The removal of contaminants from the enclosed atmospheres of manned spacecraft is essential, particularly for missions of extended duration. Contaminants can arise from a variety of sources including biological functions, off-gassing of materials, leaks, and scientific experiments. A great number and variety of contaminants have been identified (1,2,3) in spacecrafts, simulators, and materials off-gassing tests. The system selected for contaminant control will have to be very non-selective in order to remove this wide variety of contaminants and will probably consist of several subsystems each designed to remove a particular class of contaminants.

Lockheed has made a detailed study (2,3) of various systems of contaminant removal. The selected system, shown in Figure 1, consists of a high-flow fixed bed of activated carbon in parallel with a low-flow system consisting of a regenerable activated carbon bed, a catalytic oxidizer, and pre- and post-sorbent beds. The catalytic oxidizer removes carbon monoxide and hydrogen in addition to several very low molecular weight hydrocarbons which are not adsorbed in the regenerable activated carbon bed. The pre-sorbent bed contains lithium hydroxide and is intended to remove catalyst poisons, particularly SO_2, from the influent to the oxidizer. The post-sorbent bed also contains lithium hydroxide for the removal of acid gases such as HF, HCl, SO_2 and NO_2 produced in the oxidizer. Ammonia is removed by impregnating the fixed bed with phosphoric acid, and acid gases are also removed in the fixed bed by dissolution in adsorbed water. The rationale behind using a high-flow fixed bed in parallel with a low-flow regenerable bed is that certain contaminants are produced at a rate greater than can be controlled by the low-flow system. In general, the more strongly adsorbed contaminants will be controlled mainly by the high-flow bed, and the more weakly adsorbed contaminants will be controlled mainly by the low-flow bed. A trade-off study showed that the system of Figure 1 was superior to one in which a single high-flow regenerable bed was used.

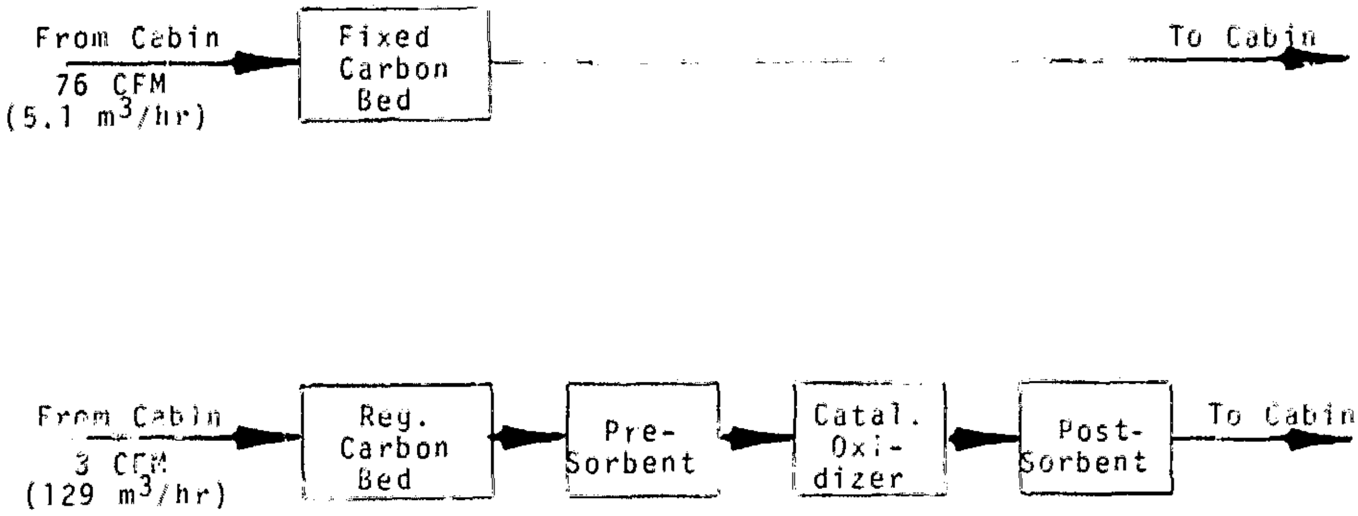

FIGURE 1. CONTAMINANT REMOVAL SYSTEM FOR 12 MAN, 180 DAY MISSION

The use of regenerable carbon results in a very significant savings in weight and volume. In the Lockheed study, approximately 500 lbs (227 kg) of carbon would be needed for a nonregenerable fixed bed system, whereas the system of Figure 1 requires only 32 lbs (14.5 kg).

The degree to which the carbon is regenerable is naturally an important factor. Typical losses in industrial regenerations range from 4-10% per regeneration (4). These losses are associated with a decrease in carbon surface area, particle size, and weight caused by high-temperature sintering and oxidation. Industrial regenerations are carried out in rotary kilns or multiple hearth furnaces. Thermal desorption of contaminants typically occurs over the range of 100-250°C. However, not all of the contaminants can be desorbed and high molecular weight, strongly adsorbed contaminants pyrolyze and decompose to form a carbonaceous residue on the carbon. This typically occurs over a temperature range of 200-650°C. This residue is then oxidized with steam, carbon dioxide, or oxygen over a temperature range of 650-1000°C.

The regeneration of carbons contaminated in spacecraft atmospheres should not be as difficult to regenerate as, for example, an activated carbon used in industrial waste-water treatment. The fact that contaminants are adsorbed from the gas phase means that they must have some degree of volatility, and significant amounts of "high boilers" should not be encountered. Furthermore the strongly adsorbed contaminants will be removed mainly in the fixed bed, allowing more efficient regeneration of the regenerable bed. Nevertheless, the possibility of pyrolysis and decomposition of some of the adsorbed contaminants must be considered.

The regenerable carbon bed used in the Lockheed study was regenerated by heating to 200°C under vacuum for 2-3 hours. Under these conditions it was observed that certain of the higher molecular weight contaminants (diisobutyl ketone and caprylic acid, in particular) could not be completely removed from the carbon. Whether this was due to an insufficient temperature for rapid desorption or to decomposition of the contaminant was not determined.

The significant losses in industrial regenerations of activated carbon and the incomplete regeneration observed by Lockheed may be remedied by the use of a catalyst-impregnated activated carbon. A nonselective catalyst could promote oxidation of carbonaceous deposits at temperatures far below the 650-1000°C typically used in industrial regenerations.

The objective of "Phase I" of this program was to evaluate the efficiency of catalyst-impregnated activated carbon in removing typical spacecraft contaminants. The seven contaminants to be investigated are listed in Table 1 along with their molecular weights and normal boiling points.

TABLE 1

CONTAMINANTS USED IN INVESTIGATION OF CATALYST-IMPREGNATED ACTIVATED CARBON

Contaminant	Molecular Weight	Normal Boiling Point (°C)
Caprylic Acid	144	238
Diisobutyl Ketone	142	168
1,1,2,2 Tetrachloroethane	168	146
Thiophene	84	84
Acrolein	56	53
Freon 114	171	4
Vinyl Chloride	62	-14

III. EXPERIMENTAL APPARATUS AND PROCEDURES

Research experiments were conducted at the City University of New York (CUNY) using a duPont thermal gravimetric analysis (TGA) apparatus and a duPont differential scanning colorimeter (DSC) apparatus. Research and engineering experiments were conducted at Abcor using a one-inch diameter by one foot long carbon column.

A. TGA APPARATUS

The TGA apparatus is shown in Figure 2 and 3 for the adsorption mode and regeneration mode respectively. For adsorption, a dried stream of nitrogen was split into a purge stream and a carrier stream. The purge stream was passed through the control end of the balance and out through the exit to avoid accumulation of contaminant in the balance. The carrier stream was sparged through a constant-temperature saturator and passed through the inner tube of the concentric furnace tube. The carrier gas passed over the carbon sample on the sample pan, was redirected by the platimum baffles,and passed out through the exit with the purge gas. The sample was held at a constant temperature during adsorption by a furnace surrounding the furnace tube.

During regeneration (Figure 3) a controlled flow of compressed air was passed through an activated carbon bed, a calcium sulfate bed, and a molecular sieve bed for organic and moisture removal. The air passed over the sample and out to the collection and analysis components. The furnace was programmed to heat the sample at a given rate. Typically 15°C/min, and the sample weight was plotted against sample temperature as measured by the thermocouple attached to the sample pan. A single carbon particle was used for the sample giving a typical weight of 40 mg.

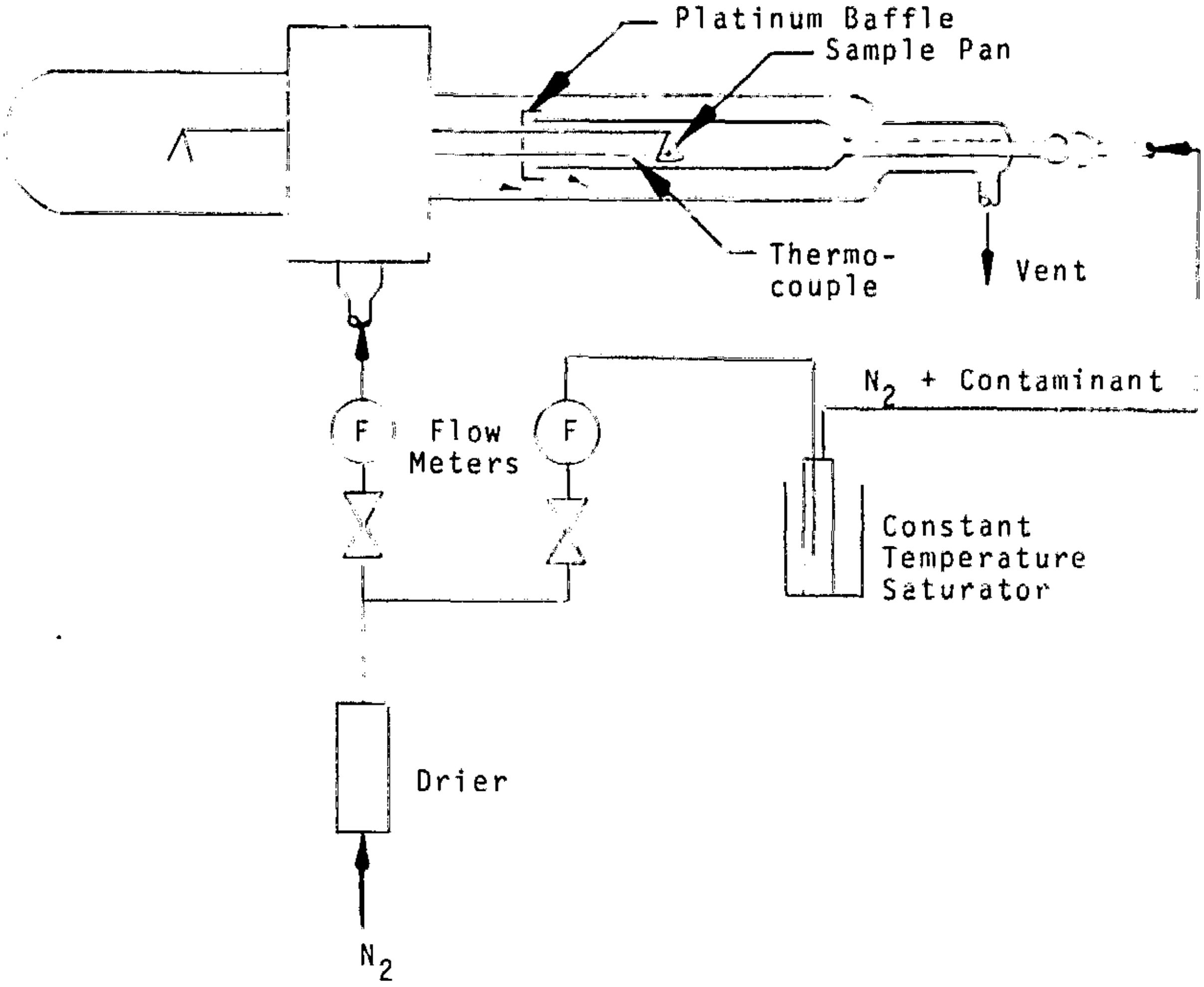

FIGURE 2. TGA APPARATUS: ADSORPTION MODE

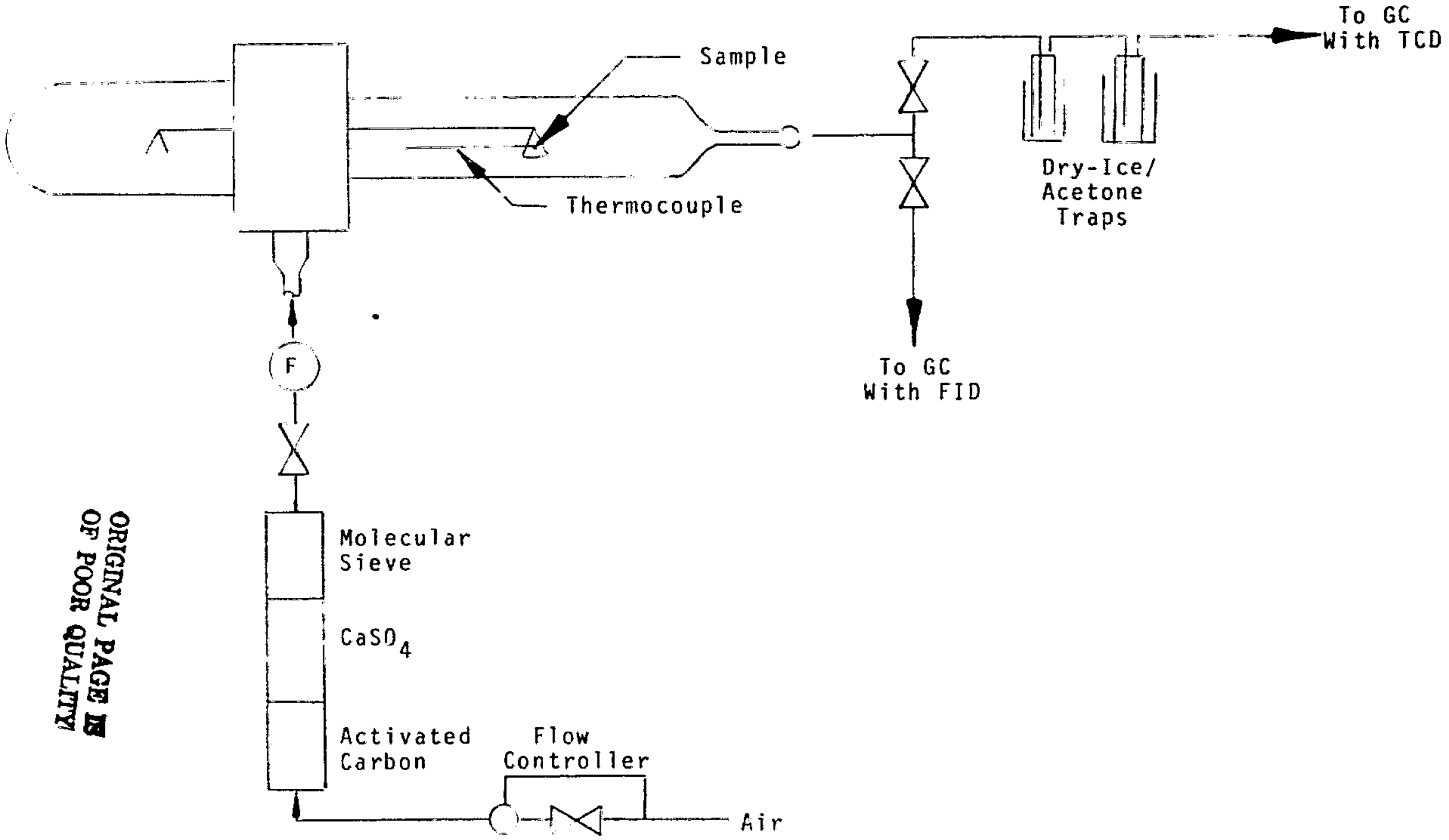

FIGURE 3. TGA APPARATUS: OXIDATION MODE

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A typical TGA trace during which oxidation occurs is shown by the solid curve of Figure 4. The weight decreased smoothly at first until the temperature reached about 200°C. Then the highly exothermic oxidation reaction caused a disproportionate temperature increase in the sample as the weight of adsorbed contaminant decreased to zero. Since the oxidation reaction was complete the sample temperature cooled back to the furnace temperature (260°C), and the sample weight remained constant at 0 mg. until about 375°C where the carbon began to oxidize. If the heat of reaction were removed, the TGA trace would follow the dashed line of Figure 4.

5. DSC APPARATUS

A cross-section of the DSC apparatus is shown in Figure 5. A contaminated carbon particle was placed in the sample pan and a flow of 300 cc/min of purified air was passed over the sample via inlet and outlet ports to the gas space over the sample. A thermocouple was attached to the sample pan with reference junction attached to the reference pan. The thermocouple measured the temperature difference between sample and reference. This difference resulted from any exothermic or endothermic process occurring within the sample. This ΔT is plotted against the cell temperature which was uniformly increased by a programmed heat input, typically at a rate of 10 to 15 °C/min.

A typical DSC trace is shown in Figure 6. The negative peak at low temperature indicates an endothermic process, i.e., thermal desorption of contaminant. The possitive peak at higher temperature indicates an exothermic oxidation reaction. The final exothermic rise in the DSC trace indicates oxidation of carbon as can be seen by comparison to the curve for no contaminant adsorbed.

