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CHARACTERIZATION OF CONTAMINATION GENERATION CHARACTERISTICS OF SATELLITE MATERIALS

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22 November 1989

Final Report for Period June 1982 - August 1989

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The objective of this program was to develop a standard test method for measuring the kinetics of material outgassing and deposition of outgassing species. The program was divided into three phases. In Phase I the current state of outgassing and deposition measurement and modeling technology was reviewed and a test approach was selected for further development. The Phase I work is reported in AFWAL-TR-83-4126 Volumes I and II. In Phase II the selected method was developed and its measurement capability was critically evaluated. The Phase II work is reported in AFWAL- TR-85-4118. Following Phase II an apparatus capable of executing the test method was built under contractor funding. In the Phase II Extension the apparatus and test method were exercised and evaluated by generating a database for 20 typical spacecraft materials. This report reviews the work performed on Phases I and II, describes the test method and apparatus, and presents the data generated under Phase II Extension. The materials tested include paints, film materials, adhesives, lubricants, and composites. The data generated include total mass loss, total outgassing rate, and mass (see reverse)

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spectrometer data for m/e=10 to 500 as functions of test time for isothermal outgassing of samples at either two or three temperatures selected from 25°C, 75°C, and 125°C; deposition rates of the outgassing products on surfaces at 90 K, 150 K, 225 K and 298 K; QCM thermogravimetric data for the collected outgassed products (obtained by controlled heating of the 90 K collector QCM at the end of an outgassing test) and mass spectrometer data obtained during the QCM thermogravimetry test. Off-line GC/MS tests were also made on the sample materials. The mass spectrometer data for one material test (R-2560 adhesive at 125°C)were further analyzed to show how the data can be used to determine the outgassing rates of each individual outgassed species.

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Section 1

INTRODUCTION AND PROGRAM BACKGROUND

This document is the final report for the Air Force Wright Aeronautical Laboratories contractual program F33615-82-C-5025, entitled "Characterization of Contamination Generation Characteristics of Satellite Materials." The contract covered the period June 1982 to August 1989. The objective of the program was to develop a standard test method for measuring material outgassing and deposition kinetics data.

The test method development program was divided into Phase I, Phase II, and Phase II Extension. In Phase I, the current state of technology for characterizing outgassing and deposition kinetics was determined and assessed, and a candidate test method was selected for further development. In Phase II, the feasibility of the selected method was demonstrated, the specifications for a single apparatus capable of executing all aspects of the test method were determined, and a draft test procedure was prepared. Technical reports were submitted at the end of Phases I and II. Following Phase II, a new test apparatus was built under Lockheed company funding. Under the Phase II Extension, the test apparatus and the test procedure were demonstrated and exercised, and a material database was developed.

This report gives the background to the program, summarizes the work performed in Phases I and II, and describes in detail the work performed under the Phase II Extension.

KEYWORDS: SPACECRAFT CONTAMINATION, CONTAMINATION TRANSPORT, MATERIAL OUTGASSING, SPACECRAFT MATERIAL SCREENING, MATERIAL CONDENSATION, REEMISSION KINETICS, CONDENSATION KINETICS

1.1 REPORT SUMMARY

Section 1.2 reviews background to the program. The limitations of materials selection solely on the basis of the ASTM E 595 screening test are noted, and the need for a more systematic approach to material selection and contamination control is identified. The contributions of this and other Air Force technology programs to develop a systematic contamination control methodology is described.

Section 2 describes the work performed on the prior phases of this program. In Phase I, a review of the literature and a survey of the industry were made. Based on the findings of the review and survey, a method for measuring outgassing and deposition kinetics was selected. The test method is based on a test and data reduction methodology which, when completely developed, will permit the outgassing and deposition kinetics of each individual outgassed species to be determined. The total outgassing and deposition rates are measured by placing the material sample in an effusion cell and collecting the flux leaving the cell on quartz crystal microbalances (QCMs) held at different temperatures.

Total outgassing rate is determined from the collection rate on one of these QCMs which is held at liquid nitrogen temperature. The species evolved from the isothermal sample are monitored using a mass spectrometer.

At the end of the outgassing test, the species deposited on the QCMs are thermally analyzed by heating the QCMs in a controlled manner. This test is referred to as QCM thermal analysis (QTA). During QTA, the QCM deposit mass changes and the evolved species mass spectra as the deposit evaporates are measured as functions of QCM temperature. These two measurements are called QCM thermogravimetric analysis (QTGA), and QCM thermal analysis combined with mass spectrometry (QTA/MS), respectively. Because QTA/MS had not been previously demonstrated, a standard off-line gas chromatography/mass spectrometry (GC/MS) analysis was added to the test method to provide backup data on the constituent species.

The effectiveness and accuracy of the QCM collection method for measuring total outgassing and deposition rates was investigated and confirmed under Phase II. Because it was not cost effective to commit substantial capital funding to a new apparatus before some of the test method principles had been verified, the Phase II development work was performed using two separate general purpose laboratory apparatuses. By the end of Phase II, most of the developmental issues had been satisfactorily addressed, and the requirements for a single dedicated apparatus capable of executing the full test procedure were identified. A draft test procedure for executing the test method was prepared.

Section 3 describes the test apparatus, which was built and checked out under Lockheed funding. The apparatus is described in sufficient detail to permit another organization to build a similar apparatus. For the most part, the apparatus functioned satisfactorily. Operational experience has suggested that some minor changes in the choice of type of QCM and method of temperature control would be desirable. The apparatus is currently being modified to incorporate these changes.

Section 4 presents the formal test procedure. This basic procedure was followed throughout the database measurement program described in Section 6. Most of the changes during the Phase II Extension were minor and evolutionary, and its current form closely resembles the draft test procedure prepared at the end of Phase II.

The objectives of the Phase II Extension were to exercise and evaluate the test method performance and to generate a multi-material outgassing/deposition kinetics database. Section 5 evaluates the data generated by the test method by analyzing in detail the data for one material test - McGhan-Nusil R-2560 adhesive at 125°C.

Section 6 introduces the material database, the main body of which is presented in the Appendix. A list of the 20 materials tested is given, and the arrangement of the database in

the Appendix is explained.

Section 7 presents Conclusions and Recommendations for the overall program.

1.2 PROGRAM BACKGROUND

Contaminant deposits can change the optical properties of thermal control surfaces and optical train components, and hence can degrade the performance of space systems which incorporate these surfaces. The amount of contamination on surfaces of this type must therefore be controlled within acceptable levels to ensure that a space system is able to function effectively over its lifetime. One of the major sources of contamination is outgassing products from materials of construction. Therefore, the impact of outgassing must be determined at the design stage before a material can be approved for use. Until recent years, the standard method for determining the acceptability of a material was to subject it to a screening test. However, there are limitations to the screening method, and we need a more systematic approach to determine material acceptability as space system performance requirements become more contamination-sensitive.

Section 1.2.1 describes the screening method and its limitations. Section 1.2.2 describes a typical systematic approach for determining materials acceptability. Material outgassing is only one of many possible sources of contamination, so Section 1.2.2 describes how control of material outgassing is folded into a comprehensive plan for systematically controlling all types of contamination. Section 1.2.2 also shows how this and other USAF technology programs contribute to the development of a systematic approach to contamination control.

1.2.1 Materials Acceptance by Screening

The standard screening procedure used by the industry is based on total mass loss (TML) and collected volatile condensable material (CVCM) of candidate materials. TML is the fraction of the initial sample mass outgassed from a material held at an elevated temperature in vacuum for a specified period of time. CVCM is the percent of the initial sample mass that condenses on a specified surface. In the early days of the aerospace industry, TML and CVCM were measured for a number of combinations of test duration, sample temperature, and collector temperature. These tests became standardized first informally by Stanford Research Institute, and then formally by the American Society for Testing Materials as ASTM E 595. A very similar test specification has been established by NASA Johnson Spaceflight Center as NASA JSC SP-R-0022A. In the standard screening test, the sample temperature is 125°C, the collector temperature is 25°C, the vacuum is $< 5 \times 10^{-5}$ torr, and the test duration is 24 hours. Spacecraft system outgassing is controlled by using only materials with very low values of TML and CVCM. The customary

materials acceptance criteria are that the TML and CVCM must be less than 1.0 percent and 0.1 percent, respectively. References 1 and 2 list TML and CVCM data for a large number of materials.

Although the screening approach has served the industry well in the past, its limitations have become increasingly apparent in recent years as space systems such as optical sensors have become more contamination-sensitive, mission lifetime goals have been extended, and cost effectiveness is being stressed more heavily. The limitations of materials screening using TML/CVCM data include the following:

(i) The test sample and collection surface temperatures used to determine TML and CVCM may be different from the temperatures of application.

(ii) The TML and CVCM tests only provide data on initial and final conditions, rather than on the variation of total mass loss and mass deposition with time.

(iii) The TML/CVCM test procedure requires the material sample to be chopped into small pieces, which is not typical of the geometry of an actual application. Since outgassing rate is usually geometry-dependent, chopping up the sample reduces the relevancy of the data.

(iv) The CVCM test uses a particular test apparatus geometry, so the data cannot be applied directly to an application with a different geometical relationship between the outgassing source and the deposition surface.

(v) The acceptance criteria of 1.0 percent TML and 0.1 percent CVCM do not take into account the total amount of material actually used in a system, the relationship between the amount of material condensed on a given surface and the change in its critical optical properties, or the sensitivity of total system performance to the change in the surface properties.

(vi) The test provides no information on the individual behavior of the several different species outgassed by most materials.

Because the screening approach uses test data for a single set of conditions in conjunction with arbitrary acceptability criteria, it cannot reflect the unique requirements of a specific system. Depending on the contamination sensitivity of the system, the screening approach may be too restrictive, and hence require unnecessarily costly materials, or not restrictive enough, which may lead to performance degradation or even failure. The more cost-effective approach is to derive allowable contamination levels by flow down from system performance requirements at the start of a program and then to systematically analyze and modify the system design and selected materials to ensure that these levels are not exceeded.

An example of the benefits of using the systematic approach is the use of General

Electric RTV 560 adhesive to bond the insulating tiles to the exterior of the Space Shuttle Orbiter. RTV 560 is a commercial grade adhesive which does not meet the 1.0/0.1 percent TML/CVCM screening requirements, but is less than one-tenth of the cost of the alternative low-volatility aerospace-grade adhesive. However, by determining allowable contamination levels systematically and then performing material outgassing and deposition tests under realistic operating conditions, NASA Johnson Spaceflight Center was able to show that RTV 560 was acceptable for the Orbiter application.

1.2.2 Materials Selection by Systematic Analysis

In the systematic approach to materials selection, the significance of materials outgassing is assessed as part of an overall systematic contamination control plan. First, maximum allowable contamination levels are derived for each contamination-sensitive surface by a flow-down analysis from system performance requirements. Contamination control procedures are established by budgeting these maximum allowable contamination levels over all phases of the program and then constraining the design and operational procedures in each of these phases to ensure that the allowances are not exceeded. Figure 1-1 is an example of systematic contamination control methodology applied to an optical sensor system with specific off-axis rejection capability and optical throughput performance requirements. Each element of the methodology is described below.

System Performance Sensitivity Analyses: The first step is to determine the maximum permissible changes in surface properties by performing system performance sensitivity analyses. For the example used, a system throughput analysis is performed to determine the minimum allowable reflectance or transmittance for each of the optical train components. Also, a system stray light analysis is performed to determine the maximum allowable scatter, expressed in terms of the bidirectional reflectance distribution function (BRDF), from optical components and other surfaces.