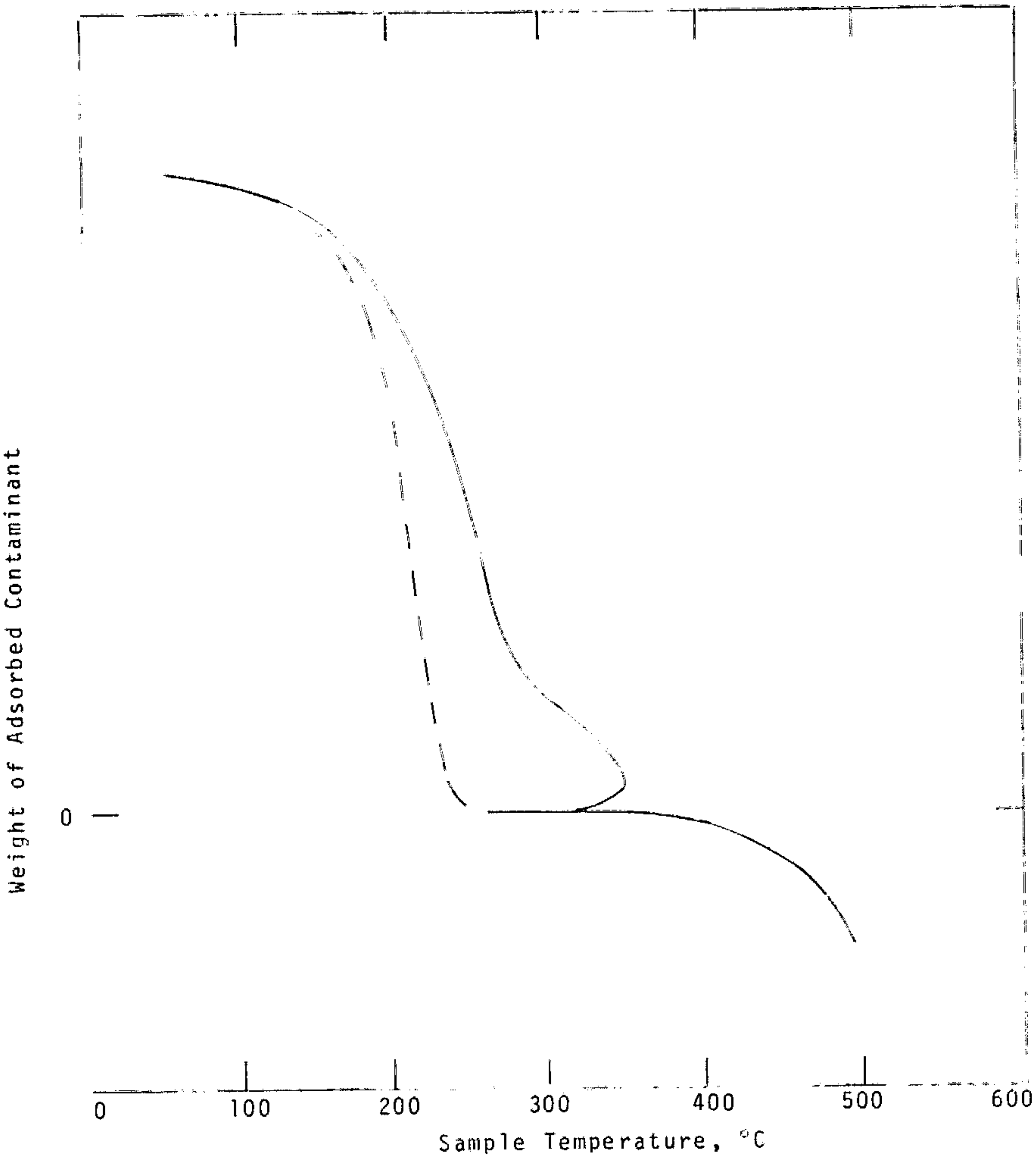


FIGURE 4. TYPICAL TGA TRACE

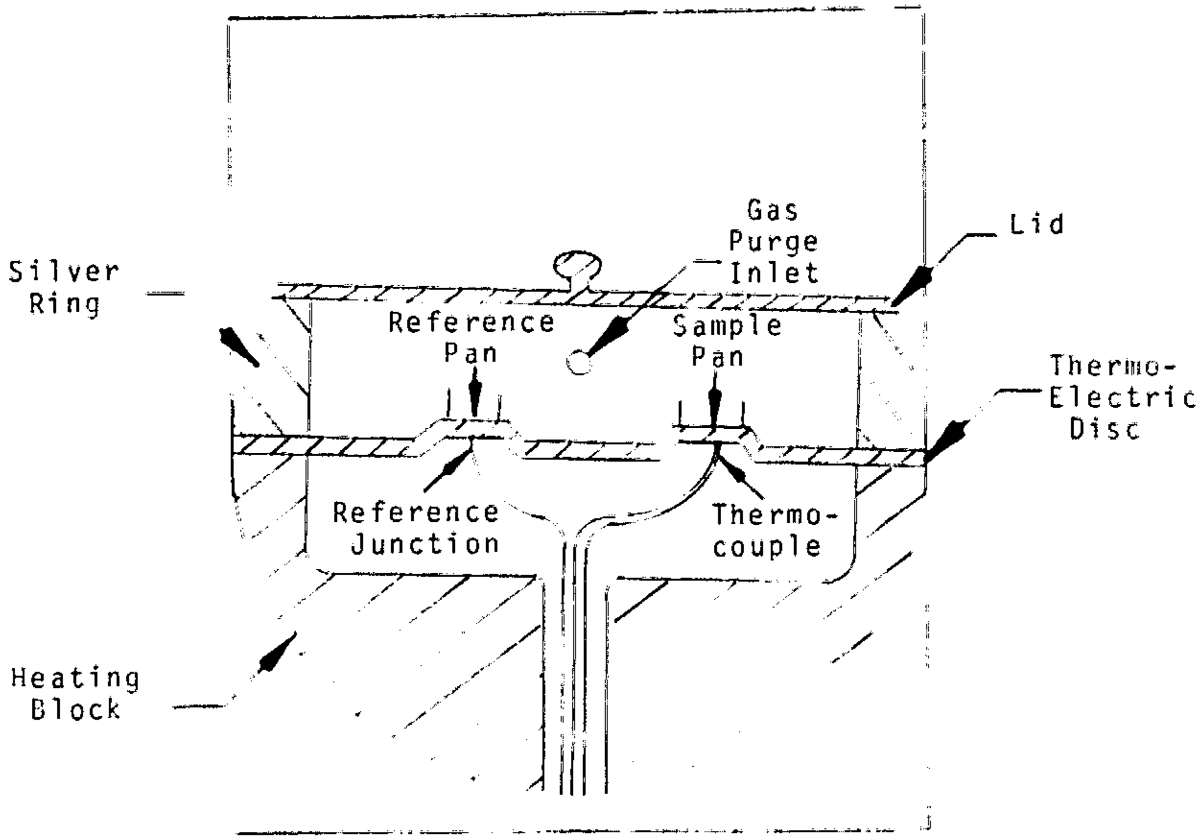


FIGURE 5. CROSS SECTION OF DSC CELL

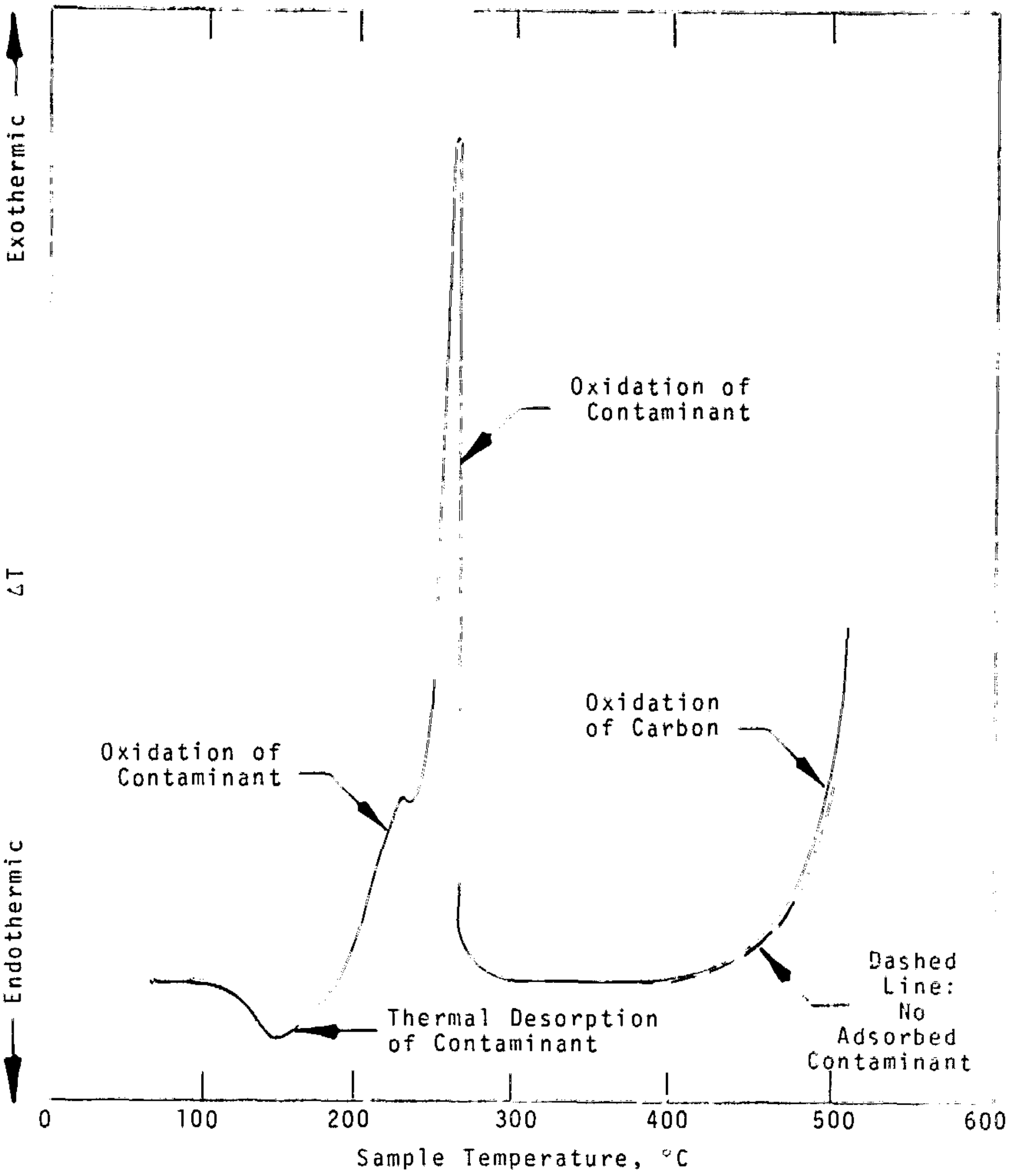


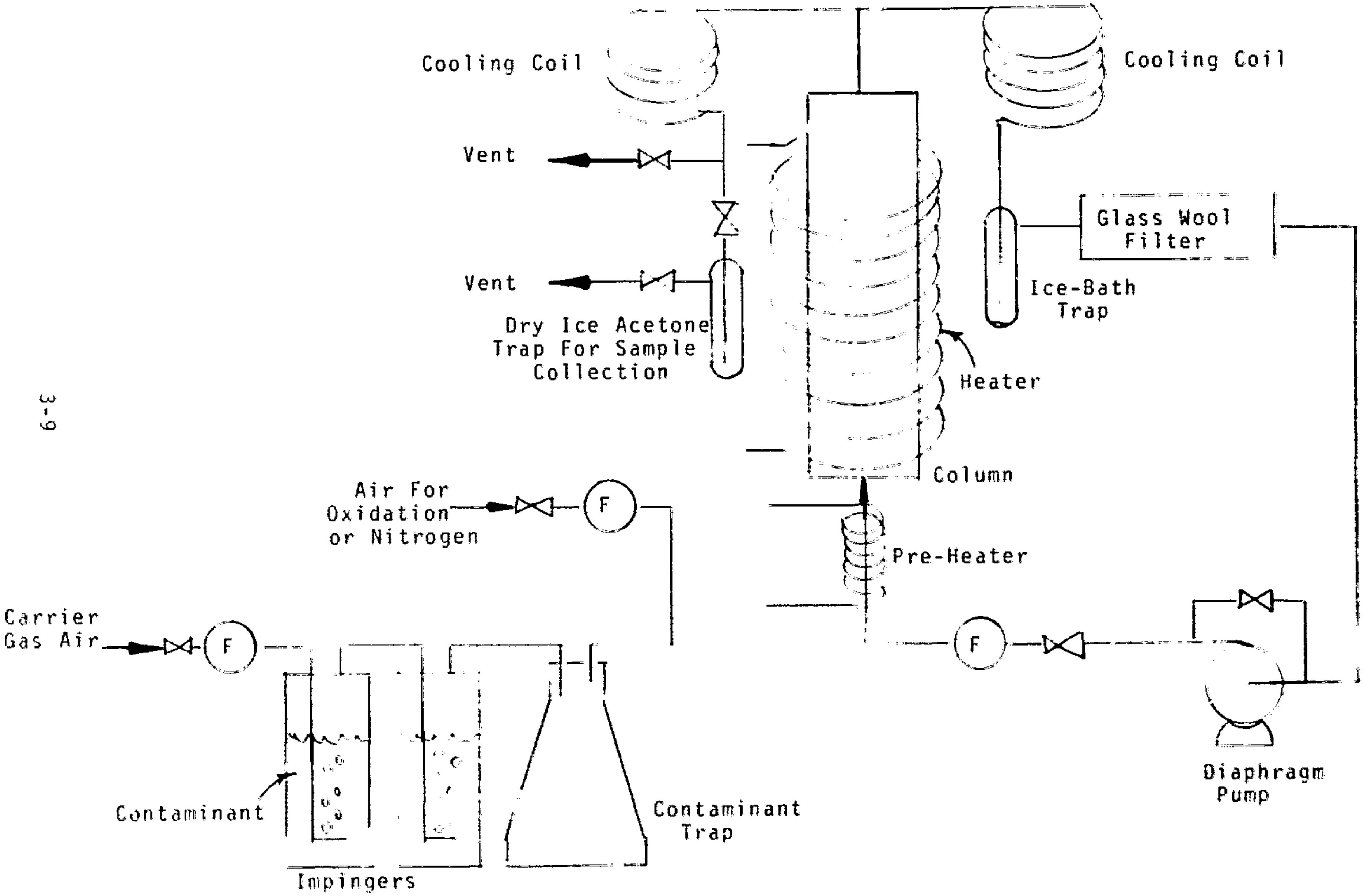
FIGURE 6. HYPOTHETICAL DSC TRACE

C. COLUMN APPARATUS

A flow schematic of the apparatus used in column studies is shown in Figure 7. During the adsorption cycle the flow rate of compressed-air carrier gas was measured and sparged through two volumes of contaminant in series. A contaminant trap removed any foam or liquid carry-over. The contaminant-saturated air was passed through the carbon column and out through the vent. The amount of adsorbed contaminant and the point at which saturation was reached were determined by removing the column at various times during adsorption and weighing it. The column was wrapped with heating tape to keep it at a constant temperature during adsorption. Typically the column was kept at 50°C above the saturation temperature of the carrier gas to prevent capillary condensation in the pores of the carbon.

Contaminant could be removed from the carbon both by thermal desorption and oxidation. Usually thermal desorption was carried out prior to oxidation, but in certain cases oxidation was started without prior thermal desorption. For thermal desorption, nitrogen was admitted to the system and was recirculated around the recirculation loop by a diaphragm pump. The nitrogen was preheated before entering the column, and the column was heated to the desired desorption temperature, typically 200-300°C. The off-gas from the column was cooled in an ambient coil and contaminant was removed in an ice-bath trap. The diaphragm pump was protected from particulate by a glass-wool filter. Samples of off-gas could be collected in the dry ice-acetone trap and combined with the contents of the ice-bath trap for future analysis.

FIGURE 7. Flow Schematic for Column Contamination and Regeneration



For oxidation a low flow of air was admitted to the recirculation loop, and the column temperature was monitored by thermocouples placed at various positions along the length of the column. The oxidation was generally controlled by fixing the recirculation rate (cooling rate) and adjusting the air flow rate as required to prevent excessive temperatures in the column or quenching of the reaction. The carbon column was removed and weighed at various times during regeneration to determine when regeneration was complete.

Details of the two carbon columns used are shown in Figure 3. The first column contained only five thermocouples inserted into thermocouple wells and proved to be very different to control. The reaction zone during regeneration was smaller than the thermocouple spacing and it was impossible to properly monitor the temperature. In addition the thermocopules worked loose and made poor contact with the bottom of the well. The second column was designed for 20 thermocouples placed directly into the packed carbon bed.

D. CARBON PREPARATION

Most experimental results were obtained using a 0.3 wt % platinum on carbon composition. The preparation procedure for column studies is given below and is based on prior research at CUNY. Carbon preparation for the DSC and TGA experiments followed a similar procidure but on a smaller scale.

- 125 grams of carbon were covered with 250 ml of solution containing approximately 0.38 grams of platinum as chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$). This gives a platinum-carbon ratio of 0.30% in sufficient solution to cover the carbon.

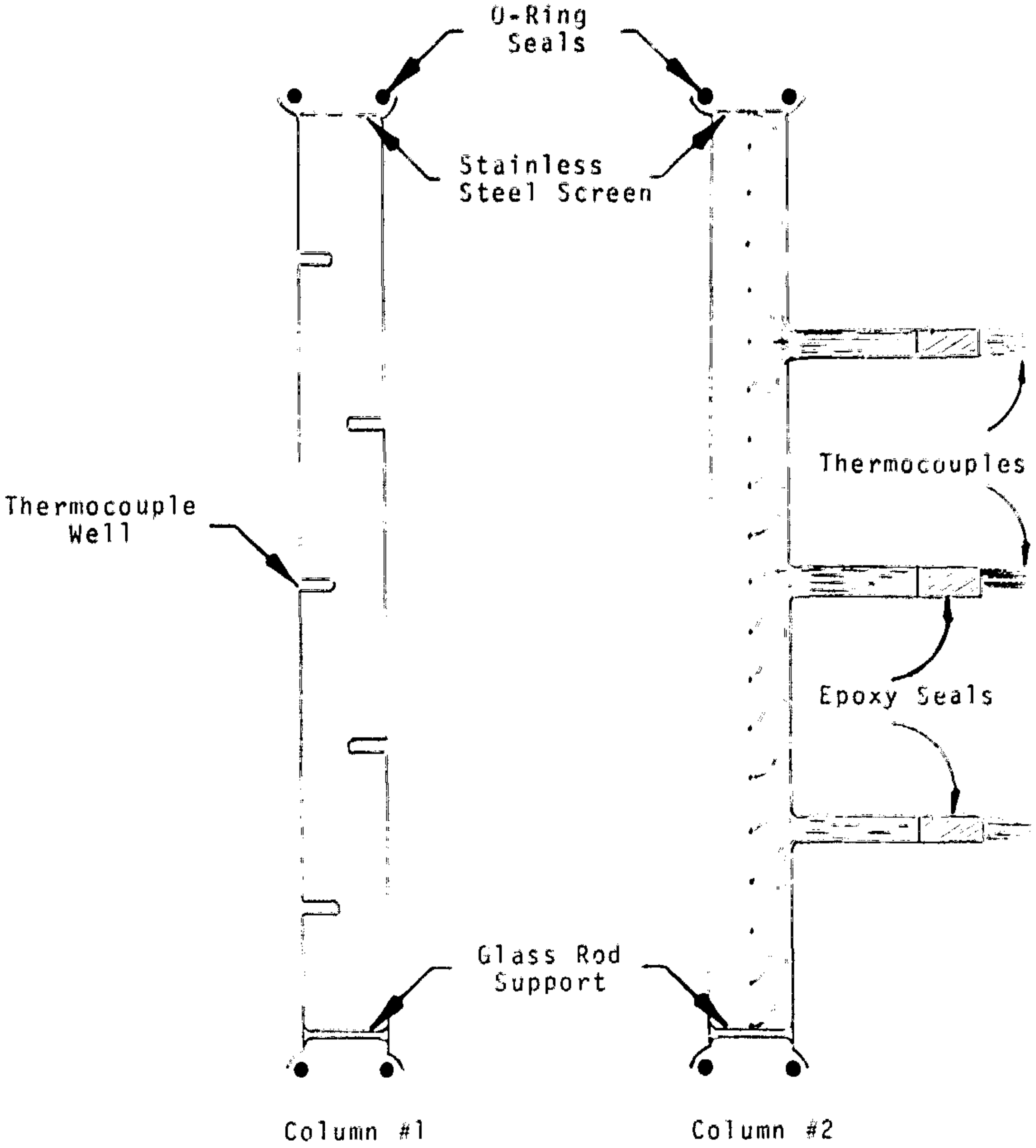


FIGURE 8. DETAILS OF COLUMN CONSTRUCTION. Scale: 1/2 Actual Size. Constructed of borosilicate glass. Externally heated by heating tape.

-- The carbon/solution slurry was evacuated to remove air from the pores.

-- The slurry was dried at room temperature to a pasty consistency and evaporated to dryness over a period of 16 hours with a heat lamp.

-- The carbon was then dried for three hours at 120°C.

-- The deposited precipitate was reduced to Pt by passing a stream of H_2 at 350°C over the carbon for one hour.

The carbon used in all tests was Pittsburgh Activated Carbon Type BPL 6 x 16 which has been shown in prior research at CUNY to have a high kindling temperature.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. CATALYST SELECTION

Various catalysts have been examined in previous research at CUNY for the oxidation of adsorbed contaminants. In general, platinum has proved to be the most efficient catalyst in terms of providing a large temperature difference between the oxidation of the adsorbate (contaminant) and adsorbent (carbon). Typical results are shown in Figure 9 for vanadia, palladium, and platinum catalysts used to oxidize adsorbed methyl methacrylate (which is a spacecraft contaminant). Platinum is clearly superior to the other catalysts giving the lowest temperature for oxidation of the adsorbate and the highest temperature for oxidation of the adsorbent. The platinum catalyst also gave superior performance with the selected contaminants. A composition of 0.3 wt.% platinum on activated carbon was selected on the basis of prior research at CUNY.

B. DSC/TGA RESULTS

DSC and TGA traces are presented below for each of the selected contaminants.

1. Caprylic Acid

The DSC and TGA traces for the oxidation of caprylic acid on platinum-impregnated carbon are shown in Figure 10. The DSC trace (solid line) shows three peaks (A, B, and C) for the oxidation of caprylic acid, in addition to the final peak (D) for the oxidation of carbon. The carbon support begins to become pyrophoric at a temperature of about 400°C.

The TGA trace (dashed line) shows the weight loss during regeneration. The weight begins to decrease at about 125°C which corresponds to the slight negative peak at the same temperature in

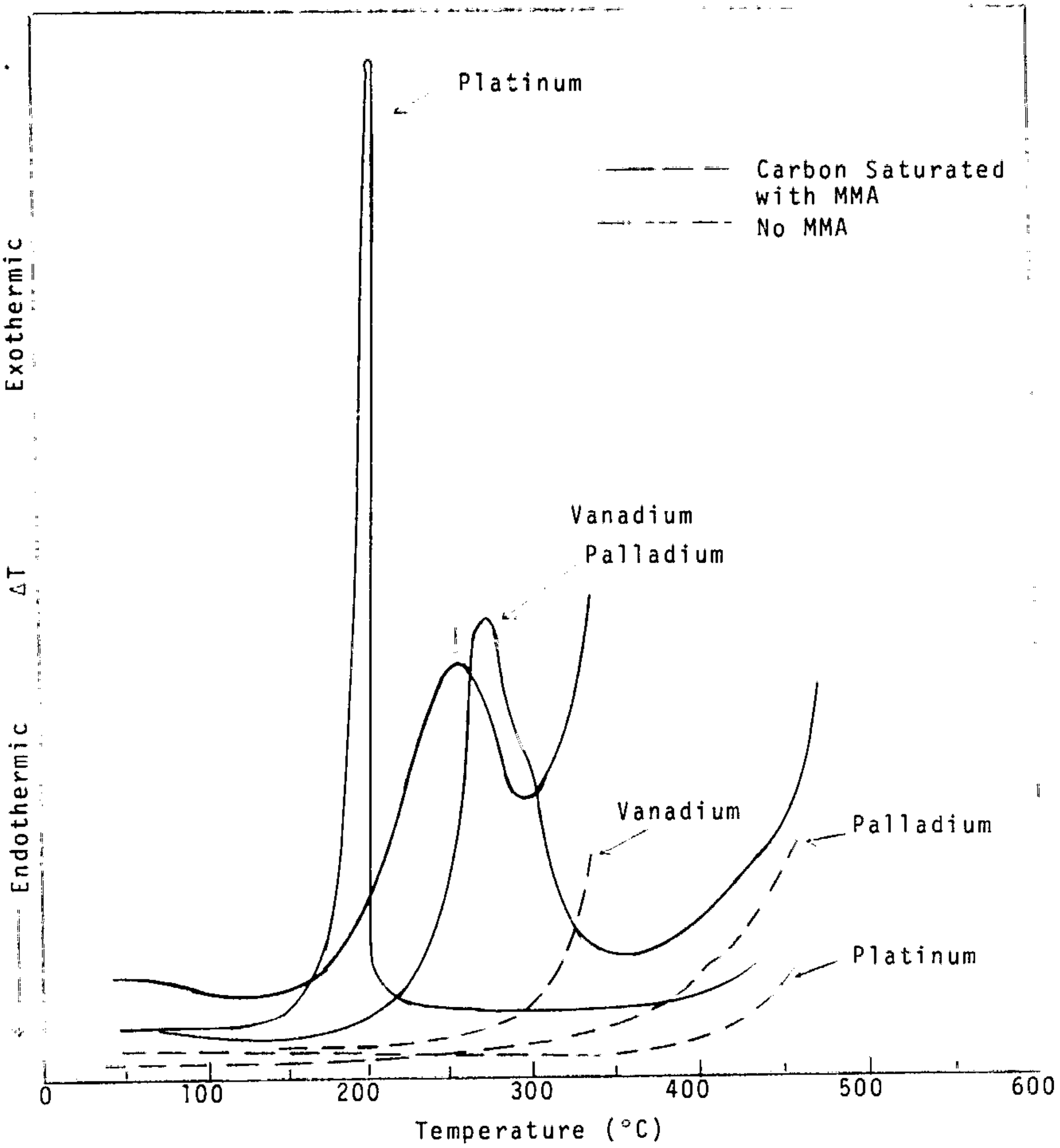


FIGURE 9. DSC Runs for Methyl Methacrylate Adsorbed on Carbon Impregnated with Various Catalysts: 0.282% Pt, 0.2% Pd, and 1% NH_4VO_3 Decomposed.

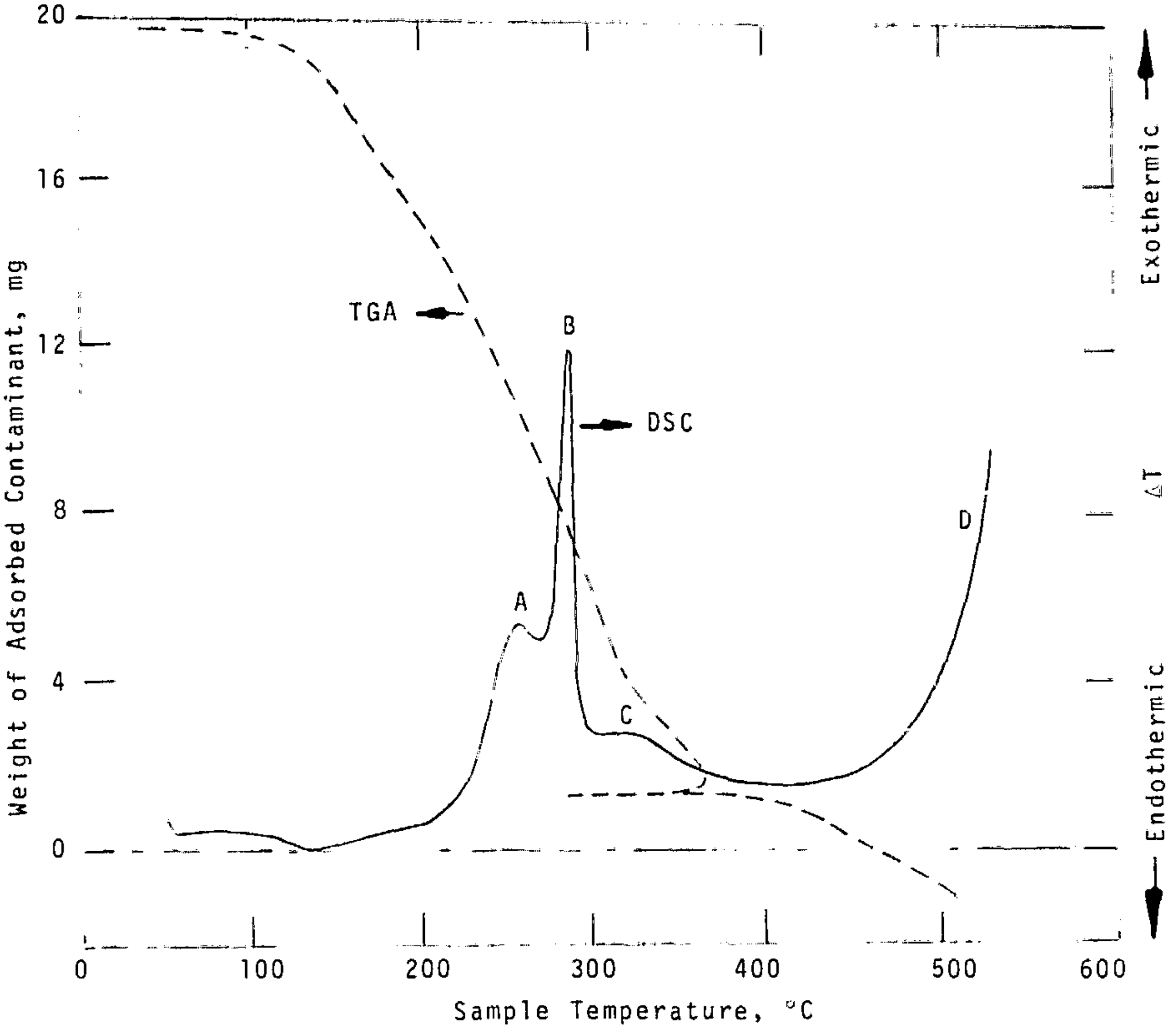


FIGURE 10. DSC AND TGA TRACES FOR CAPRYLIC ACID REMOVAL FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate= 10°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=15°C/min.

the DSC curve. The negative peak (endothermic process) indicates that the initial weight loss is due to thermal desorption of the contaminant. As the temperature is increased, the observed weight loss is probably the result of a combination of thermal desorption and oxidation of caprylic acid. Following the second oxidation peak (B) at 290°C, 8% of the original contaminant weight remains. As the temperature is increased from 300-400°C, peak "C" is evolved, but there is no weight change associated with this peak, i.e. the weight remains constant between 300 and 400°C. Above 400°C the DSC trace shows that the carbon becomes pyrophoric. Thus the weight loss above 400°C shown by the TGA trace is the result of carbon oxidation. The 8% remaining contaminant is not removed before the carbon begins to oxidize.

Figure 11 shows the DSC and TGA traces for capyrlic acid on the same activated carbon but without the catalyst. Only two peaks (A and C) are observed for the oxidation of contaminant. There is reasonably good agreement between the temperatures at which these peaks occur and the temperatures of the A and C peaks of Figure 10. Therefore the B peak of Figure 10 is the only peak that can be associated with the catalytic activity of the platinum.

The peaks of Figure 11 indicate that capyrlic acid is oxidized to an appreciable extent even in the absence of a catalyst. At low temperatures the TGA shows a weight decrease before the exotherm appears in the DSC, which can again be explained by thermal desorption. As the temperature is increased peak A is evolved indicating oxidation of the contaminant, and the weight of adsorbate decreases to about 12% of its initial value following the evolution of peak A. At higher temperatures peak C is observed. Unlike the case for catalyst-impregnated carbon (Figure 10) where the weight remained constant during peak C, the TGA trace for carbon with no catalyst shows a weight of zero at about 370°C. In addition there is a change in slope in the TGA trace as the zero weight is approached. These facts indicate that the remaining 12% contaminant is removed prior to oxidation of the carbon.

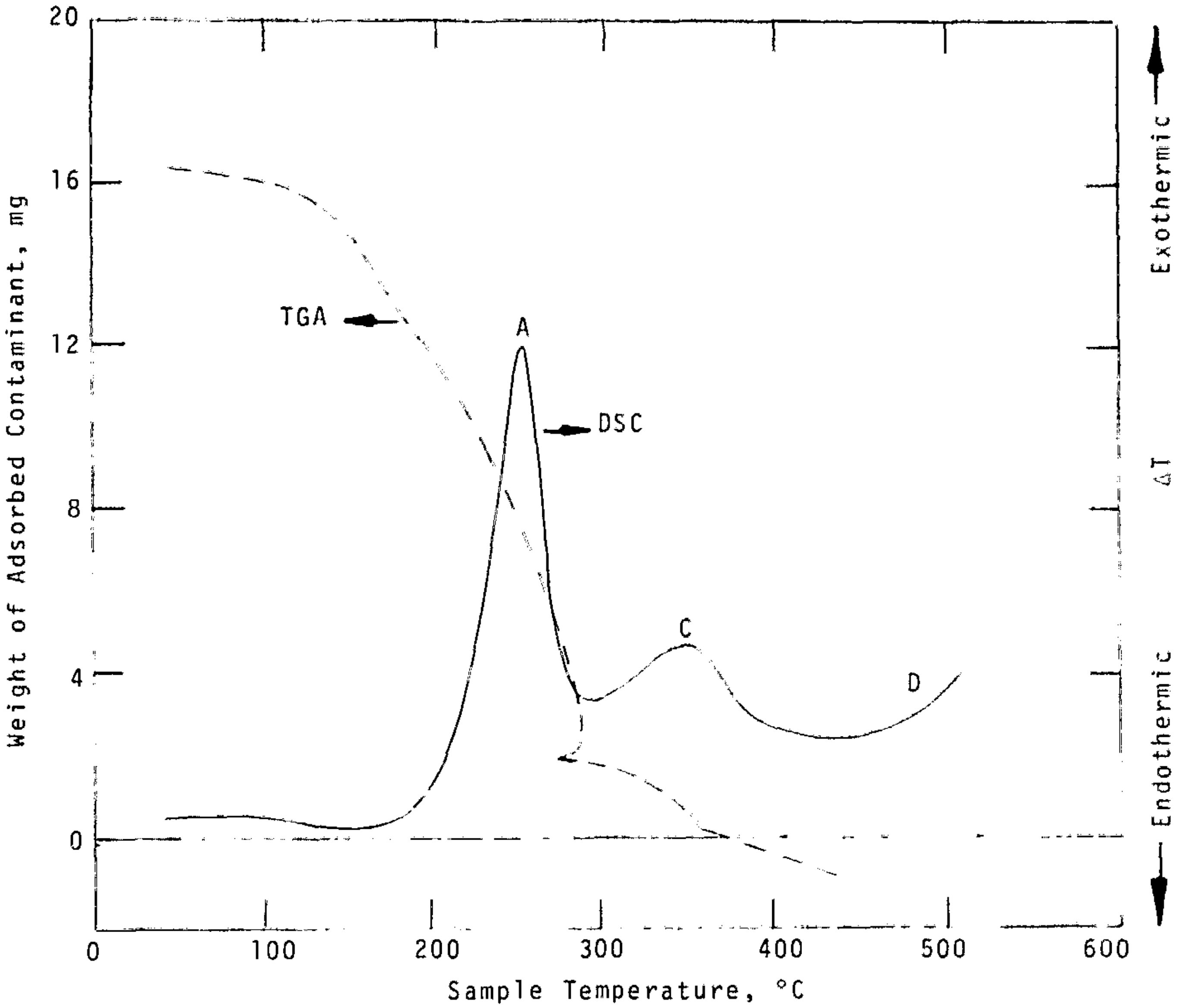


FIGURE 11. DSC AND TGA TRACES FOR CAPRYLIC ACID REMOVAL FROM NON-CATALYTIC CARBON. DSC: Heating Rate= 15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=15°C/min.

One fact that appears to be contradictory is that the weight decrease due to oxidation of the carbon begins at around 370°C in Figure 11; whereas the exotherm for carbon oxidation (peak D) does not become apparent until about 450°C. This apparent discrepancy can be rationalized somewhat by resolving the DSC trace of Figure 11 into individual peaks as shown in Figure 12. Although a theoretical peak shape was not used in this resolution, the curve for carbon oxidation can be extrapolated to a starting point of about 370°C. This explanation is not entirely satisfactory, however, since the kinetics for oxidation of the carbon do not become predominate until the resolved curves for peaks C and D cross at 425°C. Thus the change in slope of the TGA trace near zero weight in Figure 11 should occur at about 425°C rather than 370°C.

The advantages of catalyst-impregnated activated carbon for the removal of capyrlic acid are not overwhelming. The remaining 8% of contaminant present after the B peak oxidation (Figure 10) is not removed prior to oxidation of the carbon. This is particularly surprising in view of the fact that the remaining contaminant is removed from noncatalytic carbon. If the C peaks in Figures 10 and 11 result from the same surface process, then the removal of the remaining contaminant is a carbon-related reaction rather than a platinum-related one. The absence of a weight loss for the catalytic carbon would seem to imply that the products of the carbon-related reaction are strongly adsorbed on platinum.

Whether or not the failure to remove the residual 8% of contaminant is a serious limitation to the use of catalyst-impregnated carbon depends entirely on the behavior in subsequent cycles. If a residual weight of 8% occurs only on the first cycle, the loss in adsorptive capacity will be tolerable. If an 8% residue occurs for each regeneration, the capacity of the carbon will decrease at an unacceptable rate.

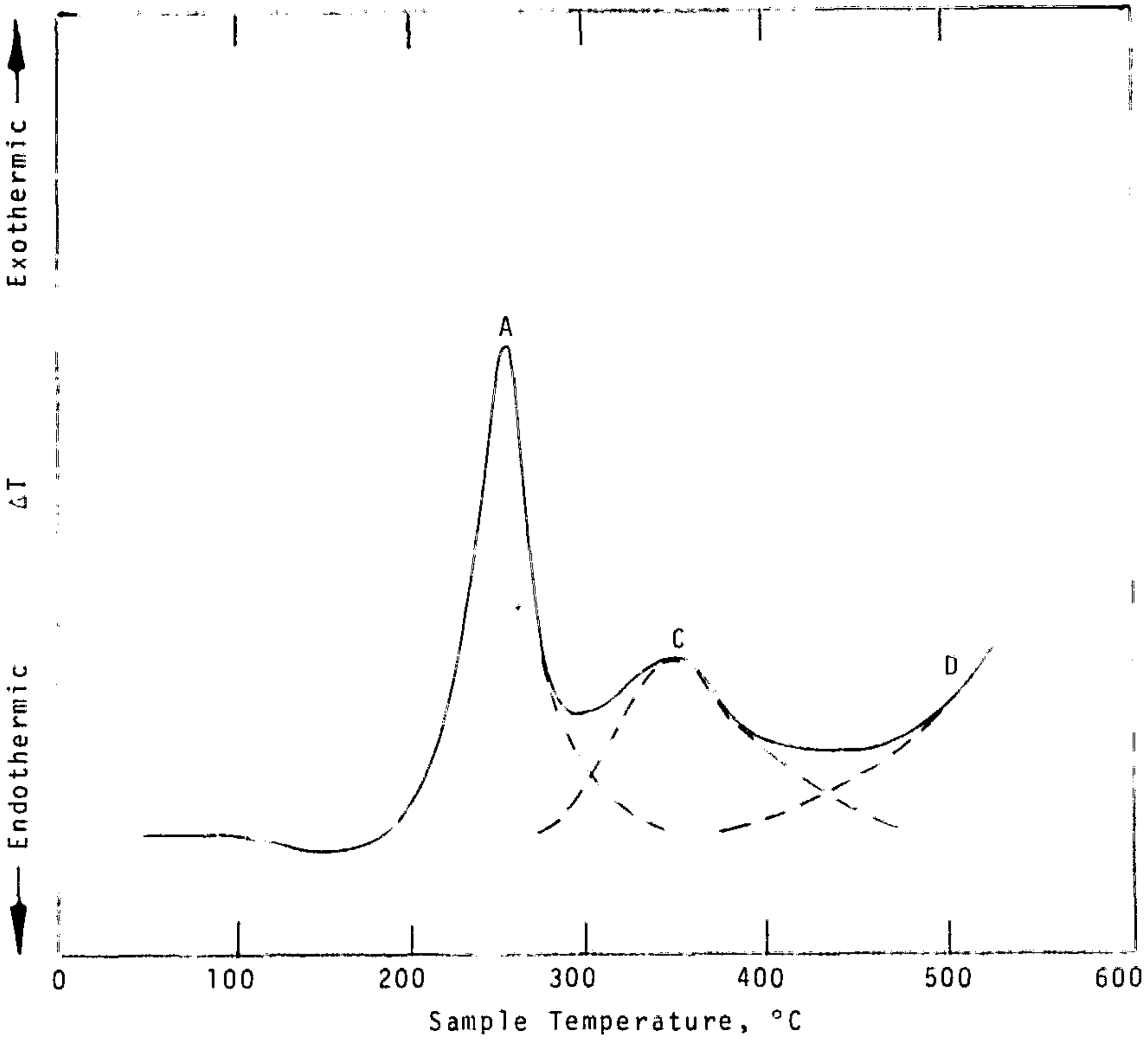


FIGURE 12. RESOLUTION OF DSC TRACE FOR CAPRYLIC ACID REMOVAL FROM NON-CATALYTIC CARBON

2. Diisobutyl Ketone (DIBK)

The DSC and TGA results for DIBK are very similar to the results for caprylic acid. DSC and TGA curves are shown in Figure 13 for regeneration of platinum-impregnated carbon and in Figure 14 for the same carbon without catalyst. For the catalytic carbon three peaks (A, B, and C) are again observed for the oxidation of adsorbate, and the final exotherm (peak D) for oxidation of carbon. By comparison to the noncatalytic carbon (Figure 14) peaks A and C result from oxidation on the carbon support and peak B results from oxidation on platinum.