Surface Property Degradation Budget: A loss of reflectance or transmittance, or an increase in BRDF can be caused by imperfections in the clean surface as well as by contaminants. The total allowable degradation of surface properties must, therefore, be budgeted between the separate contributions of surface imperfections and contaminants.

Determination of Allowable Contamination Levels: The maximum allowable surface contamination levels are determined from the budgeted maximum allowable contaminant-induced degradation of surface properties either by predicting them using analytical codes or by obtaining them directly from an experimental database. Reflectance and transmittance changes produced by molecular deposits can be predicted if they are smooth and the optical constants of the contaminant are known. However, most contaminants are uncommon chemical species whose optical constants are unknown, so the

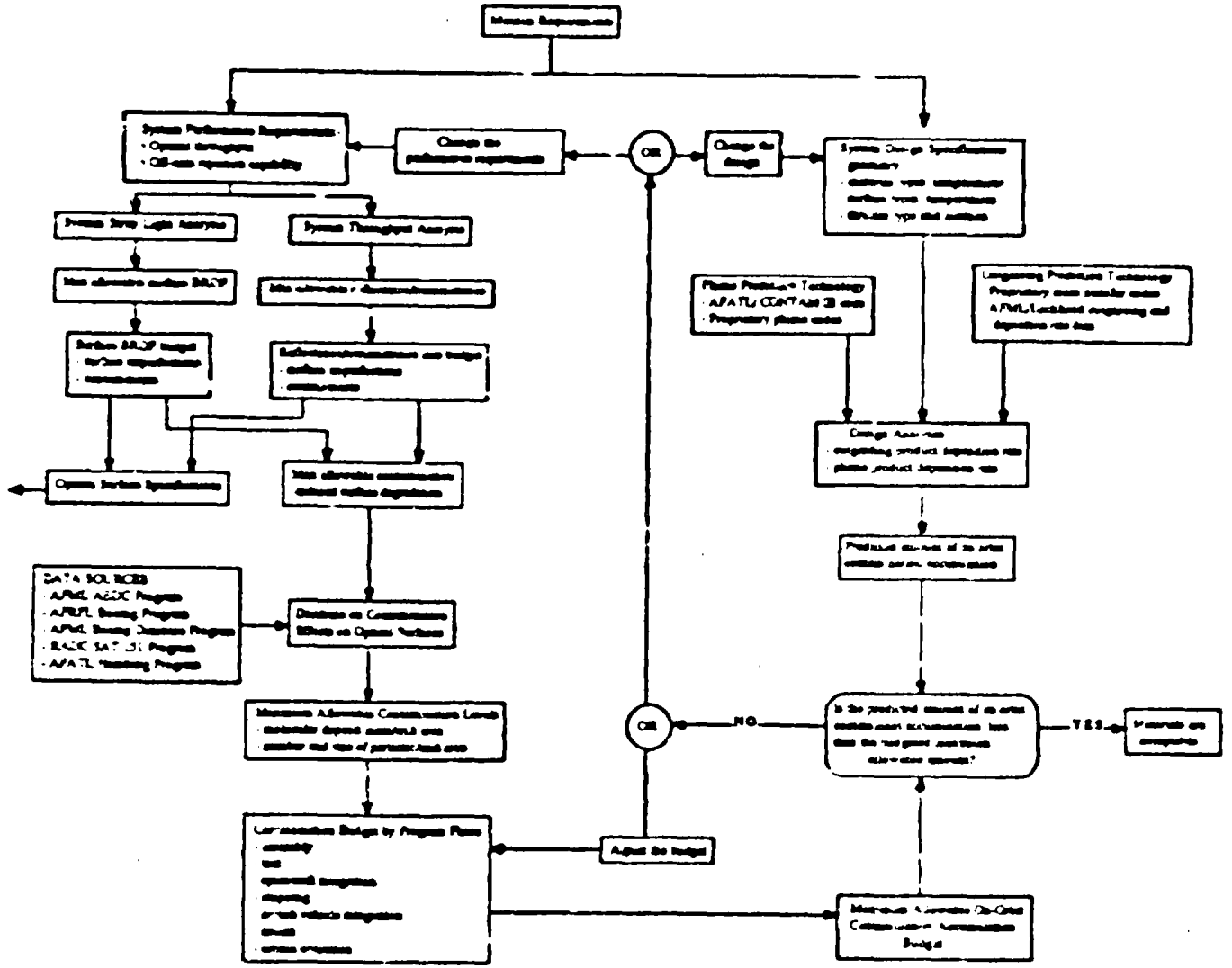


Fig. 1-1 An Example of a Systematic Methodology for Determining the Acceptability of Satellite Materials

optical effect of smooth deposits often must be determined experimentally.

It is extremely difficult to predict the reflectance, transmittance or BRDF of a surface contaminated with either island type molecular deposits or particles because the deposit geometry is usually unknown; even if it were, it would be difficult to solve the electromagnetic equations because of the complex geometrical boundary conditions of the island type configuration. Some approximate models have been proposed but their validity is for the most part untested. Thus, in practice, the amount of contaminant on a surface cannot be confidently related to the resulting change in surface optical properties without using an experimental database.

Although there are many data on the optical properties of contaminated surfaces in the literature, the materials, surfaces, and test conditions and procedures to which they apply are frequently incompletely specified. These data are, therefore, not suitable for inclusion in the type of standardized, universally-accepted optical effects database that is needed to support a systematic contamination control methodology. In response to this situation, the US Air Force funded two technology programs to establish reliable databases on the optical properties of contaminated surfaces. In 1983, the Air Force Materials Laboratory funded a program at Arnold Engineering Development Center (AEDC) to generate a database of the optical properties of surfaces contaminated by deposits of material outgassing products. The AEDC work is reported in AEDC-TMR-85-V28, September 1985, and AEDC-TR-89-2, June 1989. In 1984, the Air Force Rocket Propulsion Laboratory funded a Surface Effects Evaluation Study program with the Boeing Aerospace Company to generate a database of optical properties of surfaces contaminated by motor plume products. The Boeing work is reported in AFRPL-TR 86-093. The measurement of optical effects of motor plume contaminants is now being funded by the Air Force Armament Technology Laboratory (AFATL).

Contamination Budget by Program Phases: The total maximum molecular and particulate contamination allowances determined from system performance requirements normally apply to end-of-mission performance. Since contamination levels will increase during every phase of the program, such as assembly, acoustic and thermal/vacuum tests, shipping, integration, ascent, orbital operations, etc., a contamination allowance budget must be prepared to distribute the total allowance over all program phases.

Contaminant Control Implementation: Contamination control procedures are established for each program phase to ensure that contamination levels do not exceed the budgeted allowance. For the prelaunch phases, the control techniques used are cleaning, clean rooms, packaging, etc., for which an extensive technology shared by many terrestrial applications exists. The major on orbit contaminant sources are material outgassing and

motor plumes. These contamination sources are controlled by using computer based contamination migration models to estimate their magnitudes and then constraining material selection and system design to keep these magnitudes within budget. The computer codes model the system geometry and components, source and surface temperatures, etc., and use databases to represent plume contaminant generation, outgassing rate, and deposition kinetics.

A number of proprietary codes and databases have been developed for modeling plume and material outgassing contaminant generation, migration, and deposition, but, until recently, none of these had been standardized so that they could be used with confidence industry wide. Because of this need, the Air Force Rocket Propulsion Laboratory has undertaken development the CONTAM code to predict rocket plume contamination product generation and transport. A database of motor plume contamination product deposition kinetics has not yet been generated. Development of the CONTAM code is now being supported by the Air Force Armament Technology Laboratory.

There are currently no standard codes for predicting the migration of outgassing products. Most codes currently in use are proprietary, and to date no effort has been made to standardize them. However, all codes require a supporting database of outgassing and deposition kinetics data. The very large database of total mass loss (TML) and collected volatile condensable material (CVCM) data that has been generated by the standardized ASTM E 595 test is unsuitable for supporting modeling because, among other limitations given in Section 1.2.1, the data do not describe the kinetics of outgassing or deposition.

Because of the lack of standardized outgassing and deposition kinetics data, many aerospace organizations have developed in house test apparatuses and methods for measuring the type of kinetics data used by their proprietary model. Because of the cost involved, organizations have tended to measure only those data needed to support a particular program, using existing apparatus modified minimally, if not at all, and choosing only those test parameters directly related to the particular program. Also since these data are usually not reported in the open literature, they are frequently repeated by each organization for each application. The Air Force Materials Laboratory Non-Metallic Materials Group (AFWAL/MLBT) recognized this situation and in 1982 initiated the contractual program reported herein with Lockheed Missiles and Space Company to develop standardized methods for characterizing materials outgassing rate and deposition kinetics.

Reconciliation of Allowance with Prediction: The final step in the systematic approach is to compare the sum of the predicted amounts of on orbit deposition due to plumes and outgassing with the on orbit contamination budget. If the budget is exceeded,

then one of several changes must be made. the on orbit phase must be assigned a larger budget, the performance requirements must be relaxed on the design, including the selected materials, must be modified. If the budget is not exceeded, then all aspects of the design, including the selected materials can be considered to be acceptable from the contamination point of view.

Section 2

PROGRAM REVIEW

This section summarizes the work performed under the two previous phases of this Air Force Materials Laboratory program.

2.1 PHASE I - INDUSTRY SURVEY AND LITERATURE REVIEW

Under Phase I of this program the state of technology for measuring outgassing and deposition kinetics was determined by making a survey of the industry and reviewing the literature. This information was then assessed to determine its relevance to the program objectives. Based on the results of this assessment, a test method approach was selected for further development under Phase II.

2.1.1 Technology Survey and Review

The aerospace industry was surveyed, and the technical literature was reviewed to determine the current state of development of analytical and experimental methods for measuring the outgassing characteristics of materials and the kinetics of deposition by adsorption and condensation of molecular fluxes impinging on surfaces. The results of the survey and review are presented in Reference 3 (Phase I Report, Vol. I).

The industry survey began by circulating a questionnaire to determine how the aerospace industry currently makes these measurements. Following receipt of the completed questionnaire, a workshop with members of the aerospace industry was held at Aerospace Corporation, El Segundo, CA, where the overall problem of measurement of outgassing and deposition characteristics was reviewed. Following the workshop, a summary report presenting conclusions drawn from the workshop was prepared. The results of the questionnaire, the material presented to the workshop, and the summary report, are contained in Reference 3 (Section 2, Appendix A, and Appendix B).

The literature review used computerized searches of the relevant abstract services to identify more than 850 journal articles, reports, conference proceedings, and books. This literature was indexed according to subject. The review methodology, the bibliography, and the subject index are presented in Reference 3 (Section 3 and Appendix C).

2.1.2 Technology Assessment

The information obtained from the Technology Survey and Review was assessed with the objective of determining a preferred outgassing/deposition test method. Because the purpose of the test method was to support space system contamination migration modeling, a review of modeling methods and their database requirements was made. The

basic physical phenomena involved in material outgassing and molecular deposition were discussed, and available physical models for these phenomena were reviewed. Available experimental methods for characterizing these phenomena were evaluated, and published data were summarized. The results of this assessment are presented in Reference 4 (Phase I Report, Vol. II).

2.1.3 Test Method Selection

The requirement set for the test method is that it must be capable of generating the following types of data.

(i) The total mass loss and the outgassing rate of an isothermal sample per unit mass and per unit exposed area as a function of time.

(ii) The fraction of the total outgassing flux that will deposit on a surface as a function of surface type, temperature, and time.

(iii) The identity of each outgassed species.

(iv) The fraction of each species in the outgassing flux as a function of time.