The TGA traces are also very similar to those for capyrlic acid. In Figure 13 a weight decrease is observed before exothermic reaction occurs indicating thermal desorption at low temperatures. At higher temperatures oxidation occurs (peaks A and B) and the weight of adsorbed contaminant decreases to 4% of its initial weight. During peak C, however, the weight of contaminant remains constant and does not decrease until the carbon becomes pyrophoric. For noncatalytic carbon (Figure 14) the weight of adsorbate decreases to about 14% of its initial value after the peak A oxidation, and there is a gradual weight loss during the evolution of peak C. The change in slope near zero weight may again indicate the point at which the contaminant is completely removed. For both the catalytic and noncatalytic carbon, zero weight is not obtained until a temperature of 400°C is reached.

For a regeneration temperature between 250 and 350°C platinum-impregnated carbon can be expected to yield a lower residual contaminant weight. For a regeneration temperature between 350 and 400°C the noncatalytic carbon will yield a lower contaminant weight because of the shape of the curve.

Repetitive contamination/regeneration cycles were carried out with the DIBK contaminant. Results are given in Table 2 for

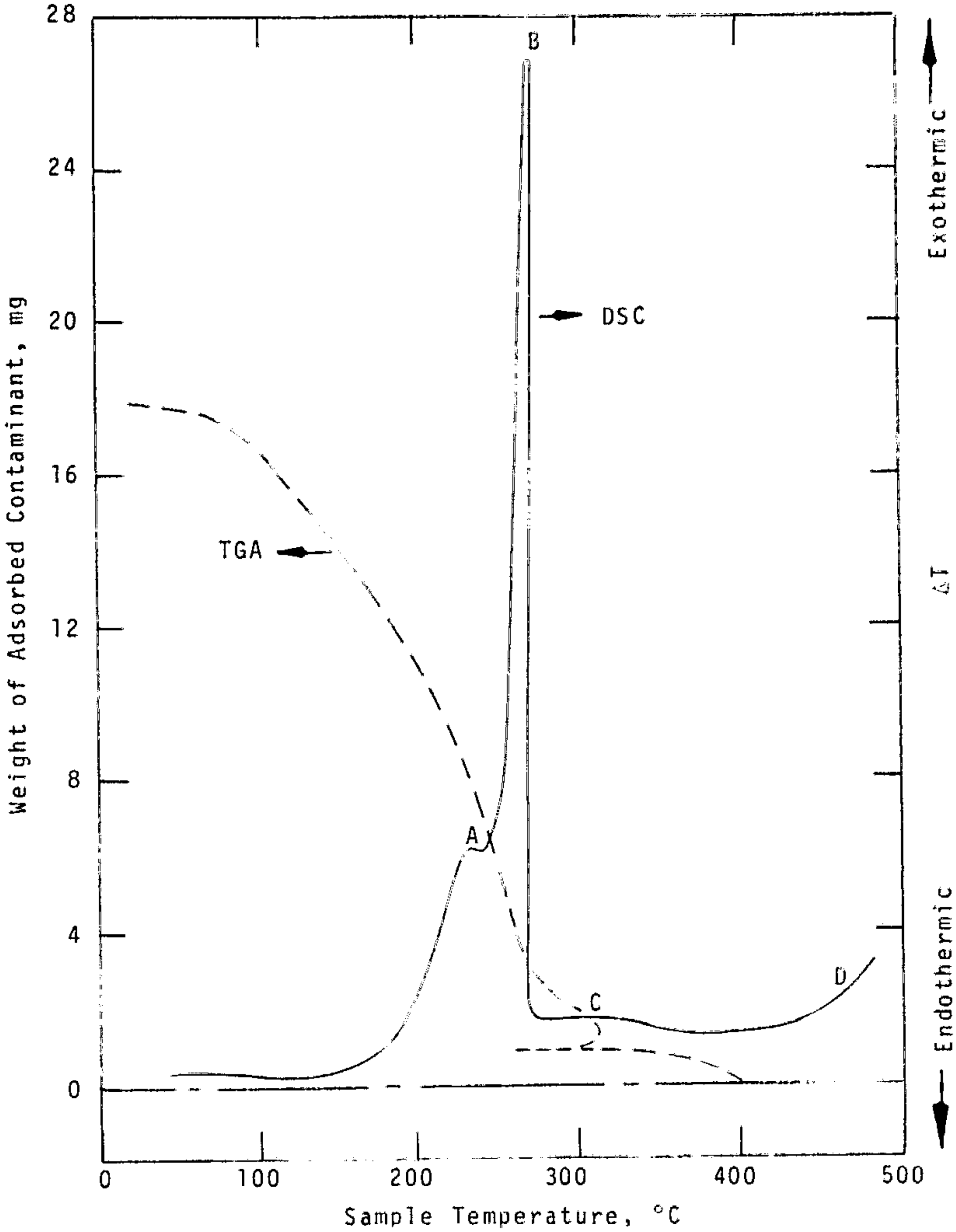


FIGURE 13. DSC AND TGA TRACES FOR REMOVAL OF DIBK FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate=15°C/min; Ordinate Scale= .04°C/in. TGA: Heating Rate= 15°C/min.

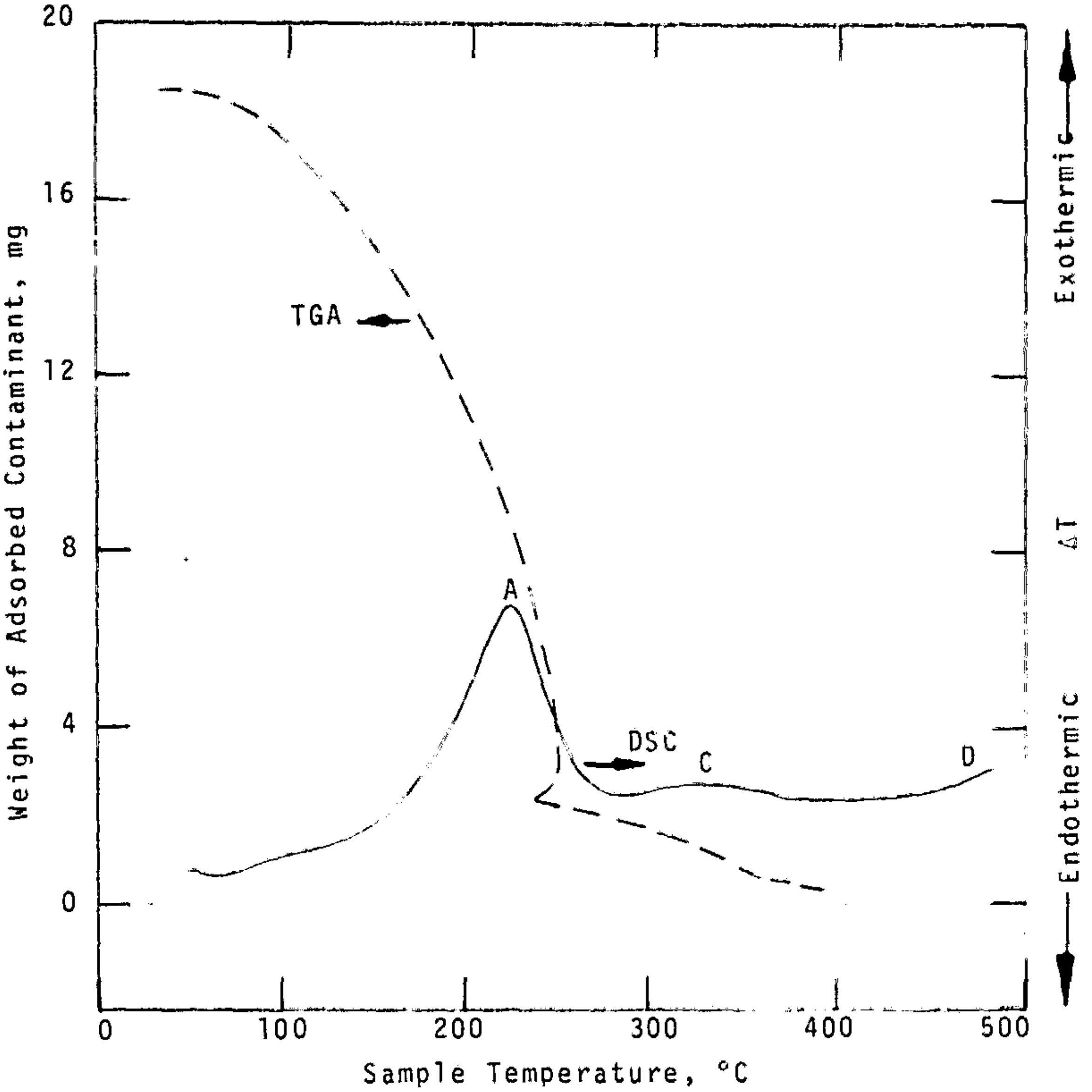


FIGURE 14. DSC AND TGA TRACES FOR REMOVAL OF DIBK FROM NON-CATALYTIC CARBON. DSC: Heating Rate=15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=15°C/min.

TABLE 2

REGENERATION DATA FOR OXIDATION OF DIBK ON PT/CARBON

Conc. of DIBK in Saturation Stream = 2100 ± 10 ppm
Saturation Temperature = 25°C
Initial wt of Pt/carbon = 53.6 mg
Optimum cut-off Temp. = 400°C

Adsorption Cycle	Adsorptive Capacity, mg/mg Carbon	Residual wt at End of Oxidation Reaction (255°C) (% of initial)
1	0.325	4.6
2	0.323	4.6
3	0.323	4.6
4	0.314	4.7
5	0.314	4.1
6	0.314	3.5
7	0.313	2.4
8	0.312	2.4

platinum-impregnated carbon. The contaminated carbon was regenerated by heating in air to 400°C. A total of eight regeneration cycles were conducted. The adsorptive capacity of the carbon decreased from 0.325 to 0.312 mg/mg carbon or an average of 0.5% per regeneration. However, most of the loss in adsorptive capacity occurred between the third and fourth cycles. Over the last five cycles the average decrease in adsorptive capacity was only 0.13% per regeneration. These losses are far below the typical industrial regenerative losses of 4-10% per cycle and are very encouraging.

Also shown in Table 2 is the residual weight of adsorbate at the end of the B peak oxidation (255°C) as a percent of initial contaminant weight. For the first several cycles the residual contaminant weight after the B peak is about 5%. However as more cycles are carried out the catalyst appears to become more efficient at removing this residue. After eight cycles the residue has decreased to about 2%. It would be very interesting to conduct repetitive cycling in which the regeneration is terminated at 260°C rather than 400°C. It would then be possible to determine whether or not the residue is cumulative.

Data for the regeneration of noncatalytic carbon is shown in Table 3. Again the carbon was heated to 400°C during each regeneration. Over a total of four regeneration cycles the decrease in adsorptive capacity was negligible. Therefore, if the carbon is heated to 400°C during regeneration the catalytic carbon has no advantage over the noncatalytic carbon. Also shown in Table 3 is the residual weight of adsorbate, as a percentage of initial contaminant weight, at the end of the A peak oxidation (230°C). The residue is 12% initially but increases to 16% after four cycles. Thus for regenerations below about 350°C the catalyst-impregnated carbon is clearly superior.

Several runs were made in which the weight of adsorbed DIBK was followed as a function of time at a constant temperature. Data for platinum-impregnated carbon and non-catalytic carbon are

TABLE 3

REGENERATION DATA FOR OXIDATION OF DIBK ON NON-CATALYTIC CARBON

Conc. of DIBK in Saturation Stream = 2100 ± 10 ppm

Saturation Temperature = 25°C

Initial wt of Carbon = 55.6 mg

Optimum cut-off Temp. = 400°C

Adsorption Cycle	Adsorptive Capacity, mg/mg Carbon	Residual wt at End of Oxidation Reaction (230°C) (% of initial)
1	0.335	11.8
2	0.334	14.0
3	0.334	15.1
4	0.334	16.1

shown in Table 4. For platinum-impregnated carbon the amount of adsorbate is reduced to about 1.5% of its initial value in two minutes at 220°C and at 245°C. This is somewhat better than the average of 4% residual at 255°C in the temperature programmed mode.

Unfortunately the non-catalytic carbon was run at a different temperature so that a direct comparison is not possible. However it appears that the catalytic carbon is superior to the non-catalytic carbon in the range of temperatures investigated.

3. Tetrachloroethane

DSC and TGA traces for tetrachloroethane on platinum-impregnated carbon are shown in Figure 15. As the temperature is increased an endothermic (negative) peak is obtained indicating thermal desorption. The weight of adsorbed contaminant decreases essentially to zero during the evolution of the endothermic peak. At higher temperatures a small positive peak is observed in the DSC trace at about 340°C. This peak is not associated with any significant weight loss and could be the result of oxidation of platinum to platinum oxide or it could result from some decomposition of the tetrachloroethane. The final exothermic increase is due to oxidation of the carbon support.

Tetrachloroethane is essentially completely removed by thermal desorption at a temperature of 350°C. No significant oxidation of this contaminant was observed with the catalysts Pt, H_2PtCl_6, $NiCl_2$, CsCl, and NaF. In all cases, however, thermal desorption was complete at a temperature of 350°C.

4. Thiophene

Thiophene is a sulfur containing organic compound and a common catalyst poison that would have to be removed from spacecraft atmospheres by carbon adsorption. The DSC and TGA traces for the removal of thiophene from platinum-impregnated carbon are shown in

TABLE 4

ISOTHERMAL TGA DATA FOR OXIDATION OF DIBK

Temperature, °C	Initial wt of DIBK (mg)	Final wt of DIBK (mg)	Elapsed Time (mins)	Wt. loss (mg)
CATALYTIC CARBON (Pt/Carbon):				
200	7.4	2.2	3.0	5.2
220	6.1	0.1	1.95	6.0
245	6.9	0.1	2	6.8
NON-CATALYTIC CARBON:				
210	10.4	2.8	2.5	7.6

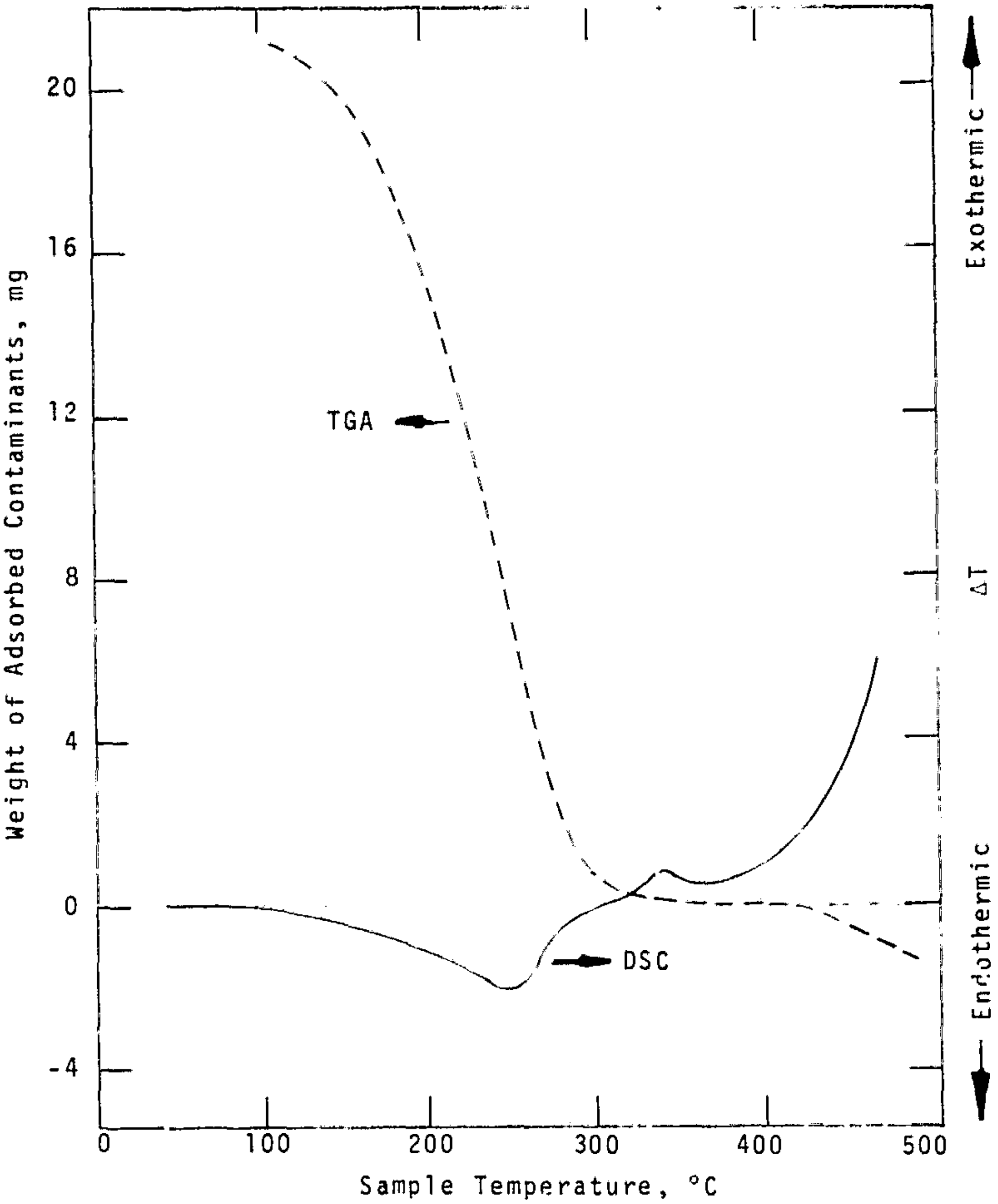
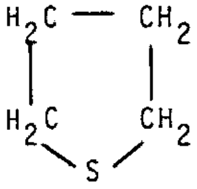


FIGURE 15. DSC AND TGA TRACES FOR REMOVAL OF 1,1,2,2, TETRACHLOROETHANE FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate=15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate= 15°C/min.

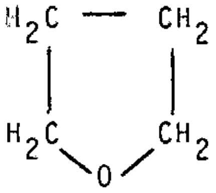
Figure 16. Thermal desorption occurs almost immediately upon heating, producing a negative peak in the DSC trace and a rapid weight loss. Thiophene is completely desorbed at a temperature of 300°C with no evidence of any oxidation. Oxidation of the carbon support begins in the range of 350-400°C.

Attempts to promote thiophene oxidation with a nickel catalyst and a vanadia catalyst were also unsuccessful.

The inability of platinum to catalyze the oxidation of thiophene is directly related to the sulfur atom in the thiophene molecule. This was confirmed in tests with furan which is similar in structure to thiophene except that the sulfur atom is replaced by an oxygen atom:



THIOPHENE



FURAN

Oxidation of furan was observed over a platinum catalyst as shown in Figure 17. Comparing the curves for platinum-impregnated and noncatalytic carbon, it is obvious that the peak at 210°C is due to platinum-catalyzed oxidation.

The desorption of thiophene was observed to poison the platinum catalyst toward oxidation of DIBK. DSC traces before and after adsorption/desorption of thiophene are shown in Figure 18. The A peak, which results from oxidation of DIBK on carbon, is not substantially altered by the exposure to thiophene. However, the B peak, which results from the platinum-catalyzed oxidation, is greatly reduced and shifted to a slightly higher temperature.

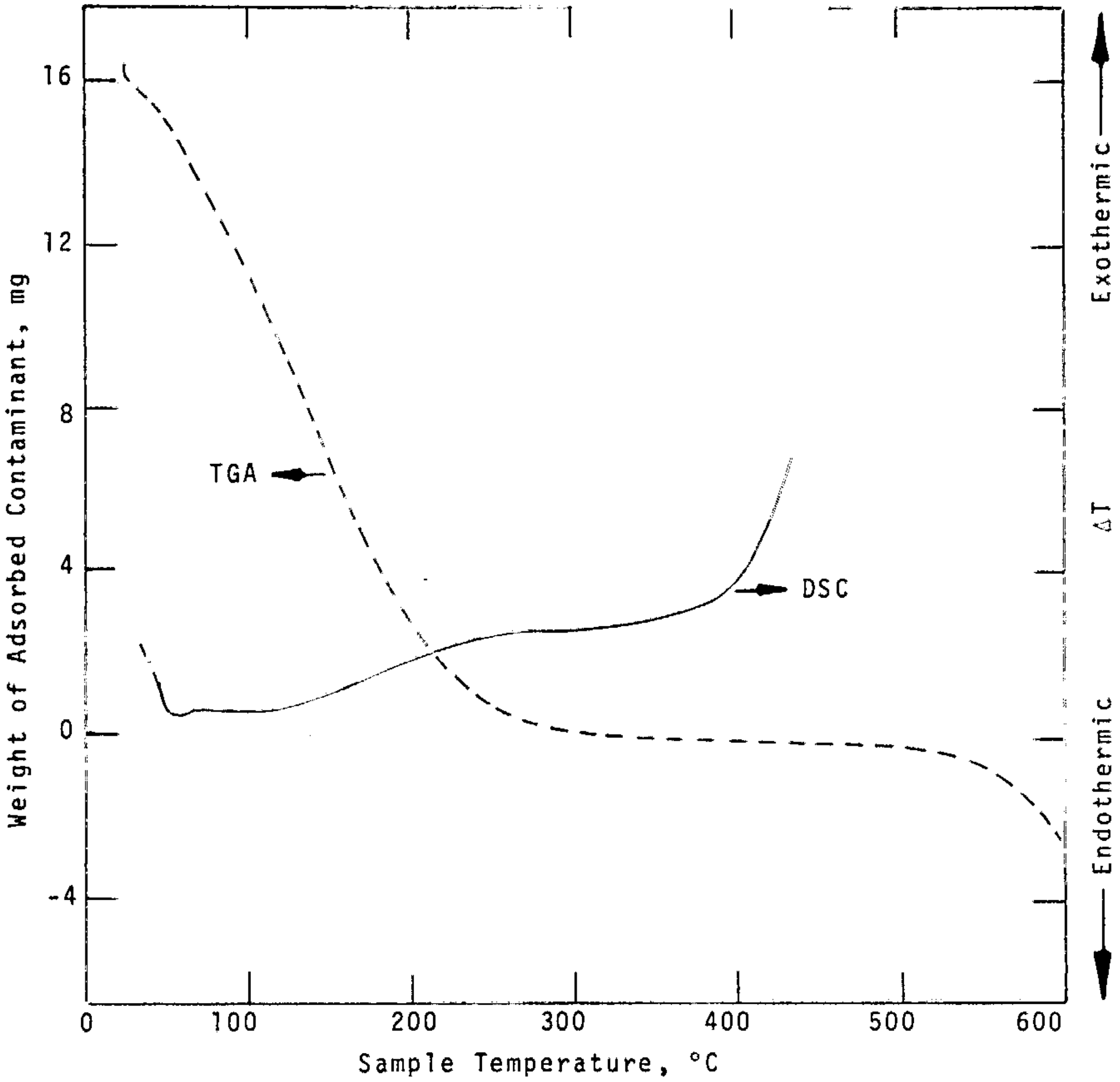


FIGURE 16. DSC AND TGA TRACES FOR REMOVAL OF THIOPHENE FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate= 15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=15°C/min.

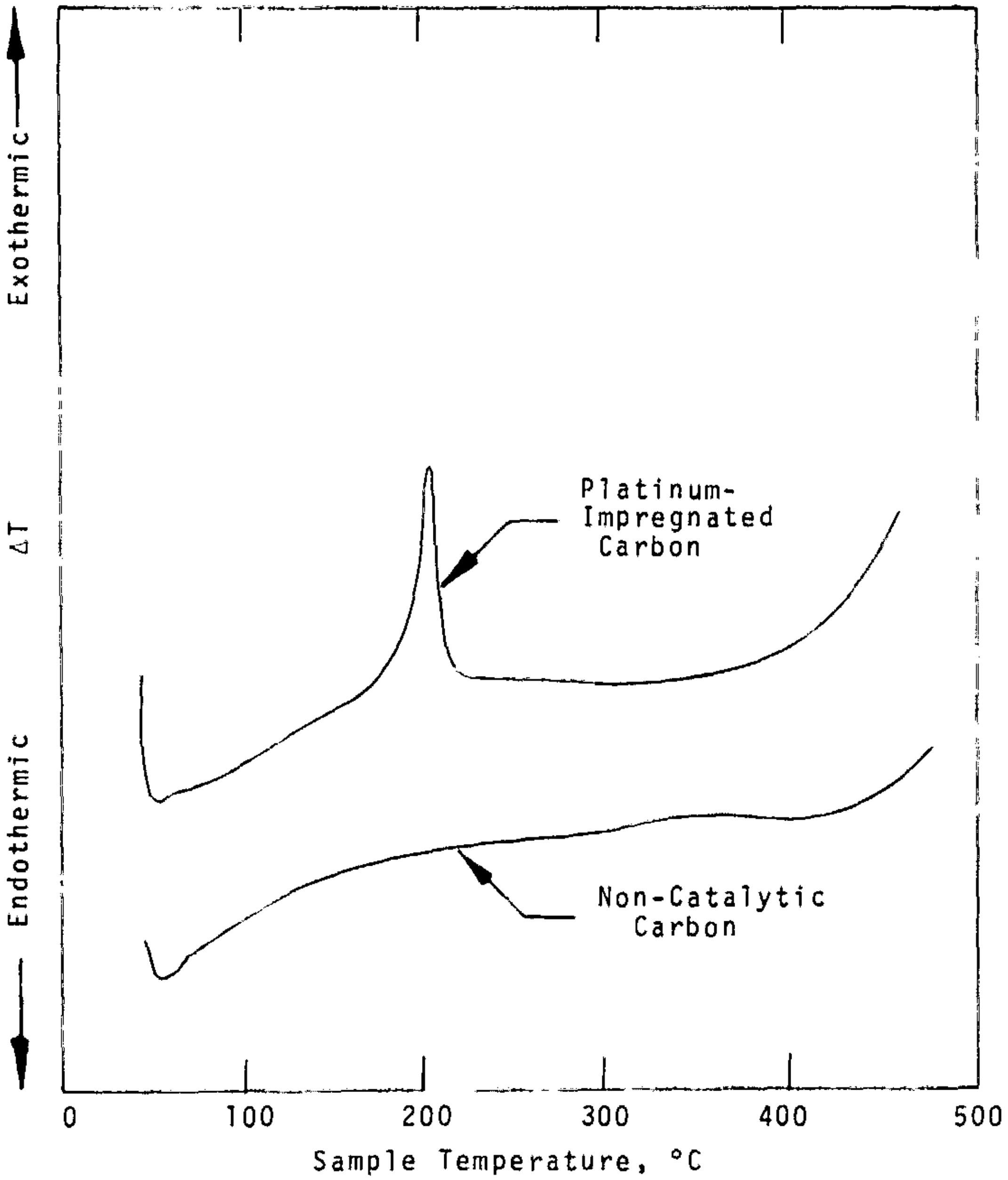


FIGURE 17. DSC TRACES FOR REMOVAL OF FURAN FROM PLATINUM-IMPREGNATED AND NON-CATALYTIC CARBON. Heating Rate=15°C/min; Ordinate Scale=.04°C/in.

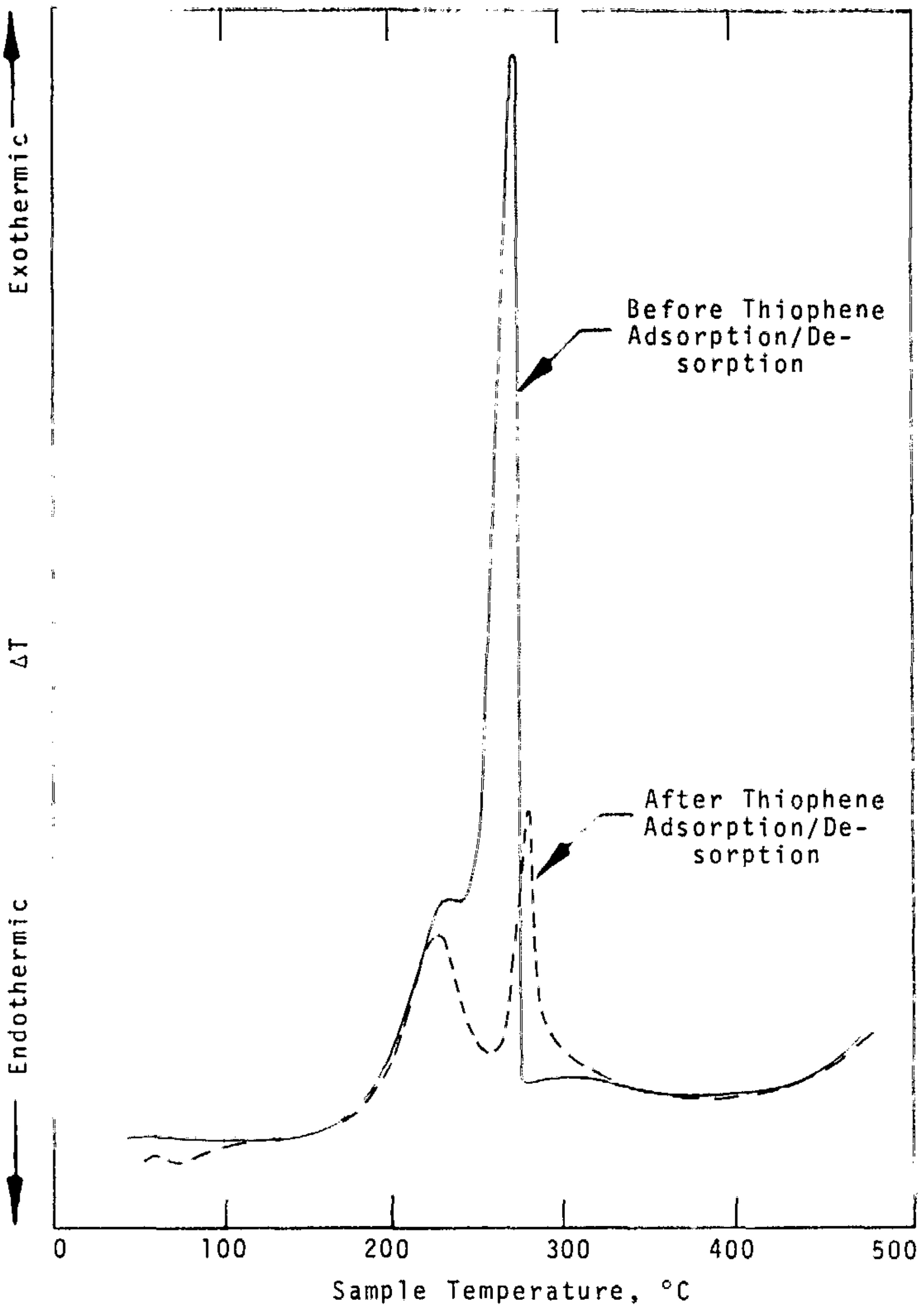


FIGURE 18. DSC TRACES FOR REMOVAL OF DIBK FROM PLATINUM-IMPREGNATED CARBON BEFORE AND AFTER THIOPHENE TREATMENT. Heating Rate=15°C/min; Ordinate Scale=.04°C/in.

5. Acrolein

The DSC and TGA traces for the regeneration of platinum-impregnated carbon contaminated with acrolein are shown in Figure 19. The endothermic peak and rapid weight loss at low temperatures indicate that an appreciable amount of contaminant is removed by thermal desorption. The exothermic peak obtained at 360°C results from oxidation on the platinum catalyst. This was confirmed in tests with other catalysts in which no exothermic peaks were obtained prior to carbon oxidation. A bismuth-molybdenum catalyst showed no activity toward acrolein oxidation even though this catalyst reportedly(5) promoted the oxidation when supported on silica gel or gamma-alumina.

6. Freon 114

The DSC and TGA traces for Freon 114 removal from platinum-impregnated carbon are shown in Figure 20. No substantial amount of oxidation occurred. The slight gradual rise in the DSC trace up to about 220°C may be the tail of an endothermic peak. This would be consistent with the rapid decline in the weight of adsorbate observed at low temperatures. It may be concluded that Freon 114 is completely removed by heating to 250°C, and that most, if not all, of the removal occurs by thermal desorption.

7. Vinyl Chloride

The TGA trace for removal of vinyl chloride from platinum-impregnated carbon is shown in Figure 21. This curve shows that vinyl chloride is completely removed by heating to 175°C. Although the DSC trace is not shown in Figure 21, no catalyst investigated was successful in oxidizing vinyl chloride. It is concluded that vinyl chloride is completely removed by thermal desorption at temperatures below the threshold temperature for oxidation.

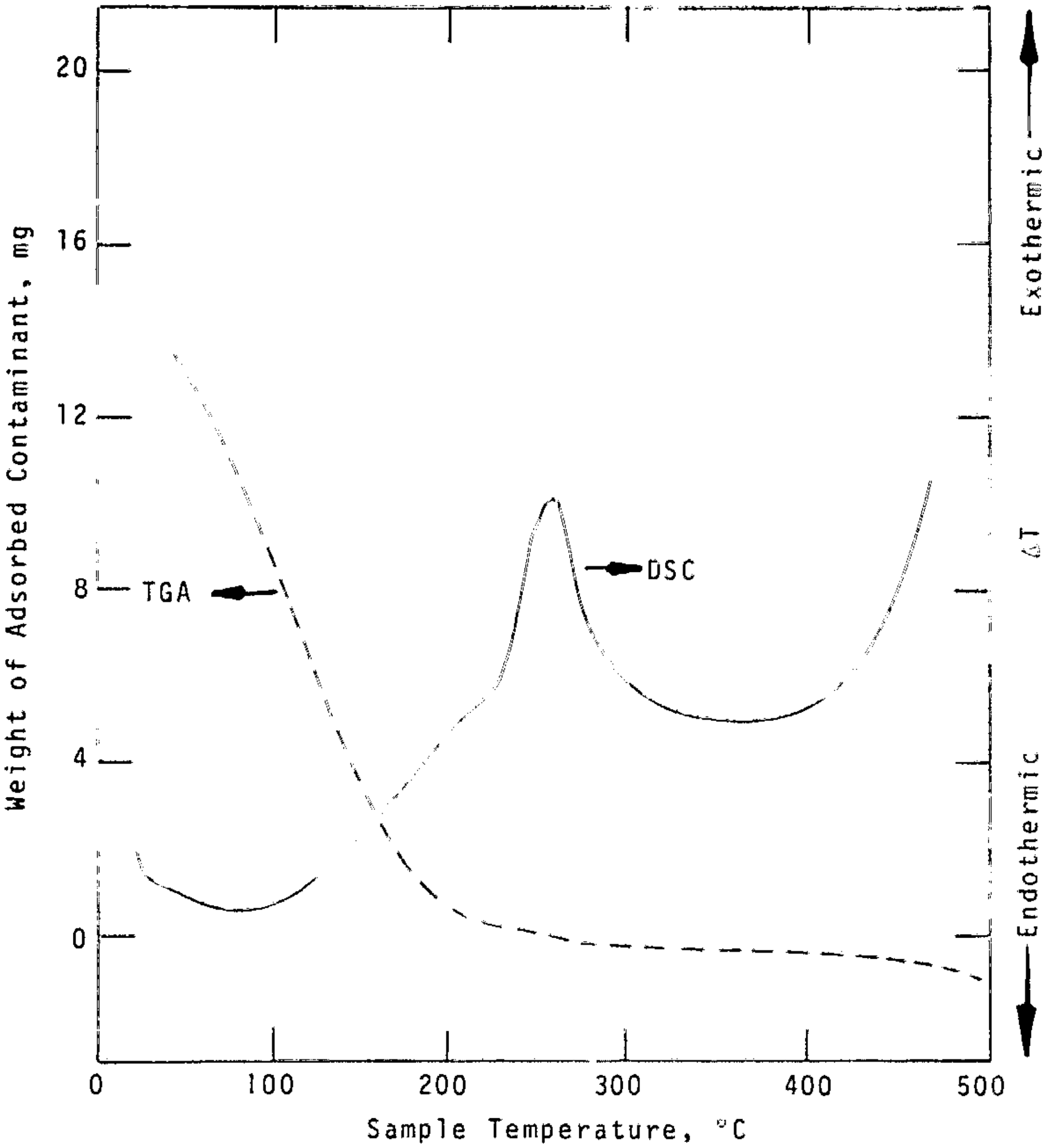


FIGURE 19. DSC AND TGA TRACES FOR REMOVAL OF ACROLEIN FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate=15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=15°C/min.

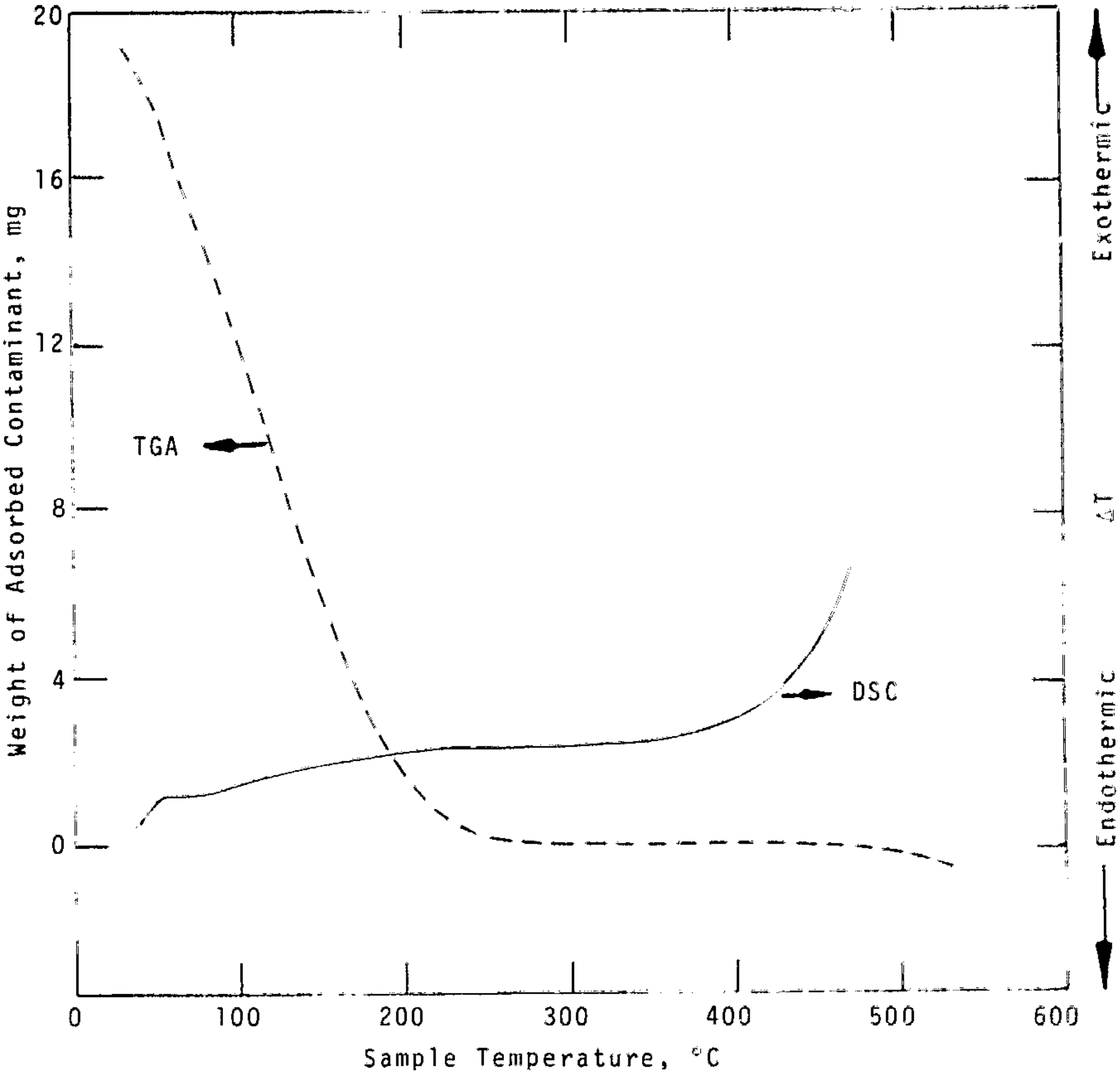


FIGURE 20. DSC AND TGA TRACES FOR REMOVAL OF FREON 114 FROM PLATINUM-IMPREGNATED CARBON. DSC: Heating Rate=15°C/min; Ordinate Scale=.04°C/in. TGA: Heating Rate=20°C/min.