(v) The rate of surface deposition of each outgassing species as a function of surface type, temperature, and time.

The total outgassing and deposition data, requirements (i) and (ii)), could be measured using technology available at the beginning of the program, but the technology for determining the contributions of each of individual species, requirements (iii), (iv), and (v), did not exist at that time. Although we hoped to base as much of the test method as possible on existing technology, we decided to develop species resolution technology on the program because it was highly desirable to be able to characterize the behavior of the individual species.

To satisfy the five data requirements, a test method made up of several different measurement techniques was selected. Figure 2-1 is a schematic of the apparatus, while Fig. 2-2 shows the overall test methodology, the data reduction procedures, and the data output. Isothermal outgassing and deposition kinetics are measured using the QCM (quartz crystal microbalance) collection technique. The total mass loss and total outgassing rate of a constant temperature material sample are determined by collecting the outgassing flux on a liquid nitrogen-cooled QCM. The deposition rates of the outgassed species on selected higher temperature surfaces are measured by collection on temperature-controlled QCMs. The sample total mass loss is also determined from ex situ pre- and post-test weighings to provide correlation with the ASTM E 595 test.

The contribution of each individual species in the outgassing flux is monitored using a mass spectrometer. The relative contributions of each species to the total outgassing flux can be determined from the total mass spectra recorded during outgassing if the

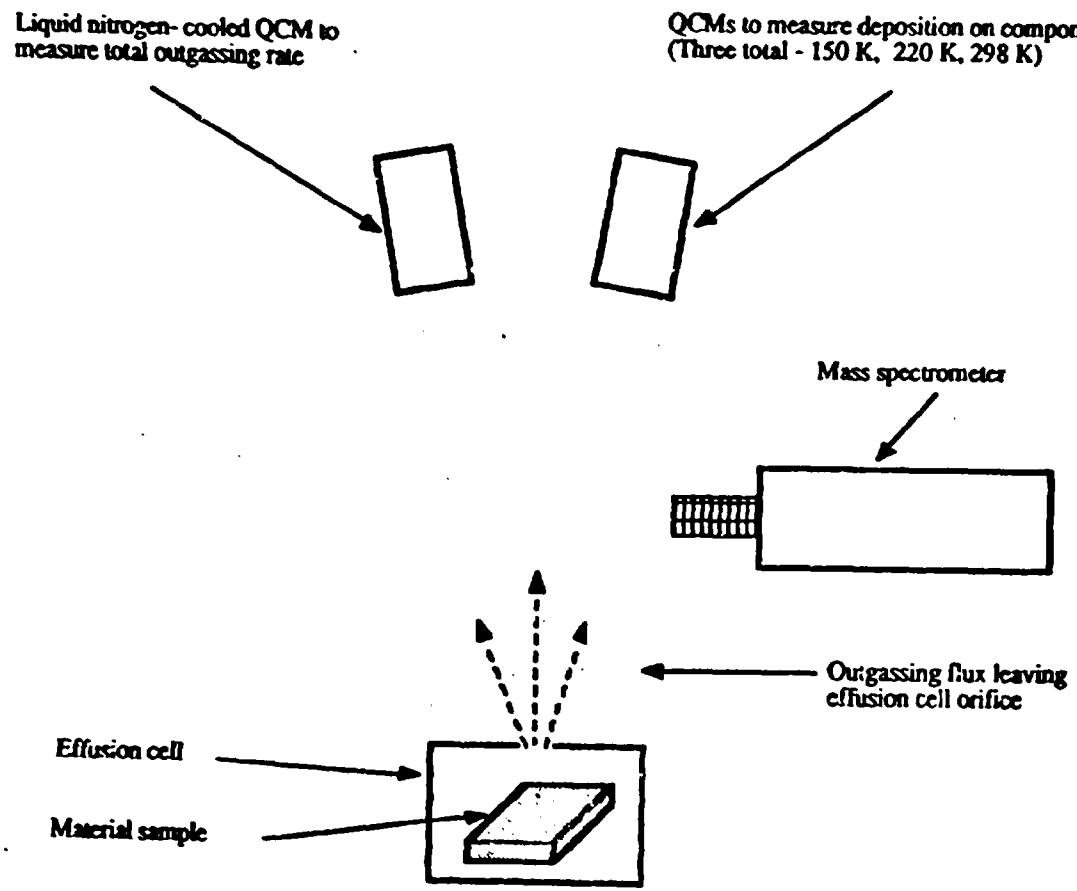


Fig. 2-1 Schematic of the Apparatus

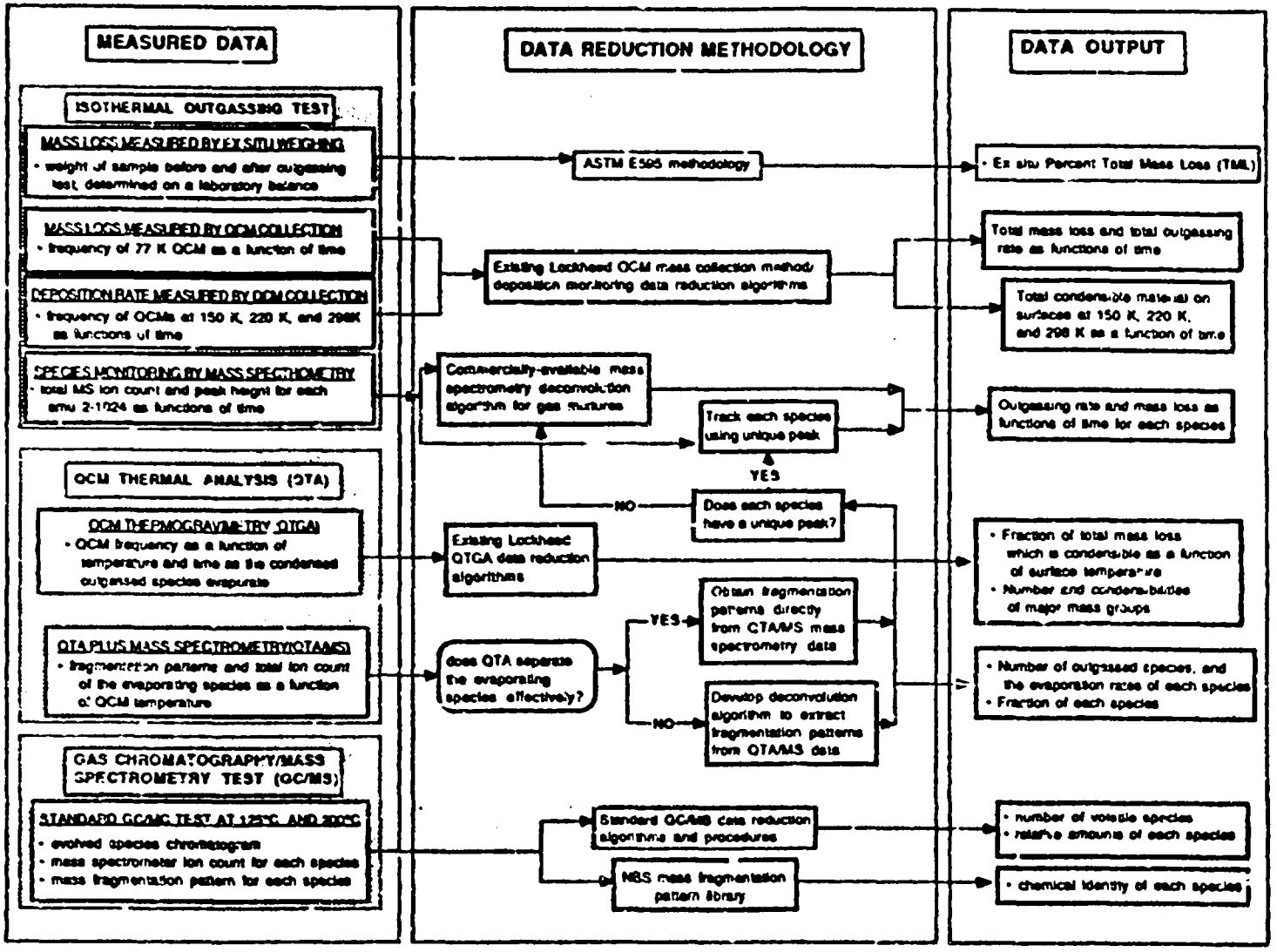


Fig. 2-2 Overall Test Methodology

fragmentation patterns of the individual species are known. The test method obtains these fragmentation pattern data using two QCM-based thermal analysis (QTA) techniques known as QCM thermogravimetric analysis (QTGA) and QTA plus mass spectrometry (QTA/MS). The QTA/MS technique appeared to offer the most potential for obtaining individual species mass fragmentation pattern data within the scope of the test method, but it required development of new technology and so had associated risk. Because of this risk, further supporting data on the behavior of individual outgassed species are obtained from a separate off-line gas chromatography/ mass spectrometry (GC/MS) test.

The elements of the test method and the reasons for their selection are discussed in the following subsections.

2.1.3.1 Isothermal Outgassing/Deposition Test

The three candidate methods for measuring total outgassing rate in vacuum are the vacuum microbalance, pressure measurement, and mass collection methods. Reference 4 presents a detailed comparison of these methods.

Outgassing rate determination by placing the sample on the scale pan of a vacuum microbalance is direct and unambiguous, but the size and shape of the sample are limited by the mass capacity of the balance, and geometric limitations are placed on the sample because of the need to position it on the balance pan. Also, it is difficult to transfer heat to the sample without disturbing the mass measurement. Vacuum microbalances must be very carefully installed, grounded, and operated if their full measurement potential is to be realized.

Outgassing rate can also be determined using one of several methods based on measurement of the pressure in a vacuum chamber with and without a material sample present. These methods are known as the rate of rise, rate of fall, and throughput methods. Pressure measurement methods are simple and inexpensive, and were widely used in the early days of the ultrahigh vacuum industry to measure outgassing rates of materials near ambient temperature. They have limited range and resolution, and are difficult to execute at temperatures lower or higher than ambient because of sorption interactions between outgassed species and the chamber walls.

In the mass collection method, the material sample is placed freely in the vacuum chamber or in an effusion cell. The outgassing flux from the sample is collected by condensation on a cooled mass-measurement device, such as a plate suspended from a vacuum microbalance scale pan or the surface of a QCM. The sample outgassing rate is calculated from the mass collection rate and the view factor between the collector and the sample or the effusion cell orifice.

The mass collection method using a liquid nitrogen-cooled QCM as the collector and

an effusion cell to hold the sample. The QCM is the preferred type of collector because of its high sensitivity, its wide dynamic range, and its ease of use. The collector QCM is cooled to liquid nitrogen temperature because most outgassed material will condense at this temperature. Cooling to a lower temperature would incur a major increase in test cost and apparatus complexity.

Use of an effusion cell permits the sample to have any size, shape, or temperature consistent with the cell design. The collector-to-cell orifice view factor becomes an apparatus constant, independent of the sample geometry. The mass collection method could be used equally well with a free-standing sample, but the collector-to-sample view factor would have to be calculated for each new sample.

The QCM collection method can be readily adapted for measuring the condensability of the outgassed species at temperatures other than liquid nitrogen temperature by using the same basic apparatus design with additional collector QCMs operating at higher temperatures.

The test method includes determination of sample total mass loss by pre- and post-test weighing on a laboratory balance. This provides a check on the total mass loss determined by the collection data, as well as correlation with ASTM E 595 data.

An additional benefit of the QCM collection method is that it permits some aspects of the behavior of different outgassed species to be characterized using QCM thermal analysis (QTA) procedures described in Section 2.1.3.2.