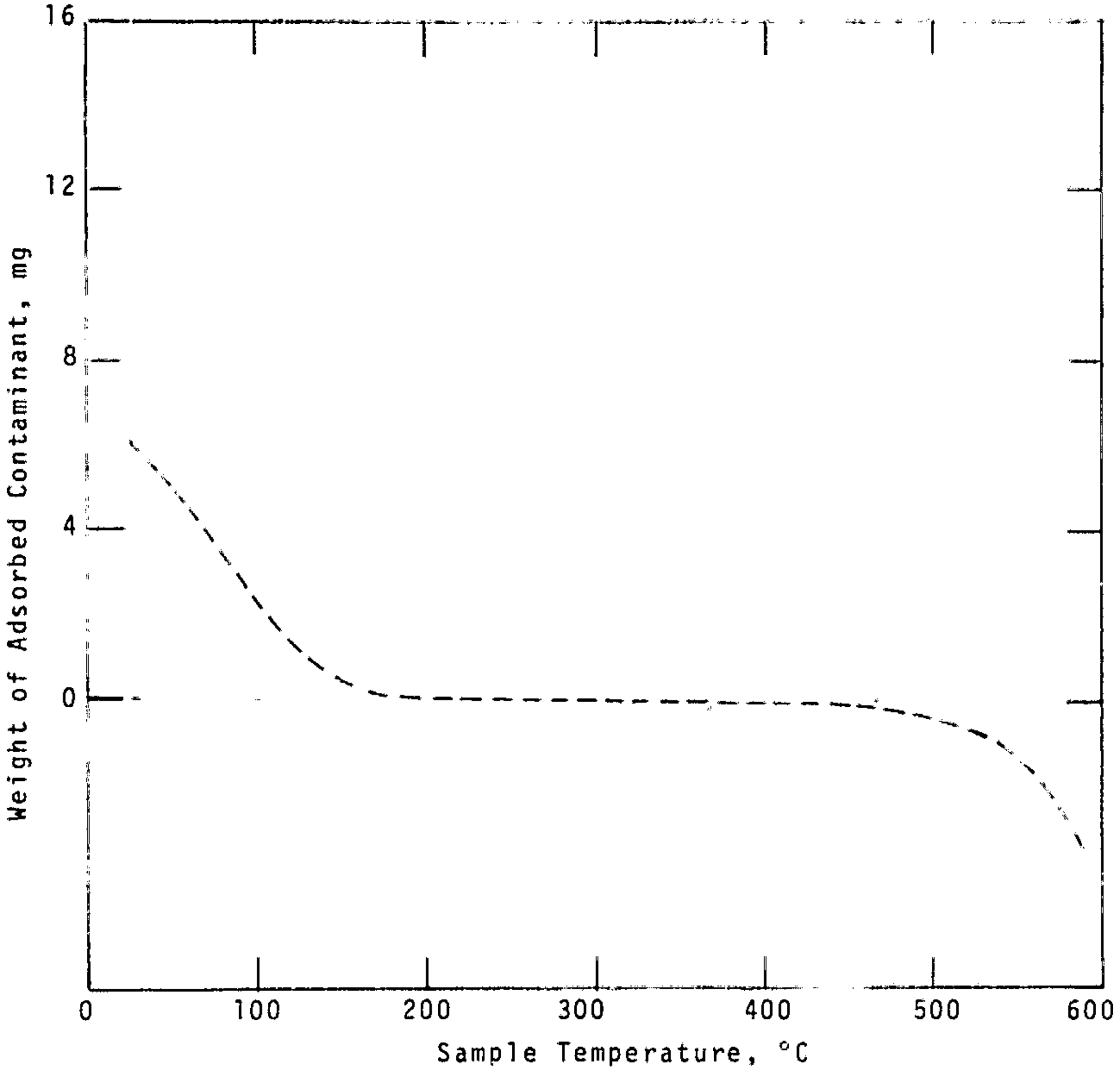


FIGURE 21. TGA TRACE FOR REMOVAL OF VINYL CHLORIDE FROM PLATINUM-IMPREGNATED CARBON. Heating Rate=15°C/min.

C. COLUMN STUDIES

The oxidative regeneration of activated carbon was examined in a small column to ascertain the feasibility of such a regeneration on a scale larger than the DSC and TGA tests. The column tests were designed to simulate the regeneration of an actual column. The objectives of these tests were to determine:

--the mode of column regeneration;

--the qualitative dependence on controllable variables such as temperature, flow rate, and oxygen partial pressure; and

--the loss in adsorptive capacity and carbon weight in repetitive cycling.

Tests were limited to three contaminants: tetrachloroethane, DIBK, and caprylic acid. All tests were conducted with a 0.3 wt.% platinum-impregnated carbon.

1. Tetrahcloroethane

The operating conditions and data for repetitive contamination/regeneration of platinum-impregnated carbon are given in Tables 5 and 6. The weight of contaminant pick-up and loss during adsorption and regeneration are shown in Figure 22 for a total clean-carbon weight of 47.5 grams. The average column temperatures are also shown. For the first two adsorptions the carrier was saturated both with contaminant and water. During adsorption the weight of adsorbed contaminant increased linearly with time until the capacity of the column was reached. The uptake of contaminant and water was dependent on the adsorption temperature. For the first adsorption the column was maintained at room temperature, which was also the temperature at which the carrier gas was saturated. Therefore, capillary condensation probably occurred within the pores of the carbon. This accounts for the unusually large weight uptake during the first adsorption, 77% based on the weight of the clean carbon. During subsequent adsorption cycles the column was held at about 75°C. This temperature should prevent condensation of water in pores greater

TABLE 5

ADSORPTION OF TETRACHLOROETHANE ON ACTIVATED CARBON

Run No.	Avg. Column Temperature(°C)	Flow Rate[(a)] (SCFH)	Time (Hrs)	Weight Increase (grams)[(b)]
1	25	10	1.0	10.2
	25	10	1.5	14.2
	25	10	2.0	17.6
	25	10	2.5	21.7
	25	15	3.0	27.4
	25	10	3.5	31.6
	25	10	4.0	33.1
	25	10	4.5	33.1
2	54	10	1.0	9.7
	60	10	2.0	15.5
	69	10	3.0	23.2
	71	20	4.0	27.0
	68	20	4.5	27.3
3	93	20	0.6	10.3
	70	20	1.17	20.5
	80	20	1.33	24.5
	77	20	1.62	23.8
4	72	30	0.5	12.0
	82	40	1.0	24.1
5	75	20	1.5	23.9
	72	20	2.0	23.9

(a) Flow rate of compressed air carrier gas. For runs 1 and 2 the carrier was saturated with contaminant and water. For runs 3-5, no water was added. 1 SCFH=.0283 m^3/hr.

(b) Weight of clean carbon = 47.5 grams.

TABLE 6

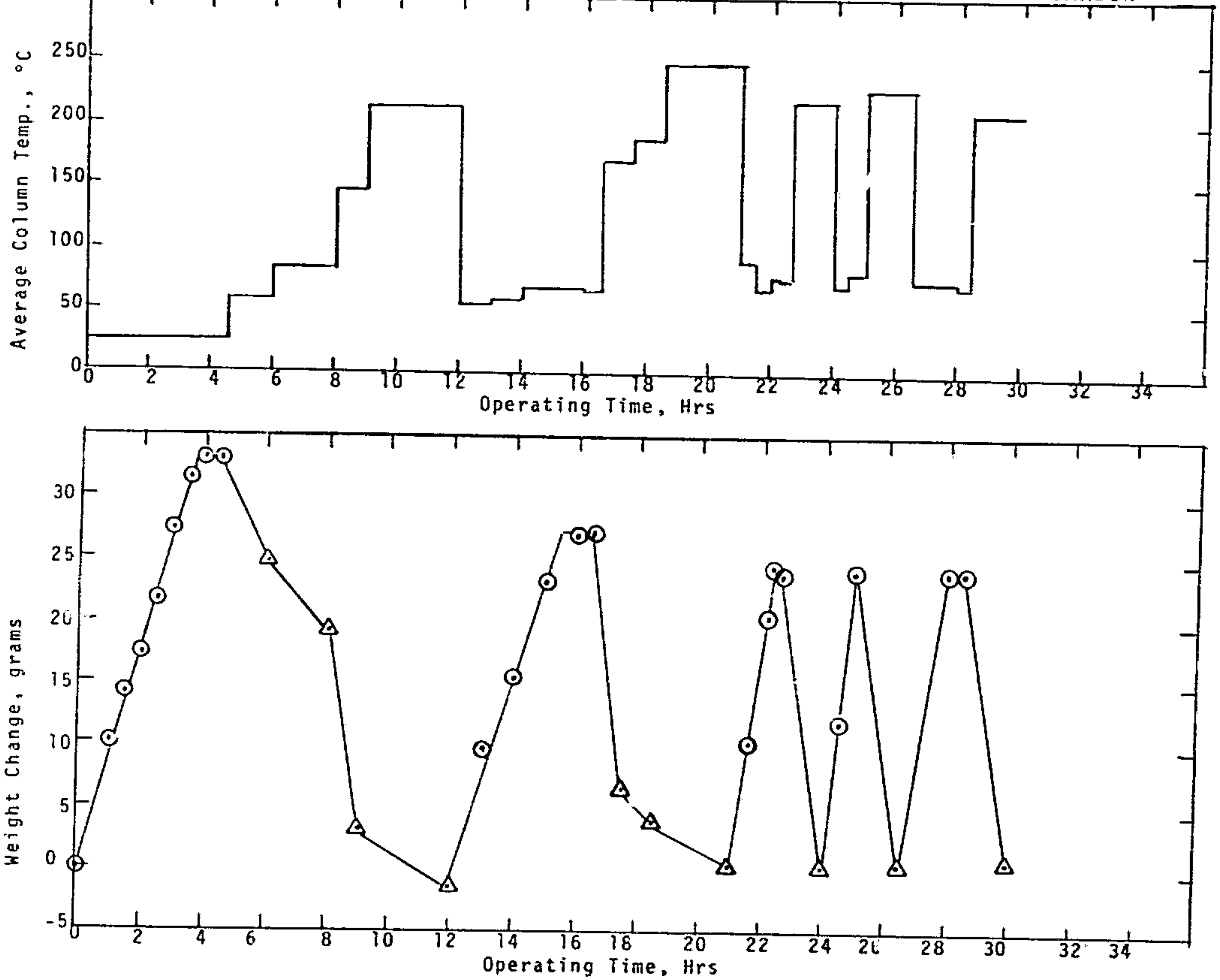
REGENERATION OF PLATINUM-IMPREGNATED CARBON AFTER ADSORPTION OF TETRACHLOROETHANE

Run No.	Avg. Column Temperature (°C)	Flow Rate[a] (SCFH)	Time (Hrs)	Residual Weight (grams)
1	60	10	1.5	24.9
	88	10	3.5	19.5
	147	10	4.5	3.4
	214	10	7.5	-1.4
2	170	10	1.0	6.7
	188	10	2.0	4.0
	103	10	3.5	--
	252	10	4.5	0.5
3	218	10	1.5	0.4
4	230	10	1.5	0.6
5	210	10	1.5	0.8

(a) Flow rate of dry compressed air. 1 SCFH=.0283 m^3/hr.

FIGURE 22.

WEIGHT CHANGE AND AVERAGE COLUMN TEMPERATURES DURING ADSORPTION AND REGENERATION: TETRACHLOROETHANE ON PLATINUM-IMPREGNATED CARBON



than 7 Å (70 nm) when the carrier gas stream is saturated at 25°C. From the pore distribution curve for the carbon, 95% of the pores are greater than 7 Å (70 nm).

The carbon capacity was nearly the same for the four adsorptions at elevated temperatures averaging 51% of the clean-carbon weight.

After the first adsorption the column temperature was increased slowly to determine the best regeneration temperature. The average column temperature was first increased to 60°C. At this temperature the weight of adsorbed material decreased to a value consistent with the saturation uptake in subsequent adsorptions, for which the column was held at about 75°C. By comparing the weight loss at various temperatures it was concluded that regeneration would be substantially complete in one hour at 200°C. This is in agreement with the endothermic peak temperature for tetrachloroethane shown in Figure 15.

After each adsorption-regeneration cycle the measured weight was very close to the clean-carbon weight. Although there appears to be a very slight trend toward lower adsorption capacity (peaks 3, 4, 5), this may result from temperature differences during adsorption. The fact that a constant pick-up and loss of contaminant is observed indicates that the regeneration is essentially complete.

During regeneration, off-gases were trapped in an ice bath and inspected visually. For the first two cycles, the carrier gas was saturated with water during adsorption. The condensate collected during the first two regenerations separated into an organic phase and an aqueous phase of approximately equal volumes. The aqueous phase had a slight blue tinge which probably resulted from corrosion in the copper lines. For a sorption cycles in which the carrier gas was not saturated with water, no separate aqueous phase was collected in the ice-bath trap.

When the column was heated during regeneration a very strong odor of tetrachloroethane was noted in the off-gas. When a column temperature of about 150°C was reached the off-gas became acidic (pH ~ 2), but no CO_2 could be detected in the off-gas by injecting samples into a gas chromatograph.

These results suggest that tetrachloroethane was being thermally desorbed rather than oxidized. This is consistent with the DSC/TGA results of Figure 15. The acidic pH of the off-gas suggests that at least some of the tetrachloroethane was decomposed to HCl, which may explain the small positive peak in Figure 15. The absence of any substantial heat generation and the absence of CO_2 and H_2O in the off-gas indicate the lack of any appreciable oxidation.

It may be concluded that regeneration of carbon contaminated with tetrachloroethane is simple and efficient. The carbon cannot be rendered pyrophoric since a rapid, highly exothermic reaction does not occur. However, the above results indicate that provisions must be made for disposal of off-gases from the regeneration cycle. This will be considered in Section VI.

2. DIBK

Repetitive contamination/regeneration cycles were carried out using DIBK and the same catalyst-impregnated carbon as used in the tetrachloroethane tests. The weight change and average column temperature are shown in Figure 23, and the data and experimental conditions are given in Tables 7 and 8. The uptake of DIBK decreased slightly over the course of the experiments as shown below.

Adsorption Cycle	Total Uptake of DIBK (grams)
1	11.1
2	10.9
3	10.3
4	10.7
5	9.4

FIGURE 23.

WEIGHT CHANGE AND AVERAGE COLUMN TEMPERATURES DURING ADSORPTION AND REGENERATION: DIBK ON PLATINUM-IMPREGNATED CARBON

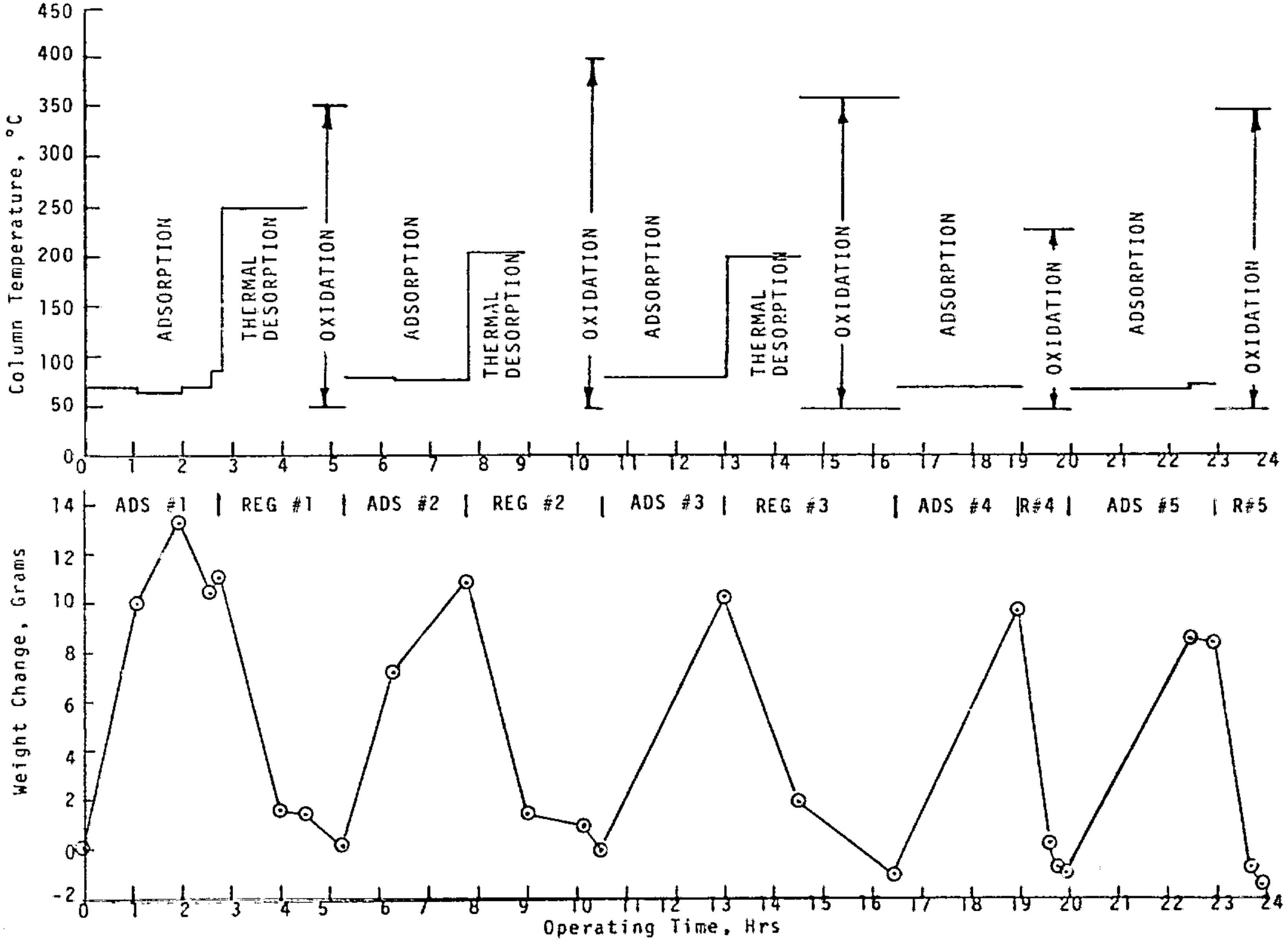


TABLE 7

ADSORPTION OF DIBK ON ACTIVATED CARBON

Run No.	Avg. Column Temp. (°C)	Flow Rate[(a)] SCFH	Time (Hrs)	Weight Increase (grams)[(b)]
1	71	20	1.08	10.0
	66	20	1.93	13.3
	70	20	2.58	10.4
	85	20	2.75	11.1
2	81	20	1.00	7.2
	77	20	2.50	10.9
3	81	20	2.50	10.3
4	72	20	2.50	9.8
5	71	20	2.50	8.7
	74	20	3.00	8.5

(a) Flow rate for compressed air carrier gas bubbled through two impingers of DIBK at 23°C. 1 SCFH=.0283 m^3/hr.

(b) Weight of clean carbon = 47.5 grams.

TABLE 8

REGENERATION OF PLATINUM-IMPREGNATED CARBON AFTER ADSORPTION OF DIBK

Run No.	Column Temp. (°C)	Flow Rate (SCFH)*	Time (Hrs)	Residual Weight (grams)	Remarks
1	250	5 - N_2	1.25	1.6	Thermal Desorption
	250	5 - N_2	1.75	1.5	Thermal Desorption
	50-350	1 - Air$^{(a)}$	2.50	0.2	Oxidation
2	205	5 - N_2	1.25	1.5	Thermal Desorption
	260$^{(b)}$	0.5 - Air	2.42	1.0	No Oxidation Observed
	50-400+	5 - Air$^{(a)}$	2.75	0.0	Oxidation
3	~200	0.2 - Air	1.5	2.0	No Oxidation Observed
	50-200	5 - Air$^{(a)}$	2.25	--	Oxidation
	50-360	5 - Air$^{(a)}$	3.42	-0.9	Oxidation
4	50-230	2 - Air$^{(a)}$	0.67	0.3	Oxidation #1
	50-230	2 - Air$^{(a)}$	0.83	-0.6	Oxidation #2
	50-230	2 - Air$^{(a)}$	1.0	-0.8	Oxidation #3
5	50-350	2 - Air$^{(a)}$	0.75	-0.6	Oxidation #1
	50-350	2 - Air$^{(a)}$	1.0	-1.3	Oxidation #2

(a) Air flow turned on and off intermittently to control temperature in reaction zone. Numerical value indicates maximum flow during "on" period.