The technology assessment task revealed that the only viable candidate technique for real time qualitative and quantitative characterization of outgassing species in vacuum is mass spectrometry. The mass spectrometer is positioned so that its ionizer sees the outgassing flux leaving the effusion cell orifice and is used to record mass peak intensities over a selected mass range as a function of time during the isothermal outgassing test. At any point in time the outgassed molecular flux may contain several different chemical species, so the recorded mass peak intensities will, in general, be the sum of the contributions of several species. The contributions of the individual species can be resolved if the mass fragmentation patterns and ionization constants of each species are known. If the fragmentation pattern of a species contains a unique peak, then the outgassing rate of the species can be tracked by following the variation of that peak with time. If the pattern does not show a unique peak, a deconvolution algorithm must be used to resolve the behavior of each species. The proposed test method calls for obtaining the individual species fragmentation pattern and ionization constant data by developing a procedure known as QTA/MS in which mass spectrometry is performed during QTA. This procedure is described in Section 2.1.3.2.

2.1.3.2 QCM Thermal Analysis (QTA)

During an outgassing test, the deposit formed on the collector QCM contains a sample of the outgassed species in the same relative proportions in which they were outgassed. This deposit can be examined by two QCM thermal analysis (QTA) techniques, which involve heating the QCM in a controlled manner and measuring the behavior of the deposit. In QCM thermogravimetric analysis (QTGA), the mass remaining on the QCM is measured as a function of temperature as the various condensed species evaporate in different temperature regimes, according to their volatilities. This measurement determines the fraction of the total outgassing product which is condensable at a given surface temperature. In work performed on a Lockheed Independent Research and Development (IRAD) project [5] prior to this contract, it was shown that if there were relatively few species in the deposit and if their volatilities differed significantly they could be separated by QTA and their relative abundances could be determined by QTGA. Further, because each species has a unique evaporation rate/temperature characteristic, it may even be possible to identify a species chemically from QTGA data.

In QTA plus mass spectrometry (QTA/MS), the flux evaporating from the QCM during QTA is monitored using a mass spectrometer. If QTA can effectively separate the individual species in the deposit, this technique becomes a form of chromatography, and the mass spectrometer will be able to determine the mass fragmentation pattern of each species directly. Also, the relative response of the mass spectrometer to each species, and hence their ionization constants, can be calculated by relating the instantaneous mass spectrometer peak intensities to the instantaneous evaporation rate indicated by the QCM.

Since mass spectrometry itself is a proven technique, the success of QTA/MS, and hence the methodology for determining the outgassing rates of the individual species, depends entirely on the ability of QTA to separate the individual species. Although QTA resolution capability had been demonstrated for simple deposits, its ability to resolve deposits with many species of similar volatilities in a routine measurement had not been proven at the outset of the program. If QTA was not able to separate the individual species adequately, then an algorithm to deconvolute the QTA/MS data would have to be developed. This would be a major new undertaking and would be outside the scope of the program. The species separation capability of QTA was therefore the highest risk component of the proposed test methodology.

2.1.3.3 Gas Chromatography/Mass Spectrometry (GC/MS)

Because QTA/MS had not been demonstrated at the time of test selection, it was decided to include a separate off-line gas chromatography/mass spectrometry (GC/MS) measurement in the test procedure to provide additional supporting species characterization

data. GC/MS is a standard analytical chemistry test in which the material sample is heated in a flowing stream of helium while the evolved species are collected in a liquid nitrogen trap. The trap is then heated and the evolved species are separated in a chromatograph column, detected by a mass spectrometer, and identified by comparing mass fragmentation pattern data with a standard library.

Because of the presence of the helium carrier gas, lower volatility species may not be evolved in detectable quantities during GC/MS. On the other hand, the relatively high sample temperature usually used in GC/MS (e.g., 250°C at Lockheed) may produce thermal degradation products which would not be present during vacuum outgassing. These issues were investigated in Phase II.

2.2 PHASE II - TEST METHOD DEVELOPMENT

Under Phase II of the program, the measurement capabilities of the test method were developed and evaluated, and a draft test procedure for implementing the test method was prepared. Work performed under this phase was reported in the Phase II Task Report [6].

2.2.1 Measurement Capability Development and Evaluation

The measurement capabilities that were addressed were as follows:

(i) The accuracy of the QCM collection technique for measuring sample total mass loss, total outgassing rate, and total deposition rate.

(ii) The use of mass spectrometry to monitor the outgassed species in the outgassing flux quantitatively over a long duration test.

(iii) The ability of QTA to resolve the individual species in a condensed deposit.

(iv) The relationship between the species identified by GC/MS and the species released in a vacuum outgassing test.

2.2.1.1 Outgassing and Deposition Rate Measurement

The practicality of the QCM collection technique for measuring the total outgassing rate of a sample held in an effusion cell had been proven in an earlier Lockheed IRAD project [7]. The use of QCMs held at different temperatures to measure relative deposition rates had been well established throughout the industry and had also been demonstrated as a basic research technique. The major remaining developmental issues were assessment of the measurement accuracy of these techniques and estimation of the effect of the effusion cell pressure on the magnitude of the measured total mass loss.

2.2.1.1.1 Measurement Accuracy

The sample outgassing rate is calculated from the change in QCM frequency, the QCM mass sensitivity constant, the fraction of the outgassing flux which is condensable on a liquid nitrogen-cooled QCM, and the distribution of flux leaving the effusion cell orifice.

The deposition rate is calculated from the change in QCM frequency and the QCM sensitivity constant. The accuracy of these measurements was assessed in two ways. First, the accuracy to which each of these individual factors could be determined was evaluated. Second, the total mass loss measured in situ by QCM collection and calculated using all of these factors together was compared with the value determined by pre- and post-test ex situ weighing.

Accuracy of Individual Factors:

The QCM frequency is stable to ±1 Hz as long as the temperature remains constant, and can be measured to an accuracy of better than 1 Hz. Since the total change of QCM frequency during an outgassing test is in the range of about 1 to 10 kHz the mass measurement error resulting from QCM frequency measurement error is negligible.

Following standard practice, the QCM mass sensitivity constant used was the theoretical value for a 10-MHz crystal of 4.43×10^{-9} g/cm^2 Hz. The literature reports many experiments in which the mass sensitivity of the QCM was calibrated against the vacuum microbalance. All of these experiments conclude that for a uniform deposit the measured QCM mass sensitivity constant is equal to the theoretical value to within ± 2 percent.

The molecular flow distribution from the effusion cell orifice was measured, and the data were compared with a theoretical relationship derived by Clausing [8]. The predicted and measured distributions agreed to within ±2 percent, so the QCM-to-cell view factor is known to this accuracy.

The apparent outgassing rate measured by a liquid nitrogen temperature QCM may be less than the true value since some possible outgassing species such as nitrogen, oxygen, hydrogen, etc, are not condensable at this temperature. Mass spectrometer measurements have indicated that for most polymeric materials, the contribution of these species is usually very small. This observation is reinforced by the excellent agreement, noted below, that was obtained between the total mass loss determined by QCM collection and by ex situ weighing. For low outgassing materials such as metals, the contribution of noncondensable gases may be more significant. However, the presence of species not condensable at liquid nitrogen temperature can be readily detected by the mass spectrometer, and the QCM-measured data can be corrected appropriately to allow for the contribution of these species.

Comparison of In Situ and Ex Situ Measurements:

The total mass loss determined by the QCM collection technique was compared with the total mass loss determined by pre- and post-test ex situ weighing. Two systematic effects can affect the accuracy of the apparent mass loss determined by each of these two

methods. Ex situ weighing will indicate an erroneously low value of mass loss if there is significant regain of water vapor and other atmospheric species between removal of the sample from the vacuum chamber and post-test weighing. The collection method will indicate a low total mass loss if the sample outgasses a significant amount of material not condensable at liquid nitrogen temperature and the QCM data are not corrected using mass spectrometer data. The two sets of data should show best agreement with each other and should give a total mass loss vale which is closer to the absolute total mass loss in vacuum when the amount of nitrogen, oxygen, and water vapor in the outgassed products is minimal.

The extent of the effects of atmospheric components on ex situ and in situ total mass loss was investigated by comparing the total mass loss determined by the two methods for a number of materials. Except for unusual cases such as mylar film which has a dramatic weight regain on reexposure to the atmosphere, we found that the data obtained by the two methods agreed to ±2 percent. We concluded from this agreement that the effect of noncondensable gases was indeed negligible in most cases.

The test-to-test repeatability was examined by testing several samples of one material under identical conditions. Repeatability was found to be in the ± 2 percent range.

2.2.1.1.2 Effusion Cell Effects

Use of an effusion cell to hold the sample makes sample preparation and insertion much simpler, and eliminates the need to calculate the QCM-to-sample view factor anew for each sample. However, to establish a net mass flow through the effusion cell orifice, the pressure in the cell must be higher than the outside pressure. The effect of finite cell pressure is to cause some of the outgassed species to be readsorbed before having the opportunity to leave the cell. This effect will reduce the measured total mass loss and outgassing rate below the values which would occur in a perfect vacuum. The magnitude of this effect on total mass loss (TML) was assessed by conducting a series of tests using a modified ASTM E 595 apparatus. The ASTM E 595 apparatus incorporates 24 sample effusion cells with screw-in caps which carry the cell orifices. The diameters of some of the cell orifices were reduced by various factors by insertion of reducer plugs, while the orifices of some cells were left at the standard ASTM E 595 diameter. The cap from one of the cells was removed entirely so as to reduce the back pressure for this cell to a minimum. A series of identical samples were placed in these cells and were exposed to vacuum for the same time and temperature. The ratio between the TML data for specimens in cells with reduced orifices to the TML for the cell without an end cap were then related to the pressure in the cell, which was calculated from the mass loss and the orifice conductance. It was concluded that as long as the cell pressure is less than about 10^{-4} torr, the effect of cell

pressure on TML is minimal, and if the pressure is lower than 10^{-5} torr the cell pressure effect can be neglected. Calculations show that for the 0.125 inch diameter cell orifice chosen for the new test apparatus (Section 3), the cell pressure may exceed these values briefly at the beginning of a test on a large or high outgassing sample, but the pressure will fall rapidly to a negligible value as the outgassing rate decays with time.

We concluded from the above investigations that the accuracy of mass loss determination by the QCM collection was at least as high as ex situ weighing, repeatability was good, and the contribution of each of the factors affecting the mass loss calculation was well understood. The accuracy with which most of the contributing factors is known is of the order of ±2 percent, so the overall accuracy should be of the order of about ±5 percent. The accuracy of the deposition measurement depends on fewer factors than the outgassing measurement, and should be accurate to ±2 percent.

2.2.1.2 Mass Spectrometry

The Phase II activities were conducted using a 1-300 amu UTI mass spectrometer interfaced with a Hewlett Packard computer. For the Phase II Extension test program, this system was replaced by a 2-1023 amu Balzers mass spectrometer interfaced with an IBM PC computer. Both systems worked very well, were very reliable, and had excellent software offering a wide variety of data acquisition, viewing, and storage options. The Balzers mass spectrometer was chosen for the Phase II Extension because of its greater sensitivity and higher mass range.

The use of mass spectrometry for in situ monitoring of different molecular species is well established and needed no further development for this program. The only area of uncertainty regarding the measurement capability of the mass spectrometer was its stability over the period of an outgassing test. Mass spectrometer stability and response to specific species is affected by a number of parameters such as ionizer emission current and efficiency, transmission of the quadrupole mass filter, and electron multiplier gain. The stability of the mass spectrometer was verified by monitoring the output signal in situations in which the mass flux through the ionizer was constant or known. In an initial test, the mass spectrometer response to the quasi-constant long-duration fragmentation pattern signatures of the vacuum chamber background was measured, and was found to be very stable. The stability was confirmed for a higher signal level by monitoring the flux evaporating from a sample of caprolactam (a monomer of Nylon 6) with the UTI mass spectrometer and a collector QCM. Correlation of the QCM data and the mass spectrometer data showed that the response of the mass spectrometer was constant over periods of several days. The response stability of the Balzers mass spectrometer was confirmed during Phase II Extension by the background monitoring technique.

2.2.1.3 QCM Thermal Analysis (QTA)

The QTA measurement technique includes both QTGA and QTA/MS. Previous work [5] has shown that QTGA can provide considerable information on the mass composition and properties of the deposit, but that it has several significant limitations. Many of these limitations could be overcome by monitoring the evaporating flux with a mass spectrometer. Since the apparatus does include a mass spectrometer, any benefits to QTGA to be gained by its use would be uncovered during QTA/MS. Because of this commonality, and that the data output from QTGA was not critical to completing the proposed data reduction methodology, further development of QTGA on Phase II was not given a high priority. The performance and limitations of QTGA are reviewed in Section 2.2.1.3.1.

The QTA/MS measurement is critical to the success of the procedure of Fig. 2-2 because it provides the mass fragmentation pattern data needed to interpret and/or deconvolute the mass spectra measured during the isothermal test. Most of the Phase II development work on QTA therefore addressed QTA/MS. The QTA/MS technique is a novel form of in situ gas chromatography which, if successfully developed, would be a significant contribution to the technology of analytical chemistry. Its development was a very ambitious task to undertake and certainly could not be completed under the scope or schedule of Phase II. The work accomplished on Phase II was thus of a preliminary nature. Areas of QTA performance needing development were identified and some preliminary performance evaluations of QTA/MS were made. Development of QTA/MS continued under the Phase II Extension and is described in Section 5 of this report.

2.2.1.3.1 QTGA Performance Factors and Limitations

The three main factors which characterize the performance of QTGA are species separation capability, temperature displacement, and detection sensitivity. Performance is also limited by liquefaction of the deposit and formation of azeotropes.

Separation capability is the ability to distinguish two species with similar evaporation characteristics. If two species have evaporation characteristics which differ by only a small amount, then, as the QCM is heated, the less volatile species may begin to evaporate at a significant rate before the more volatile species has completely evaporated. In this case, the net evaporation rate measured by the QCM will include the contributions of both species, and these contributions cannot be separated using QCM data alone. The degree of species overlap can be reduced by heating the QCM more slowly or by using a smaller initial deposit mass. Both these approaches will cause a higher fraction of the more volatile species to leave the QCM before the evaporation rate of the less volatile species becomes significant. However, both approaches are somewhat impractical. Using the current

nominal heating rate of 1 K/min, a QTGA test takes about 5 hours. The test would have to be extended excessively if the heating rate was to be reduced enough to improve species resolution significantly. Selection of a thinner deposit thickness is not a practical solution, since the deposit thickness is a function of a sample outgassing rate and cannot be selected arbitrarily.

A uniform thick deposit of a single species has a single unique evaporation rate/temperature characteristic which is a function of its vapor pressure and molecular weight. This characteristic can frequently be used to fingerprint an unknown species, or even to identify a species whose vapor pressure and molecular weight are known. However, several experimental factors can reduce or increase the apparent evaporation rate at a given temperature. This has the effect of displacing the evaporation characteristic to a higher or lower temperature, making the species appear to be less or more volatile and perhaps confusing it with another species.

One major factor causing temperature displacement is the delaying effect on evaporation of the diffusion of the more volatile species through the less volatile components in order to reach the free surface. Another factor is the reduction in net evaporation rate that occurs if the deposit has an island rather than continuous film structure. Temperature displacement to higher or lower temperatures can also occur if the species forms an azeotrope with another deposited species. Species that form azeotropes will evaporate from the QCM together and will thus appear to the QCM to be a single species. Evaporation of a more volatile species can also increase the apparent evaporation rate of a less volatile codeposited species by simple momentum transfer mechanisms.

Detection sensitivity is the ability to detect the less abundant components in the deposit on the QCM. It depends on the signal to noise ratio of the basic QCM frequency measurement. In general, the frequency of a clean QCM is temperature and heat flux dependent, and the major sources of noise during QTGA are temperature and heat flux induced changes in QCM frequency. The presence of noise means that a larger deposit mass is required to detect species with low concentrations. It may not always be possible to obtain a larger deposit mass, and in any case, larger deposits introduce species separation and temperature displacement problems as described above. If the temperature induced QCM frequency change is a repeatable function of temperature, its effects can be minimized by measuring it as a function of temperature and subtracting it from the total measured frequency change for QCM plus deposit. Heat flux induced frequency noise is caused in part by unsteady flow of heat to the QCM from the temperature ramp controller. This source of noise can be reduced by using a temperature ramp controller which provides a smoother power profile by, for example, using voltage modulation

instead of on/off modulation for power adjustment.

The performance of QTGA can be affected by deposit liquefaction. If any species in the deposit liquefies before evaporating, the coupling between the entire deposit and the QCM crystal is lost and the QCM is unable to sense the deposit mass. Coupling will be restored when the QCM has been heated to a sufficiently high temperature for the liquid components to have completely evaporated.

QTGA performance [illegible] by monitoring the evaporating flux with a mass spectrometer. Temperature displacement of a given species would be immediately apparent when its characteristic mass fragmentation pattern appeared at a higher temperature. The mass spectrometer's higher sensitivity would supplement the QTGA data for less abundant species and help improve overall system sensitivity. The use of a mass spectrometer would also make it easier to resolve the data when liquefaction and azeotropes occur. When the deposit liquefies, it will continue to evaporate and the mass spectrometer will be able to continue to monitor the evaporation rate until full QCM response is restored. Although azeotropes evaporate from the QCM at a single temperature, the components will behave as separate species in the gaseous state and will be detected separately by the mass spectrometer.

Use of mass spectrometry would also enhance species separation capability. If the mass fragmentation patterns of species with similar volatilities were known in advance, their relative contributions in overlap regions could be readily quantified. However, this creates a dilemma because the primary objective of QTA in the present context is to separate the individual species so that their mass fragmentation patterns can be determined directly using the technique of QTA/MS. However, the two objectives of improving QTGA and determining individual species fragmentation pattern data could be achieved if an algorithm to deconvolute the QTA/MS data for closely spaced species were available. Creation of algorithms of this type should be technically feasible and relatively straightforward, but the effort required would be outside the scope of this program.

2.2.1.3.2 Preliminary Study of QTA/MS

The development work on QTA/MS on Phase II addressed only the most basic measurement issue, which was determination of whether the total ion count indicated by a mass spectrometer placed in the flux evaporating from the QCM was able to track the evaporation rate indicated by the QCM both qualitatively and quantitatively during QTA. These issues were addressed in two tests using a pure species – caprolactam – as the test material.

In the first of these tests, we found that during QTA the mass spectrometer recorded two total ion count peaks during evaporation of a single species from the QCM. This was

due to detection of species evaporating from the QCM end cap as well as from the QCM crystal. In the QCM Research Inc. Mark 9 QCM unit used in these tests the measuring crystal views the effusion cell orifice through a central hole in a cap covering the end of the main QCM body. The QCM body, cap, and crystal are in thermal contact and at equilibrium they operate at essentially the same temperature. When they are cold, the impinging outgassing flux will condense on the surface of the cap as well as on the crystal. During QTA, the cap temperature will increase in unison with the QCM crystal, and if the mass spectrometer views the QCM end cap as well as the crystal, it detects the flux evaporating from both these surfaces. If these surfaces were at exactly the same temperature this situation would be beneficial, because it would provide a greater mass spectrometer signal than would be available from the QCM crystal alone. However, because of the temperature differentials that are set up in the QCM unit during transient heating, the end cap will always be at a slightly higher temperature than the crystal during QTA. A given species will therefore evaporate from the cap at an earlier time than from the crystal, and the mass spectrometer will detect two separate evaporation peaks for a given species. This problem was eliminated in the apparatus used for test development by placing an apertured baffle between the effusion cell and the QCM. The baffle reduced the amount of deposition on surfaces other than the crystal during the outgassing test, and also served to reduce the view factor between the mass spectrometer ionizer and QCM surfaces other than the crystal during QTA.

Since completion of this program, QCM Research Inc. has introduced the Mark 16 QCM in which the measuring crystal can be heated without heating the entire QCM body and end cap. Nominally, this version of the QCM appears to be well-suited for the QTA/MS application, and such a unit has been purchased.

In the second test, the response of the mass spectrometer was compared with the QCM output as the evaporation rate from the QCM increased during QTGA. We found that the total ion count indicated by the mass spectrometer tracked the evaporation rate indicated by the QCM in a satisfactorily linear and repeatable manner.

Since the separation capability of QTA depends strongly on the particular set of outgassed species deposited on the QCM, it was decided to address this issue as part of the Phase II Extension when multispecies deposits from actual test samples would be available. Funding limitations also contributed to this decision. No examination was made in Phase II of the enhancement of QTGA that would be provided by the addition of mass spectrometry. Such enhancement was not critical to the success of the test method and could also be evaluated in parallel with the Phase II Extension test program.

2.2.1.4 Gas Chromatography/Mass Spectrometry (GC/MS)

Since mass fragmentation patterns are determined for each evolved species as part of the standard GC/MS test, this test could, in principle, provide useful backup data in case these patterns could not be obtained from QTA/MS. The outgassing products from polymers frequently include a number of homologues which have fragmentation patterns which are very similar, and in order to resolve homologues with different molecular weights the individual species fragmentation pattern data must be quantitatively very self-consistent. However, in general, different mass spectrometer ionizers produce slightly different fragmentation patterns. A comparison was therefore made of the patterns produced by the ionizers used in the GC/MS and outgassing test apparatus mass spectrometers. As expected, both ionizers produced the same patterns qualitatively, and both systems identified the same principal mass peaks. However, there were significant quantitative differences between the patterns, and we concluded that it would not be possible to use fragmentation pattern data determined by the ex situ GC/MS test to deconvolute the peak height data obtained during an in situ isothermal outgassing test.

The standard Lockheed GC/MS test uses a sample temperature of 250°C. At this temperature, additional volatile species not present in the vacuum outgassing test may be created by thermal degradation. Therefore, it seemed appropriate to use a lower GC/MS temperature in the present context. On the other hand, the presence of the helium atmosphere in the standard GC/MS test will suppress outgassing to some extent, and it might be necessary to use a higher sample temperature in GC/MS than would be used in the highest vacuum outgassing test temperature of 125°C to evolve the same species. To investigate this issue the GC/MS test was repeated at temperatures of 125°C, 150°C, 200°C, and 250°C to determine how high above 125°C the GC/MS test temperature could be raised without producing thermal degradation products. The species identified at each temperature by GC/MS were compared with those found in a 125°C outgassing test. As a result of this comparison, it appeared that the GC/MS test temperature could be raised to 200°C without noticeable production of thermal degradation products. However, it was recognized that the comparison was not rigorous and that the ideal compromise temperature would be different for different materials.

2.2.2 Test Procedure Development

Based on experience obtained while developing the various aspects of the test in Phase II, a draft procedure for implementing the test method was developed. The draft procedure covered sample preparation, test parameters, sequence of events, and operation of the apparatus and was presented in the Phase II Task Report [6]. Since the test method was intended to support organizations throughout the industry, a workshop was held at

Lockheed in November 1984 to discuss the test procedure and to obtain an industry consensus on test parameters. The draft test procedure, including test parameters, was largely the same as the current version of the procedure presented in Section 4.