(b) Temperature measured at the column inlet after the pre-heater.

* 1 SCFH=.0283 m^3/hr.

The average decrease is 3% per cycle. The average uptake of DIBK at saturation was 0.2 grams per gram of carbon which is considerably below the saturation uptake for tetrachloroethane of 0.5 grams per gram of carbon. For the first adsorption run, the high point of 13.3 grams may be the result of a weighing error or may result from a nonuniform column temperature.

The regeneration of the contaminated carbon occurred in a very interesting pattern. The recirculation loop was operated during regeneration at a flow rate of 20 SCFH (157 s.cc/min). During the first three regeneration cycles, DIBK was thermally desorbed before oxidation was attempted. This was accomplished by admitting only nitrogen to the recirculation loop and heating the column to a temperature of 200-250°C while recirculating nitrogen. Approximately 85% of the DIBK could be thermally desorbed by this procedure. It is possible that the remaining 15% could also have been removed by going to higher temperatures.

Following thermal desorption, the remaining 15% was removed by oxidation. Oxidation was initiated by heating the bottom two inches of the column to about 200°C and slowly admitting air to the recirculation loop. Once the oxidation was started no further heating of the column was required. Oxidation occurred in a narrow band of approximately 2 cm in height. This band moved upward along the length of the column at a rate dependent upon the rate of admission of oxygen. The temperature above and below the reaction zone (typically 50-100°C) was not greatly different from ambient; the temperature within the reaction zone was a strong function of the oxygen flow rate.

The oxygen flow rate was a very important parameter. If the flow rate was too slow the reaction would be quenched; if too fast, the temperature within the reaction zone would become excessive. The control problem was complicated experimentally by the fact that the thermocouples along the column were spaced at two-inch intervals, and the reaction temperature could not be monitored when the reaction zone was between two adjacent thermocouples. It is quite possible that excessive temperatures could have occurred when the reaction zone was in such a position.

The optimum air flow rate was determined to lie between 0.5 and 1 SCFH (3.9 and 7.9 s.cc/min) at a recirculation rate of 20 SCFH (157 s.cc/min). Typically a flow rate of 1-2 SCFH (7.9-15.7 s.cc/min) of air was admitted intermittently as required by the temperature of the reaction zone.

The temperatures shown in Figure 23 give the minimum and maximum observed temperatures during oxidation. Temperatures above those shown could have occurred when the reaction zone was between thermocouples.

In the second regeneration, oxidation was again successful in removing the residual DIBK. Although the maximum regeneration temperature of 400°C was higher than desired it appears that not much carbon was lost.

Some carbon was lost on the third regeneration cycle, however, and this is attributable to a run-away in temperature after the reaction zone had passed the final thermocouple. Too much oxygen was admitted, and the carbon at the top of the column glowed red hot indicating a temperature of about 500°C.

Regenerations #4 and #5 show the effect of repeated oxidation without prior thermal desorption. A single oxidation should be sufficient to remove all of the adsorbed contaminant. However, gases passing through the recirculation loop are saturated with contaminant and, as the reaction zone moves up the column, contaminant from the recirculation gases may adsorb at the bottom of the column. In subsequent oxidations the heat of reaction was observed only in the bottom portions of the column. The oxidation time for the second or third oxidation cycles was much shorter than for the first and recontamination was not a serious problem.

Thermal desorption could not be eliminated by initiating the regeneration cycle under oxidation conditions. Heat from the reaction zone caused considerable desorption of DIBK before reaction could occur. Most of the liquid collected in the recirculation-loop trap was DIBK. In addition DIBK condensed at the outlet of the column and formed a liquid layer on the stainless steel screen at the top of the column. The recirculating gas bubbled through this layer and prevented its running back down into the column. When the reaction zone reached the top of the column the DIBK was vaporized and disappeared.

It may be concluded that the oxidative regeneration of platinum-impregnated carbon contaminated with DIBK is essentially complete. The net carbon loss of 1.3 grams out of 47.5 grams (0.5% per cycle) is probably the result of poor control of conditions during regeneration. It is expected that this loss can be reduced with better control.

3. Caprylic Acid

The regeneration of platinum-impregnated carbon contaminated with caprylic acid proved to be the most difficult to control. Initially the same catalytic carbon and column were used for caprylic acid as for tetrachloroethane and DIBK. In the first two regeneration runs the loss of carbon was 3% and 52% of the initial carbon weight, respectively. These losses were a direct result of poor temperature control. The 3% loss probably resulted from excessive temperatures being reached between thermocouples where the temperature could not be measured. The 52% loss occurred when a thermocouple near the top of the column became loose and made poor contact with the thermocouple wall. The low temperatures observed at that position during regeneration were attributed to contaminant oxidation when actually oxidation of carbon was being observed.

At this point a new column was fabricated which contained 20 thermocouples inserted directly into the carbon column as described in Section III. A new charge of platinum-impregnated carbon was used, and four adsorption/regeneration cycles were conducted. The control of temperature was greatly improved with the new column.

Because of the low vapor pressure of caprylic acid the carrier gas was saturated at 115°C and the column was maintained in the vicinity of 160-190°C. Nitrogen was used as the carrier gas to prevent any oxidation during the adsorption cycle. When the saturation point of the carbon column was reached, break-through was observed visually in the form of a smokey vapor passing out the top of the column. The weight increase at this point is given in Table 9. The variation in uptake of caprylic acid may result from the inability to obtain a uniform column temperature during adsorption. However, no definite trend toward lower adsorptive capacities can be noted over the four cycles.

A considerable portion of the adsorbed caprylic acid could be thermally desorbed by heating the column under a recirculated nitrogen flow. Table 10 gives the amount of remaining contaminant after thermal desorption at the given conditions. As much as 92% of the contaminant was removed by desorption, and it is possible that even more could be removed at higher temperatures.

The oxidation of adsorbed caprylic acid was very similar to the oxidation of DIBK. An oxidation band or reaction zone moved up the length of the column. Heat carried forward from the reaction zone caused thermal desorption to occur before reaction. Caprylic acid condensed on the column walls above the desorption zone, and it also collected in the ice bath trap in the recirculation loop. The weight loss as a function of time and temperature during desorption/oxidation is shown in Table 11. The weight of contaminant remaining at the end of each oxidation cycle was small, averaging 2% of the initial weight for the four cycles. It may be concluded

TABLE 9

ADSORPTION OF CAPRYLIC ACID ON ACTIVATED CARBON*

Run No.	Avg. Column Temp. (°C)	Breakthrough Time (min)	Weight Increase at Breakthrough (grams)**
1	185	<20	13.6
2	168	17	15.9
3	187	<20	16.0
4	183	15	13.5

---

* Nitrogen carrier gas at a flow rate of 20 SCFH (157 s.cc/min) was sparged through a heated (115°C) flask of caprylic acid.

** Weight of clean carbon = 44.4 g.

TABLE 10

THERMAL DESORPTION OF CAPRYLIC ACID FROM ACTIVATED CARBON

Run No.	Avg. Column Temp. (°C)	Cum. Desorption Time (min)	Weight Remaining (% of initial)
2	242	30	31
	323	60	13
3	252	53	23
4	304	60	8

TABLE 11

OXIDATION OF CAPRYLIC ACID ON PLATINUM-IMPREGNATED CARBON

Run No.	Avg. Column Temp. (°C)	Cum. Regeneration Time (min)*	Weight Remaining (% of initial)
1	183	104	20
	161	254	18
	217	344	13
	252	434	4
2	--	98	11
	--	143	5
3	304	90	10
	--	126	0
4	334	96	.7

---

* Includes time for regeneration by thermal desorption.

that no significant loss of carbon weight or capacity occurred over the four cycles

V. MODEL OF THE REGENERATION

A mathematical model of the regeneration process would be very useful in predicting the behavior of the column during regeneration. Such a model could be used to predict the effect of different operating variables, such as flow rate and oxygen partial pressure, on the maximum temperature during regeneration and the regeneration time. It could also be used to determine the limits of stability and instability in the regeneration process.

There are a number of processes that can occur during the regeneration cycle. Oxygen diffuses through the gas film surrounding a carbon particle, diffuses through the pores of the carbon, and adsorbs on the catalyst surface. The contaminant diffuses along the surface of the carbon, is adsorbed at a catalyst site, and reacts with adsorbed oxygen. If reaction is complete CO_2 and H_2O desorb from the catalyst, diffuse through the carbon pores, and into the gas phase. The regeneration can be further complicated by the variety of reactions that can occur. The parent compound may be partially oxidized to a stable intermediate which is then oxidized to the final products in a sequential-reaction scheme.

In general the regeneration process will be limited by the "slow" step in the series of events. When the regeneration is diffusion controlled the mathematical analysis of the regeneration is considerably simplified. When the regeneration is controlled by reaction kinetics, the analysis is more complex. The overall column regeneration is, of course, a direct function of the regeneration of an individual carbon particle. Various models are considered below for the regeneration of a single carbon particle.

A. SHRINKING-CORE MODEL

In the shrinking-core model, reaction begins at the particle exterior and proceeds into particle as a spherical reaction zone receding into a shrinking core. This model has been found to be applicable to a number of practical processes including the regeneration of carbon-deposited catalysts. In the general case this model can be either diffusion limited or reaction-kinetics limited. However, in order for reaction kinetics to be rate limiting the rate of diffusion through the reacted outer shell must be much greater than the rate of diffusion through the unreacted inner core. This could occur, for example, in the noncatalytic oxidation of a carbon particle which would leave behind a porous ash of high effective diffusivity relative to a nonporous interior core of low effective diffusivity. In the regeneration of a contaminated particle of activated carbon, it is unlikely that a large change in effective diffusivity could occur. If it is assumed that there is no change in effective diffusivity in going from the reacted outer shell to the unreacted inner core, then, for this model to be applicable, pore diffusion must be rate limiting. If pore diffusion is not rate limiting (i.e. is fast relative to the reaction kinetics) then there is no means by which reaction can be localized to the surface of an interior core.

For the shrinking-core or pore-diffusion-limited model the rate of regeneration is entirely independent of the reaction kinetics, obviating the need for a surface reaction rate equation. This model has been successfully applied (6) to the regeneration of industrial catalyst particles contaminated by carbon deposits. The fraction, y, of initial contaminant remaining at time t is given by:

$$\frac{(1 - y^{2/3})}{2} - \frac{(1 - y)}{3} = Kt \qquad (1)$$

and,

$$K = nDC_{ox}/R_o^2 C_c \qquad (2)$$

where,

n = Stoichiometric ratio: moles of organic removed per mole of oxygen consumed;

D = effective diffusivity of oxygen in the porous carbon granule (cm^2/sec);

C_{ox} = molar concentration of oxygen in the bulk gas phase ($moles/cm^3$);

R_o = radius of carbon particle (cm)
C_c = initial molar concentration of contaminant (moles/ cm^3 of bed volume).

From equation (1) the time required for any desired degree of burn-off can be calculated. For total burn-off:

$$t_{100} = \frac{0.167}{K} \qquad (3)$$

A value for K can be estimated from the physical properties of the carbon. The assumptions and procedures are given in Appendix A, and the estimated value is:

$$K = 1.85 \times 10^{-5} \text{ sec}^{-1}.$$

By equation (3) the time for regeneration of a single carbon particle is about 2.5 hours.

If the rate of oxygen supply to the column is not a limiting factor, the partial pressure of oxygen will be uniform throughout the column, and all particles will regenerate simultaneously. Thus the total regeneration time will be 2.5 hours.

The experimental observations are not in accord with the shrinking-core model. The DSC traces show that the regeneration of a carbon particle is complete in minutes rather than hours as predicted by the model. In addition, K is proportional to $T^{-1/2}$ so that as the temperature is increased the rate of regeneration should not change substantially. This is in marked contrast to the experimental DSC curves where the rate of reaction (which is proportional to the displacement in the positive Y-axis direction) is very strongly dependent on temperature. The strong temperature dependence of the peaks suggests an exponential temperature dependence characteristic of a reaction limited process. Furthermore, the fact that multiple peaks are often obtained also rules out the shrinking-core model for which a single broad peak should be observed. It may be concluded that the regeneration is not pore-diffusion limited, and the shrinking-core model does not apply.

B. CONTINUOUS-REACTION MODEL

The continuous-reaction model is often proposed as an alternative to the shrinking-core model. The continuous-reaction model assumes that oxygen enters the particle with little resistance and reacts throughout the particle at all times. Thus the concentration of contaminant decreases uniformly throughout the particle. For the regeneration of activated carbon, the continuous-reaction model can apply only if pore diffusion is rapid enough to keep a uniform concentration profile throughout the particle. Therefore, the continuous-reaction model is applicable only if the reaction kinetics are rate limiting.

However, this model is also at odds with the experimental results. A particle cannot regenerate any faster than the pore diffusion calculations indicate. That is, the continuous reaction model could be invoked to explain a regeneration longer than the 2 1/2 hours calculated for pore diffusion but cannot explain the rapid regenerations observed experimentally.

C. EXTERIOR SHELL MODEL

Since neither of the commonly-invoked models are consistent with the experimental facts, it is necessary to devise a new model, based on the experimental data and capable of predicting the column behavior during regeneration. It is evident from the DSC traces that the regeneration is limited by the reaction rate rather than by diffusion. If pore diffusion were rate limiting, the increase in temperature during a DSC run would have no substantial effect on the reaction rate since the diffusion process is only weakly temperature dependent. The fact that sharp peaks are obtained, the fact that peaks are obtained at different temperatures for different catalysts, and the fact that multiple peaks are often obtained all indicate that surface interactions are responsible for the DSC peaks. For the oxidation of diisobutyl ketone over platinum (Figure 13) the oxidation is substantially complete in eight minutes. This is difficult to rationalize in light of the pore diffusion calculations which show that even if the reaction kinetics are "infinitely fast", the minimum regeneration time is 2-3 hours.

These results can be rationalized by the exterior shell model in which most of the reaction occurs at the exterior surface of the carbon particle and in the openings of the pores rather than at the interior of the particle. The contaminant must diffuse to the surface of the particle before it can be oxidized. The previous models tacitly assumed that the contaminant was uniformly distributed throughout the particle and remained uniformly distributed until it was oxidized. Thus oxygen had to diffuse to the interior of the particle. The diffusion of contaminant to the exterior of the particle, as assumed in the present model, can be much more rapid. This is particularly true in the light of the experimental observations that oxidation was always accompanied by thermal desorption. Rapid thermal desorption occurring within a pore could provide a substantial pressure driving force for flow of the contaminant to the exterior of the particle. In addition to flow of contaminant through the voids of the carbon particle, contaminant can diffuse along the surface of the pores. In order for oxidation to occur at a catalyst site, the contaminant must, in any case, diffuse along the surface to that site. Therefore, at oxidation temperatures, surface diffusion is a reasonable mechanism for transport from the interior to the exterior of the particle. Since it has been shown (7,8,9) that a mobile adsorbed molecule can move across a surface with the velocity of a two dimensional ideal gas, the surface diffusion rate can be rapid. In addition, for DIBK for example, only one molecule of contaminant must diffuse to the exterior, as opposed to 13 molecules of oxygen that must diffuse to the interior if reaction occurred within the pores. It is likely that the contaminant moves to the exterior of the particle by a combination of flow through the pore voids and adsorption-surface diffusion-desorption.

The exterior shell model can be limited by the rate of mass transfer of oxygen from the bulk gas stream, by the rate of chemical reaction at the surface, or by the rate of diffusion of contaminant from the interior to the exterior of the particle. Again the strong temperature dependence of the regeneration and the multiple DSC peaks rule out the possibility of mass transfer limitations from the bulk gas stream to the particle surface under the experimental conditions. The surface diffusion and gas phase transport of the contaminant from the interior to the exterior of the particle will involve an activation energy and will be strongly temperature dependent. For a non-mobile adsorbed contaminant molecule there is an activation energy that must be overcome before the molecule can diffuse, and, of course, for desorption to occur the activation energy for desorption must be provided. Therefore, the strong temperature dependence of the regeneration is consistent with a rate limitation by contaminant transport. However, if contaminant transport were rate limiting, the rate of regeneration should be independent of oxygen partial pressure. This contradicts experimental observation: the rate of regeneration was very dependent on the rate of oxygen supply and thereby on oxygen partial pressure. Furthermore, thermal desorption of contaminant was observed to occur in column tests prior to oxidation indicating that the rate of transport of contaminant from the interior to the exterior of the particle was greater than the rate of oxidation of contaminant at the surface. It is concluded that under the experimental conditions investigated, the regeneration followed the exterior shell model and was limited by the rate of surface reaction.

D. DEVELOPMENT OF MATHEMATICAL MODEL

A rigorous mathematical treatment of the regeneration process is quite complicated, and it is expedient, at the outset, to make a number of simplifying assumptions:

1) The column is operated adiabatically, and therefore there are no radial temperature gradients.
2) The heat transfer in the direction of fluid flow occurs only by convection.
3) The gas velocity across the column diameter is uniform, and the change in molar flow rate of the gas phase by chemical reaction is negligible.
4) The temperature gradient from the surface to the interior of the particle is negligible allowing an average particle temperature to be used.
5) The rate of reaction follows an expression of the form $r_c = k\ e^{-E_r/RT_s}\ y^n C^m$ (see Table 12 for nomenclature).
6) The rate of desorption is not limited by pore diffusion and is of the form $r_d = k_d e^{-E_d/RT_s}\ C$, i.e. desorption is first order and readsorption is negligible.

The mathematical model is based on the following idealized description of the regeneration process. A recirculated nitrogen stream is used as a carrier gas during regeneration. The stream is heated to a temperature of T_o before it is admitted to the column, and, upon leaving the column, it is cooled to a temperature sufficient to remove any desorbed contaminant. With no oxygen present, nitrogen is circulated through the column, which eventually reaches the temperature T_o. Thermal desorption is allowed to proceed until, at T_o, the rate of desorption is negligible. The concentration of remaining contaminant is C_o. At this point (time zero) the mole fraction of oxygen in the feed to the column is increased from zero the y_o. Provided T_o is chosen so that reaction will occur when oxygen is present, reaction will be initiated at the bottom of the column producing a large release of heat. Essentially all of the oxygen is consumed in the reaction zone at the bottom of the column and no reaction occurs above the reaction zone. As contaminant is consumed at the bottom of the column, the reaction zone moves upward at a rate dependent upon the rate of oxygen supply. Below the reaction zone heat is transferred from the regenerated carbon to the gas phase. Above the reaction zone heat is transferred from the gas phase to the contaminated carbon particles increasing their temperature above T_0 and causing additional thermal desorption. The desorbed contaminant is swept away by the regeneration carrier gas. Thus a thermal desorption zone moves up the bed ahead of the reaction zone.

Material and energy balances were made on a differential cross-sectional slice of the column of height Δx. The differential equations, boundary conditions, and nomenclature are given in Table 12. There are two independent variables: distance up the column, x; and time, t. There are four dependent variables: oxygen mole fraction, y; contaminant concentration, C; gas temperature, T_g; and solid temperature, T_s. Table 12 gives the four simultaneous partial differential equations that must be solved for the four dependent variables. These equations are first order but are coupled and highly nonlinear requiring numerical techniques for solution.

The particular mode of regeneration described above was chosen for its simple boundary conditions. A more practical method of initiating the regeneration would lead to more complicated boundary conditions.

E. DETERMINATION OF RATE EXPRESSION

The most difficult task in developing a mathematical model to simulate the regeneration is obtaining accurate rate data for the reaction and desorption of contaminant. The problem is further complicated by the occurrence of multiple peaks in the DSC trace each of which must be represented by a different kinetic expression. In addition, the weight loss during oxidation probably results from a combination of oxidation and thermal desorption.