Section 3

TEST APPARATUS

This section describes the outgassing/deposition kinetics measurement apparatus and its operational characteristics. The apparatus was built under Lockheed funding before the Phase II Extension. Lockheed funding covered apparatus detailed design, hardware, data aquisition software, and functional checkout, as well as modifications made to the apparatus during the course of the Phase II Extension.

The apparatus is shown in Figs. 3.1, 3.2, and 3.3. Figure 3.1 is a general view of the apparatus test hardware. Figure 3.2 is a schematic of the main test chamber. Figure 3.3 is a schematic of the data aquisition system. Sections 3.1 through 3.3 give detailed descriptions of the three main subsystems of the apparatus - the vacuum system, the outgassing/deposition measurement system, and the mass spectrometer system. Component manufacturer names and model numbers are given in order to describe the performance capabilities of the Lockheed apparatus. They are not necessarily the only or best components which could be used to build an apparatus capable of executing the test method.

The baseline measurement sensitivity of the apparatus was evaluated by performing the standard test procedure of Section 4 with no material sample in the effusion cell. Section 3.4 presents the results of this test.

3.1 VACUUM SYSTEM

The principal components of the vacuum system are the main vacuum chamber, the pumping system, the interlock chamber, and the mass spectrometer insertion mechanism. The vacuum system, including the main and interlock chambers, effusion cell and mass spectrometer insertion mechanisms, electropneumatic valves, liquid nitrogen reservoirs and shrouds, QCM and effusion cell shutters, and all vacuum feedthroughs were made and assembled by R.J. Munns Mfg., Inc. of San Leandro, CA.

3.1.1 Main Vacuum Chamber

The main vacuum chamber is a stainless steel cylinder 20 inches high by 12 inches diameter, oriented with its axis vertical. It has attachment flanges around its diameter for the pumping system and for the mass spectrometer insertion mechanism. The vacuum interlock chamber attaches to the bottom end flange. The QCM assembly mounting flange is attached to the top of the chamber.

The chamber contains two concentric liquid nitrogen-cooled shrouds to prevent

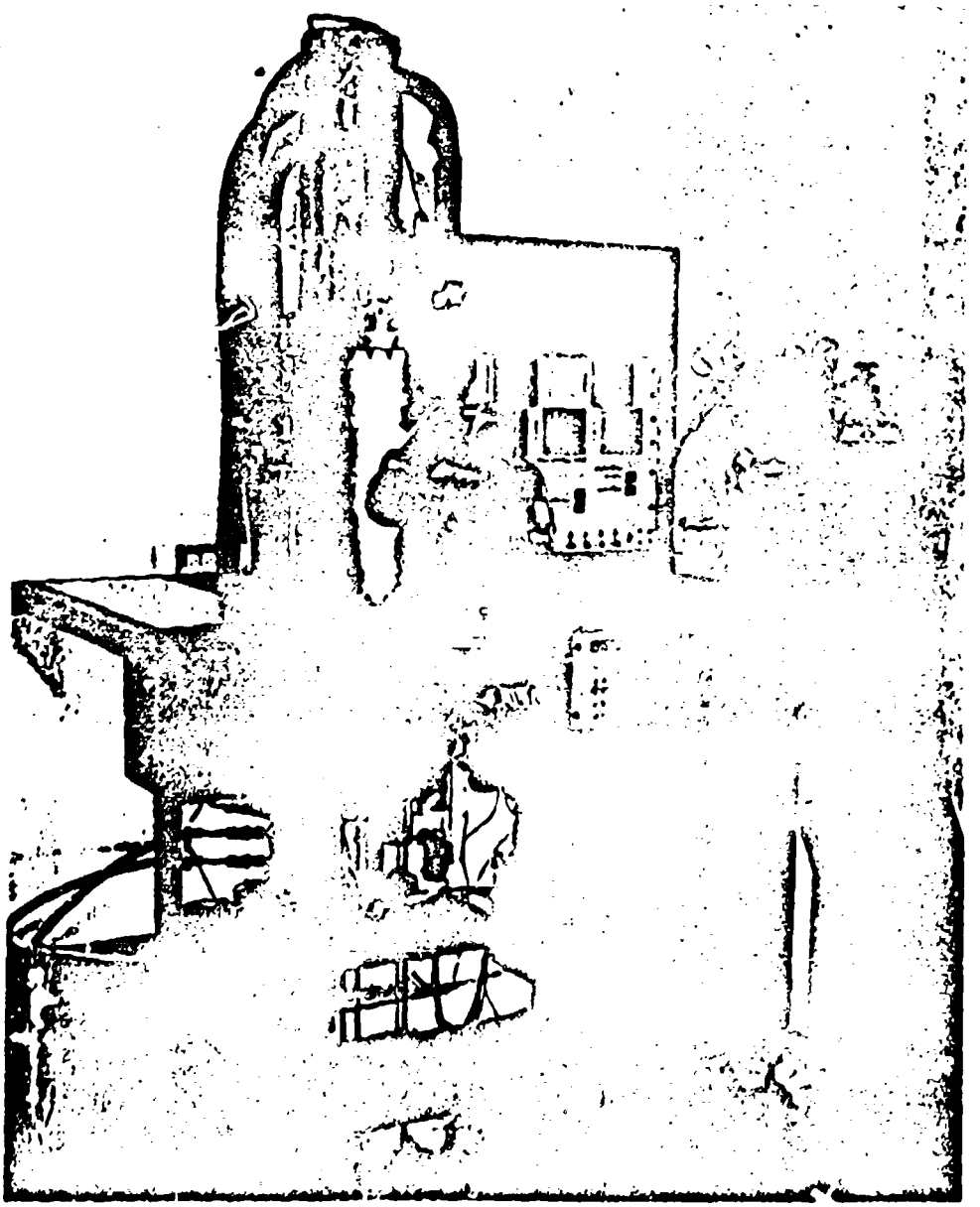


Fig. 3-1 General View of the Test Apparatus

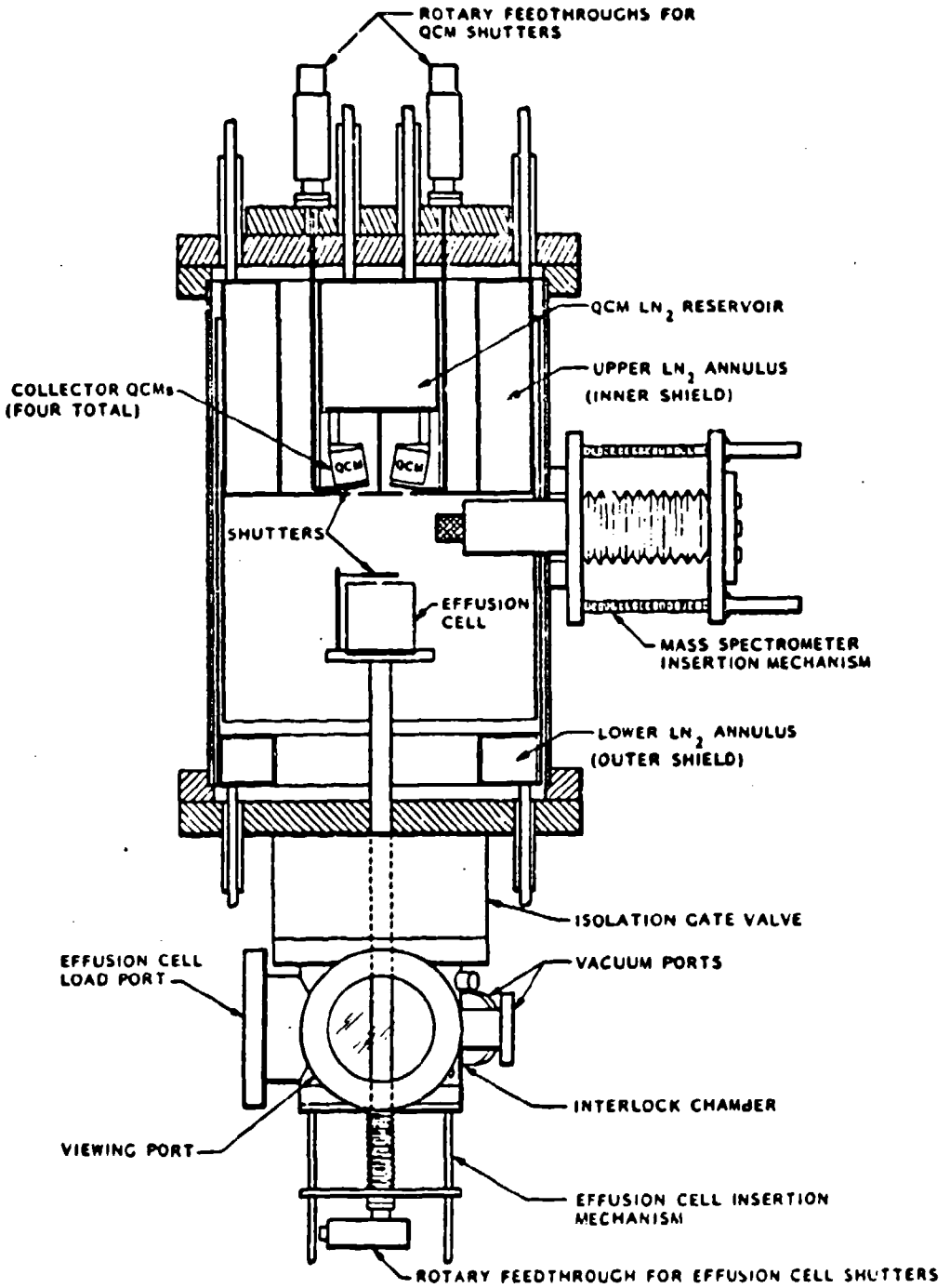


Fig. 3-2 Schematic of the Main Test Chamber

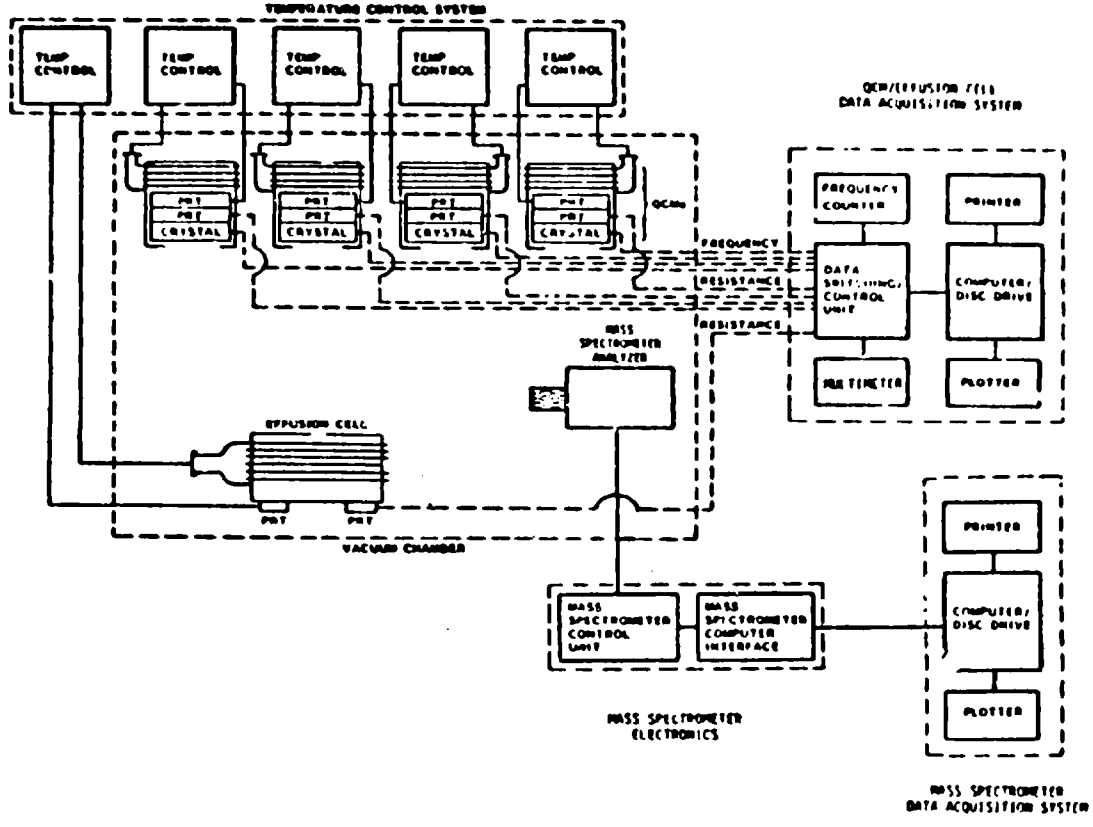


Fig. 3-3 Schematic of the Data Aquisition System

contamination from sources other than the effusion cell from reaching the QCMs and to reduce the heat load on the QCMs by radiation from the environment. A liquid nitrogen reservoir in the upper section of the vacuum chamber cools an inner shroud that surrounds the central volume in which the effusion cell and QCMs are located. A second liquid nitrogen reservoir located in the lower portion of the vacuum chamber cools an outer shroud that surrounds the upper reservoir and inner shroud. This dual shroud system was incorporated in the chamber design to ensure a stable cold-wall temperature around the central region at all times. However, operational experience showed that the outer shroud did not improve the chamber background pressure or shroud temperature stability so the chamber is operated using the inner shroud alone. Openings are provided in the shrouds to improve system pumping speed and to permit insertion of the mass spectrometer analyzer into the evaporating molecular flux fields of the effusion cell and QCMs.

Liquid nitrogen is supplied to the shroud reservoir from 160 liter dewars pressurized to 20 psig. The liquid nitrogen level in the upper reservoir is maintained using a Huntington Model LNC-200 liquid nitrogen level controller. The controller utilizes two temperature probes to determine the low and high levels of liquid nitrogen in the reservoir. The low level probe is positioned near the bottom of the reservoir to sense a low liquid nitrogen level condition and hence open the liquid nitrogen fill valve. The high level probe is placed in a tee in the vent line from the reservoir to detect a high level liquid nitrogen condition and hence close the fill valve. The high level temperature probe is situated in a tee off-axis from the vent line to avoid false triggering due to cold nitrogen gas venting from the reservoir during a fill. A small vent is required downstream from the temperature probe to avoid a vapor lock condition in the tee. A vapor lock would effectively isolate the high-level probe, and would result in an endless fill. Both probes have integral heating elements to avoid false triggering due to frost buildup. Approximately 10 minutes are required to fill the 7.5-liter capacity cold shroud reservoir. The filled reservoir provides shroud cooling for about 10 hours.

3.1.2 Interlock Chamber

An interlock chamber is provided so that the effusion cell containing the test sample can be removed from and replaced in the apparatus without having to warm up and repressurize the main chamber. The interlock chamber is connected to the main chamber via an electropneumatic gate valve. It carries an access port through which the effusion cell can be passed. A window on the front of the interlock chamber aids in placement of the effusion cell on its mount. The chamber can be filled with a clean, dry gas via a repressurization valve or purged by opening a second valve. The interlock chamber also contains a small liquid nitrogen-cooled annular shroud which can be used to precool the effusion cell for

special test applications.

The effusion cell is mounted on the end of a vertical rod and can be moved between the interlock chamber and the main chamber through the open gate valve by moving the rod. The mounting rod linear motion feedthrough is sealed with a bellows rather than a lubricated O-ring to minimize contamination and to ensure ultrahigh vacuum conditions. The isolation valve separating the main chamber from the interlock chamber is activated by a double solenoid so that, in case of a power failure, the valve position will remain unchanged. This insertion mechanism was simple, relatively inexpensive, and functioned well and reliably.

Because the mounting rod is used to hold the effusion cell in position in the main chamber, the gate valve must remain open during an outgassing test. The additional surface area and volume of the interlock chamber adds a pumping load to the main chamber pumping system, which extends the time required for the system to equilibrate after cell insertion and raises the ultimate pressure in the main chamber. If an insertion mechanism were used which would permit the transfer rod to be detached from the effusion cell after the cell had been positioned in the main chamber, the interlock chamber could be isolated from the main chamber and a lower ultimate pressure could be reached more rapidly. However, this type of mechanism would be much more complex mechanically and hence more costly. Also, it would be difficult to arrange electrical connections to the cell, and adjustment of the position of the cell after insertion would require even more mechanical complexity.

3.1.3 Pumping System

The apparatus is equipped with an Alcatel 2020A direct-drive mechanical pump, an Air Products AP-8S cryopump, and a Balzers TPU-050 turbomolecular pump. The 8 l/s capacity mechanical pump is used as a forepump for the turbomolecular pump. Appropriate valving allows the mechanical pump to also be used for initial evacuation of the main chamber and regeneration of the cryopump. The cryopump has a 1500 l/s pumping speed for nitrogen and is used to maintain high-vacuum in the main chamber. It is attached to the chamber via a large diameter elbow which isolates the cryosorbing baffles from heat sources inside the chamber (i.e., mass spectrometer ionizer and effusion cell) without sacrificing much pumping speed as a result of conductance limitations. The turbomolecular pump has a pumping speed of 50 l/s and is used to evacuate the interlock chamber. The turbomolecular pump and the cryopump can be isolated from their respective chambers with electropneumatic gate valves. The gate valves on the high vacuum pumps and the poppet valves in line with the mechanical pump are normally closed to isolate the pumps in case of a power failure.

System pressures are monitored by a Granville Phillips Series 303 vacuum process controller. The controller simultaneously operates two nude ionization gauges and two

convectron gauge tubes. The ionization gauges monitor pressures in the range from 5×10^{-11} to 1×10^{-3} torr, while the convectron gauges measure pressure from 1×10^{-3} torr to one atmosphere. One of the ionization/convectron gauge pairs monitors the main chamber pressure while the other pair monitors the interlock chamber pressure. A third convectron gauge tube is mounted at the inlet to the mechanical pump to permit occasional verification of mechanical pump operation or monitoring of cryopump pressure during regeneration.

Figure 3.4 shows typical curves for the main and interlock chambers before, during, and after effusion cell insertion using the interlock chamber. Before insertion the interlock chamber is at atmospheric pressure and the main chamber is at about 4×10^{-9} torr. At this time, the turbomolecular pump is at operational speed and is pumping on its gate valve. The insertion process starts with evacuation of the interlock chamber. To reduce the risk of pump failure when the gate valve is opened to the atmospheric pressure of the interlock chamber the turbomolecular pump control unit is switched off to allow partial slow-down of the rotors before starting interlock chamber evacuation. The mechanical pump provides foreline pumping to the turbomolecular pump at all times during the insertion process. Interlock chamber evacuation starts when the turbomolecular pump rotational speed has fallen to about 50 percent of its operational value, which occurs about 10 minutes after the control unit is switched off. At this time the gate valve between the interlock chamber and the turbomolecular pump is opened and the turbomolecular pump control unit is switched back on to allow full spin-up of the rotors. Immediately following the opening of the gate valve, the mechanical pump operates in the viscous flow regime by pumping through the accelerating turbomolecular pump. As the interlock chamber pressure drops below 1×10^{-3} torr the free-molecular flow regime is reached, the rotor blades reach full speed, and the turbomolecular pump begins to dominate pumping.

The isolation valve between the main chamber and the interlock chamber is normally opened after about 5 minutes of pumping, at which time the interlock chamber pressure has fallen to about 4×10^{-5} torr. The timing of isolation valve opening represents a compromise, and can be changed to suit the requirements of a particular te It is desirable to reduce the interlock chamber pressure as much as possible before opening the isolation valve to minimize the ensuing rise in main chamber pressure. However, we also need to insert the effusion cell into the main chamber as soon as possible so early time outgassing rate data can be obtained.

When the isolation valve is opened, the pressure in the main chamber rises because of the introduction of gas from the interlock chamber and then slowly falls as the combined system is evacuated by the cryopump.

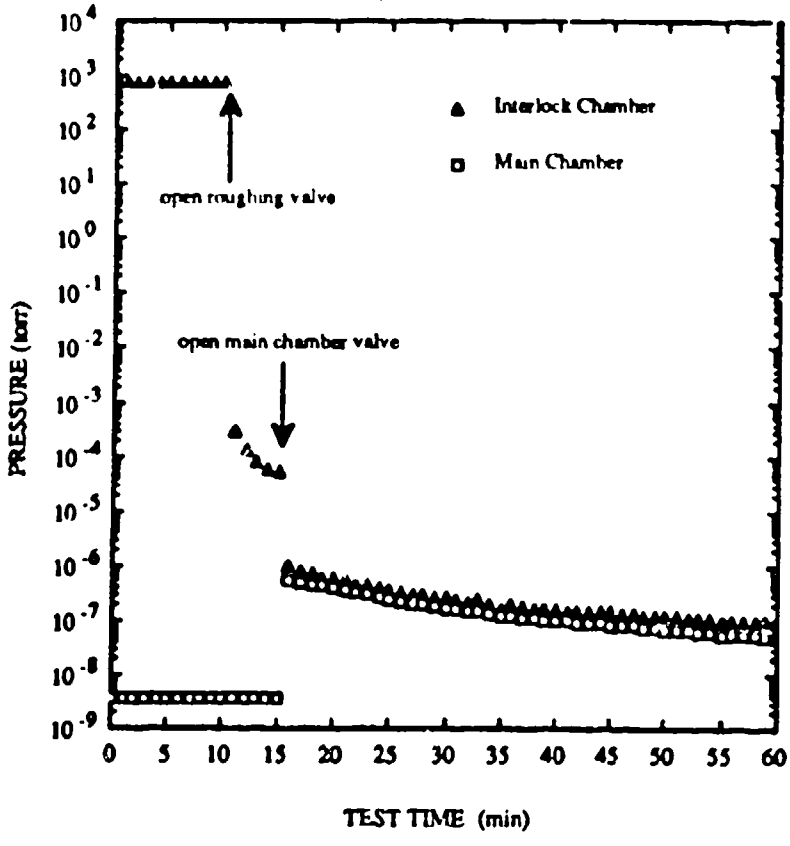


Fig. 3-4 Main and Interlock Chamber Pressures during Effusion Cell Insertion.

3.1.4 Mass Spectrometer Insertion Mechanism

The mass spectrometer head is mounted on a bellows-sealed linear motion feedthrough so that it can be postioned to give the ionizer a better view of either the effusion cell orifice or the QCM crystals during the isothermal outgassing test or QTA/I..S, respectively. The flange supporting the linear motion feedthrough carries a valved inlet line to allow a calibration gas to be introduced to the main chamber in the vicinity of the mass spectrometer ionizer. Perfluorotributylamine (PFTBA) is used for mass scale calibration and can also be used to check the transmission of the mass spectrometer.