Nevertheless an attempt was made to experimentally determine the order of reaction with respect to adsorbed contaminant (exponent m

TABLE 12

MASS AND ENERGY BALANCE EQUATIONS FOR A DIFFERENTIAL CROSS-SECTIONAL VOLUME ELEMENT OF COLUMN DURING REGENERATION

(1) Oxygen Balance

Net input by flow - Depletion by reaction = Accumulation

$$-G \frac{\partial y}{\partial x} - s\ k\ e^{-E_r/RT_s}\ y^n\ C^m = \frac{\epsilon P}{R}\ \frac{\partial}{\partial t}\left(\frac{y}{T_g}\right)$$

Boundary Condition: $y = y_0$ at $x = 0$ all t

$y = 0$ at $t = 0$ all x

(2) Contaminant Balance

Depletion by reaction + Depletion by desorption = Accumulation

$$k e^{-E_r/RT_s}\ y^n\ C^m + k_d e^{-E_d/RT_s}\ C = \frac{\rho_b}{M_c}\ \frac{\partial C}{\partial t}$$

Boundary Condition: $C = C_0$ at $t = 0$ all x

(3) Overall Energy Balance

Net input by flow + Production by reaction - Depletion by desorption = Accumulation

$$-GM_g c_g \frac{\partial T_g}{\partial x} + k e^{-E_r/RT_s}\ y^n C^m\ M_c Q_r - k_d e^{-E_d/RT_s}\ C M_c Q_a$$

$$= (1-\epsilon)\ \rho_c c_s\ \frac{\partial T_s}{\partial t} + \cancelto{0}{\frac{\epsilon P c_g}{R}\ \frac{\partial}{\partial t}\left(\frac{T_g}{T_g}\right)}$$

Boundary Condition: $T_g = T_0$ at $x = 0$ all t

$T_s = T_0$ at $t = 0$ all x

(4) Gas Phase Energy Balance

Net input by flow + Heat transfer from solid = Accumulation

$$-GM_g c_g \frac{\partial T_g}{\partial x} + h\ a\ (T_s - T_g) = \frac{\epsilon P c_g}{R}\ \frac{\partial}{\partial t}\ \left(\frac{T_g}{T_g}\right) = 0$$

TABLE 12
(continued)

Boundary Condition: $T_g = T_0$ at $x = 0$ all t

Nomenclature:

a = surface area of carbon per unit volume of bed (ft^2/ft^3)
C = concentration of contaminant (#/# carbon)
C_0 = concentration of contaminant prior to oxidation (#/# carbon)
c_g = heat capacity (at constant pressure) of gas phase (Btu/#°F)
c_s = heat capacity of carbon (Btu/#°F)
E_d = activation energy of desorption (Btu/#-mole)
E_r = activation energy of reaction (Btu/#-mole)
G = molar velocity of gas phase (# moles/ft^2-hr)
h = heat transfer coefficient from carbon to gas (Btu/hr-ft^2°F)
k = pre-exponential factor for reaction (consistent units to give reaction rate in # moles/hr-ft^3 of bed)
k_d = pre-exponential factor for desorption (consistent units to give desorption rate in # moles/hr-ft^3 of bed)
M_c = molecular weight of contaminant (#/# mole)
M_g = molecular weight of gas phase (#/# mole)
m = order of reaction with respect to contaminant
n = order of reaction with respect to oxygen
P = total pressure during regeneration (atm)
Q_r = heat of reaction (Btu/# contaminant)
Q_a = heat of adsorption (Btu/# contaminant)
R = gas constant (appropriate units)
r_c = rate of reaction (# moles contaminant/hr-ft^3 bed)
r_d = rate of desorption (# moles contaminant/hr-ft^3 bed)
s = stoichiometric ratio (moles O_2 consumed/mole contaminant)
T_g = gas phase temperature (°F)
T_s = solid phase temperature (°F)
T_0 gas inlet temperature = initial bed temperature (°F)
t = time (hr)
x = distance along column; measured from bottom (ft)

TABLE 12
(continued)

Nomenclature (continued):

y = mole fraction of oxygen in gas phase
y_o = mole fraction oxygen at inlet to column

ε = void fraction of bed
ρ_b = bed density (# carbon/ft^3 bed)
ρ_c = particle density (# carbon/ft^3)

in the rate expression) for the oxidation of DIBK. The contaminated carbon was rapidly heated under a nitrogen atmosphere to a temperature at which only the desired reaction occurred. Oxygen was then admitted and the weight loss as a function of time was measured. The exponent m was to be determined from a plot of log (-dc/dt) vs. log C. Isothermal TGA traces were obtained at 200°C, 220°C, and 245°C for platinum-impregnated carbon. In all cases the plot of log (-dc/dt) vs. log C was highly nonlinear indicating that the gross weight loss does not follow the simple kinetic expression assumed above. These preliminary results indicate that it may be impossible, within a reasonable level of effort, to unravel the complex and interrelated kinetic expressions governing desorption and reaction. It may be necessary to resort to assuming a simple kinetic expression (such as first order in oxygen and contaminant concentrations) in order to develop at least a qualitative model of the regeneration.

VI. DEVELOPMENT OF CONCEPTS FOR SPACECRAFT SYSTEMS

The method of carbon regeneration considered in the Lockheed study was thermal desorption under vacuum. There are three potential limitations to this mode of regeneration:

1) Under the desorption conditions investigated by Lockheed and investigated in this study, desorption of certain contaminants was incomplete. It is not known at this point whether or not higher regeneration temperatures and longer regeneration times could reduce the adsorbed contaminants to an acceptably low level. Furthermore it is not known to what degree the non-desorbed residue is cumulative.
2) Since thermal desorption is an endothermic process the entire heat of desorption must be supplied from external sources in addition to the sensible heat required to raise the bed temperature to the desired level.
3) If discharge of contaminants to space is banned, alternatives or modifications of vacuum desorption must be considered. The modifications may be as simple as installing a cryogenic trap on the exhaust line to space if the ban does not cover elemental gases such as oxygen, nitrogen, hydrogen, etc. If the ban is total, a nitrogen recirculation loop should be considered with removal and storage of contaminants by cold trapping.

The primary advantage of oxidative regeneration is that contaminants remaining after thermal desorption, or carbonaceous deposits resulting from decomposition of contaminants can be removed. This is considered to be a very significant advantage. There are many design, engineering, and control problems associated with *in-situ* regeneration by oxidation, and these have not been fully addressed in this "feasibility" phase of the program. Nevertheless, it is worthwhile to consider in general terms the form that such a regenerative system might take. A generalized flow schematic for spacecraft application is shown in Figure 24. The feed from the cabin is passed through a lithium hydroxide bed to remove acid gases which could poison a catalyst-impregnated carbon. The air is then passed through one of two carbon columns in parallel, column #1 in this case.

While column #1 is adsorbing, column #2 is being regenerated. The exact control procedure used in oxidative regeneration is yet to be determined, but in general an air stream is recirculated by a pump through the regenerating column. Oxidation is initiated by appropriately heating the column to a temperature at which oxidation will occur and maintained by admitting a small controlled flow of air through a by-pass between the two columns. Desorbed contaminant and oxidation products are removed and stored in a cold trap. There will be a gradual increase in the number of moles of gas in the recirculation loop because of nitrogen admitted with the oxidation air and oxidation products, CO and CO_2, which may pass through the trap, depending on its temperature and trapping efficiency. Excess gas is removed from the recirculation loop through the back-pressure regulator (BPR) which maintains a constant pressure at the suction of the recirculation pump. This excess gas may contain acid gases and is therefore passed through the lithium hydroxide sorber before readmission to the first carbon column and back to the cabin.

To this point the relative energy requirements for desorptive and oxidative regeneration have not been considered. Approximate calculations (presented in Appendix B) compare the energy requirements for vacuum thermal desorption with contaminant trapping, air-sweep desorption with contaminant trapping, and oxidation with contaminant trapping. The calculations indicate that there is very little difference (less than one pound penalty) between the various modes of regeneration. This is primarily the result of the low production rate of 17 grams of contaminant per day (3) that must be removed by the activated carbon system.

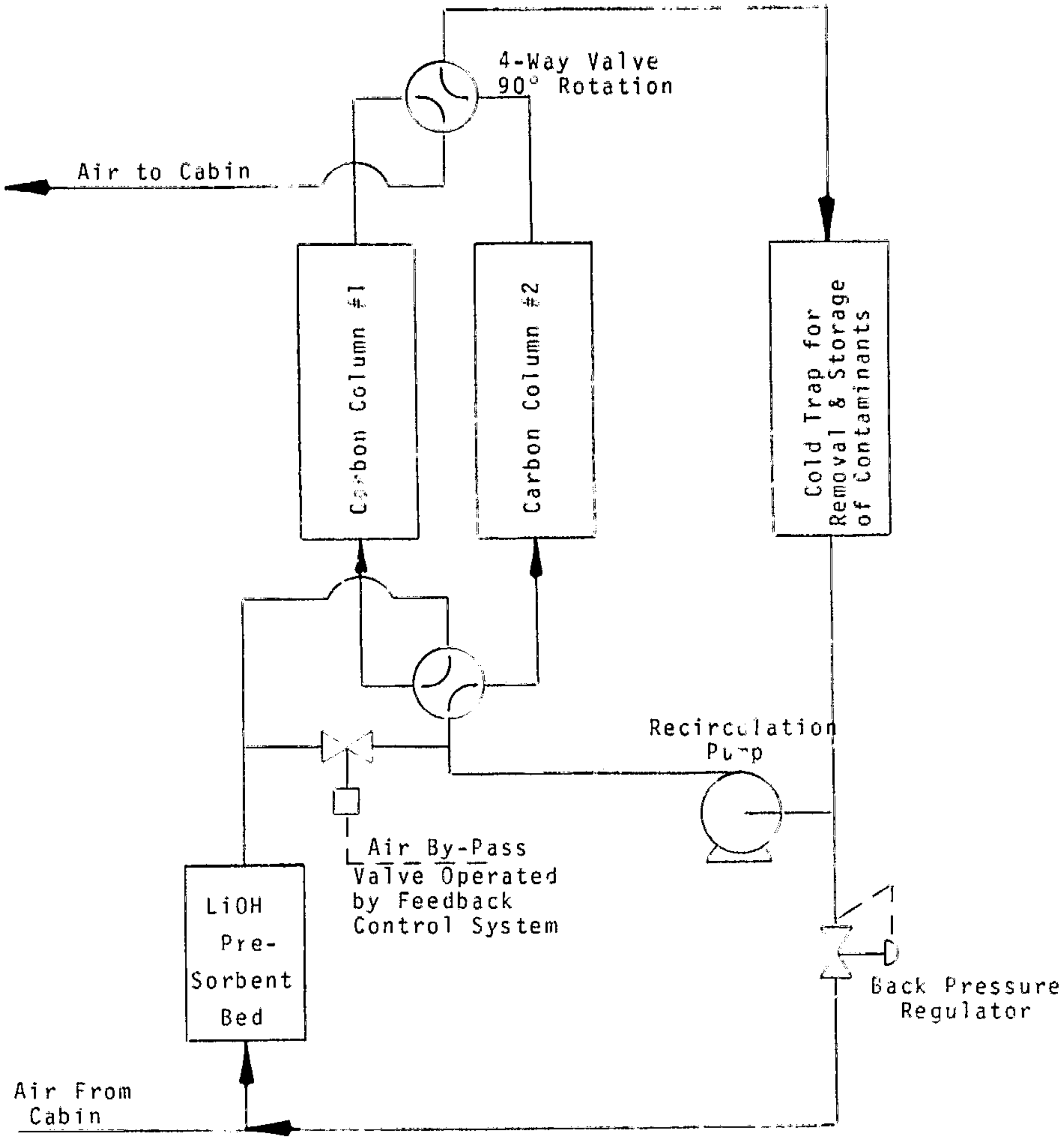


FIGURE 24. GENERALIZED FLOW SCHEMATIC FOR REGENERABLE CARBON SYSTEM USING CATALYTIC OXIDATION

VII. RECOMMENDATIONS FOR FUTURE WORK

The very low losses in adsorptive capacity incurred during oxidative regeneration are very encouraging and suggest that additional development of this mode of regeneration would be worthwhile. A program on two levels is recommended: continued adsorbent research, and system development.

The research effort should be conducted at CUNY using DSC and TGA to study single carbon particles. Additional exploratory work should be conducted looking at different catalyst concentrations and impregnation procedures. The selected catalytic carbon should be thoroughly compared to non-catalytic carbon in repetitive contamination/oxidation cycles. The degree to which the residue is cumulative following low temperature oxidation should be determined for both the catalytic and non-catalytic carbons. Thermal desorption should be extended to higher temperatures and longer times to see if adsorbed contaminants can be reduced to an acceptable level by this method of regeneration. Other contaminants encountered in spacecraft atmospheres should be examined, and tests should be made with all classes of compounds encountered.

The development work should be conducted at Abcor and should be applicable to oxidative regeneration with or without the presence of a catalyst. Various methods of control should be attempted and the optimum method specified. Sufficient data should be generated to conduct a trade-off study between oxidative and desorptive regeneration. Details of the system design should be specified, and a bench-scale model of the system should be constructed and operated to demonstrate the feasibility of automatic operation.

The details of our recommendations for future work will be submitted shortly in a continuation proposal.

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APPENDIX A

Estimation of K

The effective diffusivity is the series sum of the effective diffusivities for bulk diffusion and Knudsen diffusion:

$$\frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}} \qquad \text{(A-1)}$$

$$D_{12,eff} = \frac{D_{12}\theta}{\tau}$$

where, D_{12} = diffusion coefficient (cm^2/sec)
θ = fraction of voids in carbon granule = 0.40
τ = tortuosity factor.

For the diffusion of oxygen in nitrogen, $D_{12} = 0.18$ cm^2/sec, and

$$D_{12,eff} = \frac{(0.18)(0.40)}{\tau} = \frac{.072}{\tau} .$$

For Knudsen diffusion,

$$D_{K,eff} = \frac{19,400\ \theta^2}{\tau\ Sg\ \rho_p} \sqrt{\frac{T}{M}}$$

where, Sg = total surface area = 1.1×10^7 cm^2/g
ρ_p = particle density = 0.8 g/cc
T = temperature (°K) = 473°K
M = molecular weight = 32

$$D_{K,eff} = \frac{1.356 \times 10^{-3}}{\tau}$$

Substituting in equation (A-1) gives:

$$D_{eff} = 1.331 \times 10^{-3} \text{ cm}^2/\text{sec}.$$

For the oxidation of diisobutyl ketone

$$C_9H_{18}O + 13O_2 \rightleftarrows 9CO_2 + 9H_2O.$$

The stoichiometric ratio of organic to oxygen is:

$$n = 1/13 = .077.$$

At 200°C and 1 atm the molar concentration of oxygen in air is:

$$C_{ox} = \frac{0.21}{(22{,}414)(\frac{473}{273})} = 5.4 \times 10^{-6} \text{ g-mole/cc}.$$

The average particle diameter for 6 x 16 carbon is 0.24 cm. Therefore:

$$R_o = 0.12 \text{ cm}.$$

Assuming a loading of 0.3g contaminant/g carbon and a bed density of 0.5g carbon/cc bed, the molar concentration of diisobutyl ketone is:

$$C_c = \frac{(0.30)(0.5)}{(142)} = 1.056 \times 10^{-3} \text{ g-moles/cc}.$$

Then,

$$K = \frac{nD\,C_{ox}}{R_o^2\,C_c} = \frac{3.7 \times 10^{-5}}{\tau} \text{ sec}^{-1}.$$

The tortuosity factor can vary over an order of magnitude but a typical value is 2. Thus,

$$K = 1.85 \times 10^{-5} \text{ sec}^{-1}.$$

APPENDIX B

COMPARISON OF ENERGY REQUIREMENTS FOR VARIOUS MODES OF REGENERATION

It is of some interest to determine the relative merits of various modes of regeneration in relation to heating and cooling penalties. This can be done in a very approximate manner by assuming no heat conservation and approximate weight penalties of 300 lb/kw for heating and .01 lb/Btu/hr for cooling (10). Three regeneration modes are compared below:

1) Vacuum desorption with contaminant trapping;
2) Air-sweep desorption with contaminant trapping; and
3) Oxidative regeneration with contaminant trapping.

1. Vacuum Desorption Vs. Air-sweep Desorption

For vacuum desorption it is assumed that the carbon column is evacuated to space and there is no weight penalty associated with evacuation. Vacuum desorption and air-sweep desorption will require the same amount of energy input for heating the carbon and column to the desorption temperature and for providing the heat of adsorption required to remove the contaminant. The same amount of cooling will be required to trap out the contaminant. The difference in energy requirements for the two operational modes is the amount of heat required to raise the air stream to the desorption temperature and the amount of cooling required to cool it to the trap temperature plus the pumping energy required to recirculate the air stream. Of course the energy requirements can be minimized by operating at as low an air flow rate as possible. It is quite possible that an effective air sweep can be achieved at low flow rates. It is assumed for the purposes of calculation that an effective air sweep can be achieved with a flow rate of 100 moles of air for each mole of contaminant removed. The total production rate for contaminants removed by carbon adsorption (3) is 17 grams per day. Assuming daily regeneration and an average contaminant molecular weight of 100, the gross amount of air required for sweeping is 17 moles. The net amount of air is much less since the air is recirculated. At an average heat capacity of 7 cal/mole°C, the air heating and cooling requirement for desorption at 300°C and trapping at -80°C is 4.5×10^4 cal or 0.052 kw-hr. Assuming a heating penalty of 300 lb/kw and a 24 hour regeneration period the weight penalty for heating is only 0.65 lbs (.29 kg). Assuming a cooling penalty of 0.01 lb/Btu/hr the weight penalty for cooling is only .07 lbs (.0317 kg).

The pumping power can be calculated from the equation:

$$P = 1.236 \times 10^{-4} \frac{T_a q_o}{n\eta} \left[\left(\frac{p_b}{p_a} \right)^n - 1 \right]$$

where:

P = brake horsepower

T_a = absolute temperature at suction (°K)

q_o = volume of gas compressed (SCFM)

η = mechanical efficiency (assume 50%)

n = $(K-1)/K$

K = ratio of specific heats C_p/C_v (1.4 for air)

p_a = absolute pressure at suction

p_b = absolute pressure at discharge.

Assuming a 5 psi pressure drop through the column and trap,

$$P = (1.236 \times 10^{-4}) \frac{(347)(9.3 \times 10^{-3})}{(0.286)(.50)} \left| \left(\frac{20}{15} \right)^{.286} - 1 \right|$$

$$= 2.4 \times 10^{-4} \text{ hp}$$

$$= 1.79 \times 10^{-4} \text{ kw.}$$

Assuming the same weight penalty as for heating the penalty for pumping energy is only .05 lbs (.023 kg).

It may be concluded that the weight penalties for air-sweep desorption as opposed to vacuum desorption are not significant.

2. Air-sweep Desorption Vs. Oxidation

A comparison of the energy requirements for thermal desorption and oxidation will depend on the procedure used for oxidation. While it is, in principle, possible to initiate the oxidation by heating a single carbon particle and sustain the oxidation with no external heat input, it may be difficult to control the oxidation by this procedure. An alternative procedure, which is less favorable toward oxidation in terms of energy requirements, is to externally heat the column to oxidation temperature, to heat the incoming oxidation air to the same temperature and to externally cool the column to remove the heat of reaction.

If the same recirculation rate is used for oxidation as for thermal desorption the heating and cooling requirements will be approximately the same for the two modes of regeneration except for the heat of reaction which must be removed. If it is assumed that 10% of the daily contaminant production (17 grams) is removed from the carbon by oxidation (the other 90% is removed by thermal desorption), the total heat of reaction (assuming a typical value of 20,000 Btu/lb = 11.1 kcal/g = 46.4 kJ/g) is 19 kcal (79.5 kJ). Over a 24-hour period this amounts to a cooling penalty of only .03 lbs (.0135 kg). It may be concluded that the daily production rate of contaminants is so small that the cooling requirement for removal of the heat of oxidation is insignificant. (At the flow rate assumed in this calculation, a 50/50 mixture of oxygen and nitrogen would provide approximately a 5000% excess of oxygen over stoichiometric.)