3.2 OUTGASSING/DEPOSITION MEASUREMENT SYSTEM

The outgassing/deposition measurement subsystem consists of the QCMs, effusion cell, the temperature control system, and the data acquisition equipment which monitors or controls the other devices.

3.2.1 QCM Assembly

The QCM assembly consists of four QCMs, each with its own mounting strut and shutter, a liquid nitrogen reservoir, a lower shield system, and a chamber mounting flange. The assembly is shown in Figs. 3-5 and 3-6. Figure 3-5 is a general view of the entire assembly. Figure 3-6 shows the QCMs and shutter assembly as viewed from the effusion cell orifice.

The QCMs are QCM Research Inc. Mark 9 units, with aluminum cases, a 77 K to 400 K operating range, unpolished crystals, and full crystal overcoats of Al_2O_3. Each QCM contains two 10-MHz crystals, oscillator electronics, and two platinum resistance thermometers (PRTs). One crystal is used for mass collection while the other is used for reference. One PRT is used for temperature control feedback while the second is monitored by the data acquisition system.

Each QCM is individually suspended from the liquid nitrogen reservoir by bolting its back side to a plate attached to the bottom end of a vertical strut. The top end of the strut is attached to the bottom of the liquid nitrogen reservoir. The four support struts are arranged symmetrically around the chamber axis, so that each QCM has the same view factor to the effusion cell orifice. The support plates are angled at 10° to the support struts so that the axes of the QCMs intersect the chamber axis at a common point about 5.90 inches below the bottom of the QCM liquid nitrogen reservoir. This point is the location of the effusion cell orifice when the cell is placed in its standard position. At this point, the distance from the effusion cell orifice to the face of each of the QCMs is 6.00 inches.

The test procedure calls for the QCMs to be maintained at 90 K or less, 150 K, 220 K, and 298 K. The support struts and plates for the 90 K and 150 K QCMs are made from

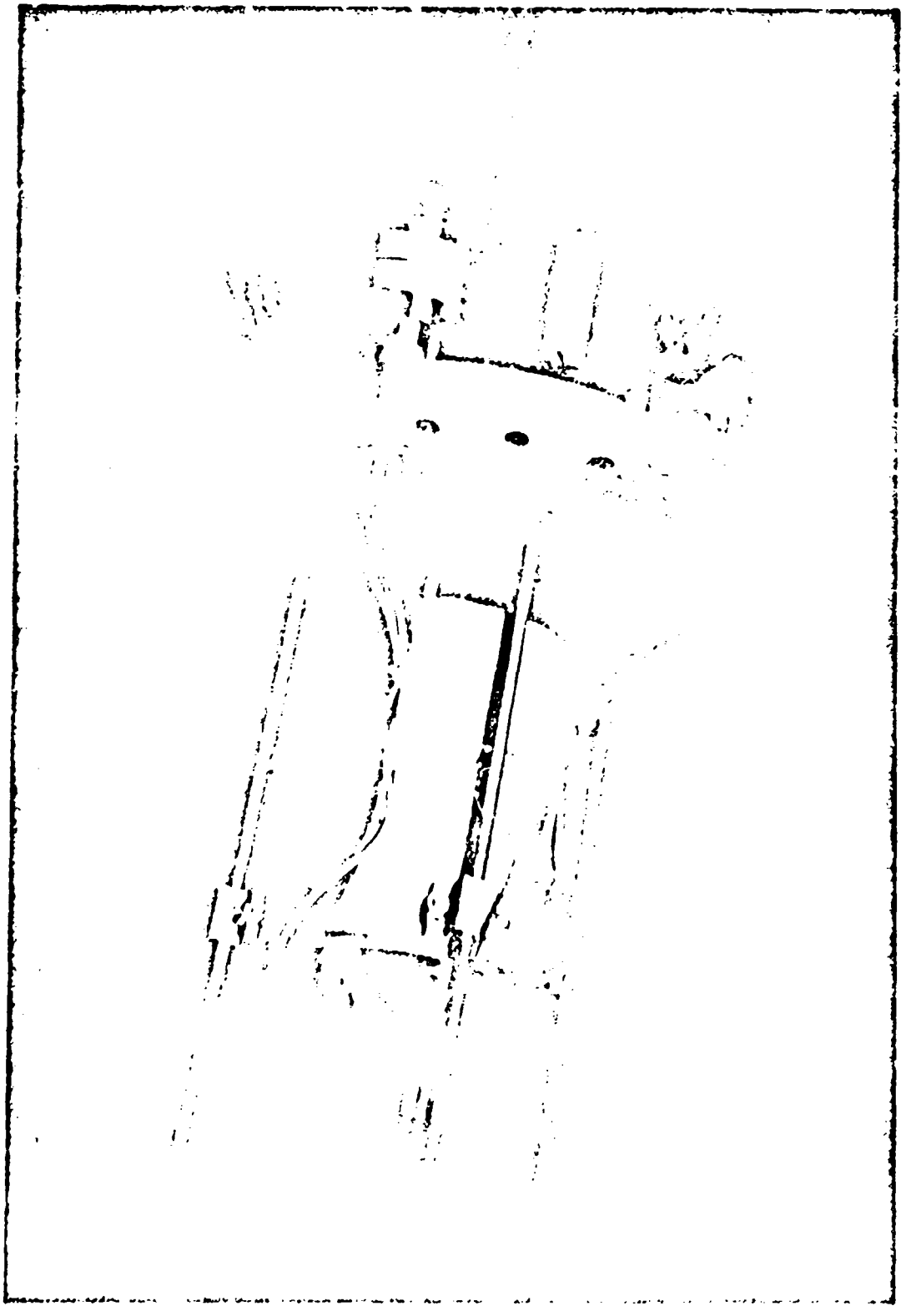


Fig. 3.5 General View of the QCM Assembly

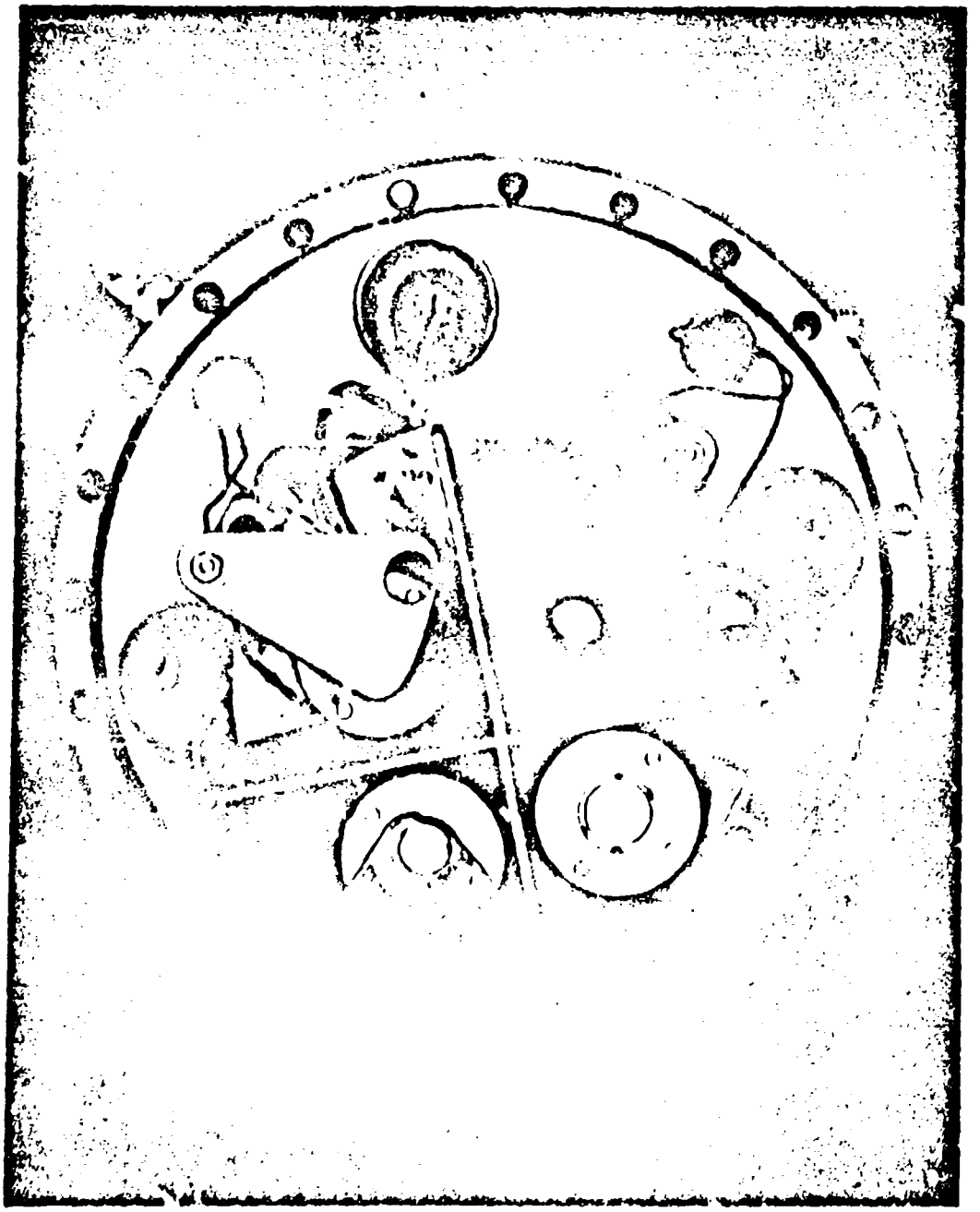


Fig. 3.6 View of the QCM Assembly Looking Up from the Diffusion Cell Orifice

copper, while those for the 220 K and 298 K QCMs are made from stainless steel to minimize the power required for temperature control.

The temperature requirement for the lowest temperature QCM should be as cold as possible. With good heat-sinking, this QCM could be maintained within a degree or so of the 77 K reservoir without difficulty. However, in this case a very large amount of heat would be needed to heat the QCM to 400 K during QTA. The magnitude of the thermal conductance of the cold QCM support strut is, therefore, a compromise between the desire for the lowest temperature possible and the need to be able to heat to 400 K. Because less than perfect heat-sinking was used and because of internal heat generation by the QCM electronics, the lowest attainable QCM temperature is about 88 K.

Each QCM has a shutter which can be operated from outside the chamber. The shutters are cooled by heat sinking their guides to the liquid nitrogen reservoir. Each shutters has three positions - fully closed, fully open, and apertured. In the apertured position, the QCM views its surroundings through a hole in the shutter which has the same diameter as the QCM crystal. The apertured shutter minimizes the number of molecules reaching the mass spectrometer ionizer from sources other than the QCM crystal during QCM heat up, which improves the resolution of QTA/MS.

The QCM assembly is provided with a separate liquid nitrogen reservoir to improve temperature stability by maximizing the degree of isolation from the external environment. The reservoir is vented to the atmosphere to maintain the liquid at 77 K. The liquid nitrogen level in the reservoir is maintained using a Huntington Model LNC-200 liquid nitrogen level controller. This unit uses two temperature probes to determine the low and high levels of liquid nitrogen in the reservoir. The basic operation of this controller was described in Section 3.1.1. However, because of the temperature sensitivity of the QCMs, the liquid nitrogen fill technique differs slightly from the shield reservoir. Liquid nitrogen is normally supplied in storage dewars pressurized to 20 psig, at which pressure the equilibrium temperature is about 85 K. When the reservoir is filled with this warmer liquid, its temperature rises a few degrees and then falls to its one atmosphere equilibrium value of 77 K by evaporation to the environment. In the case of the QCM reservoir, this effect produces a temperature transient in all QCMs, although the extent of the transient on the higher temperature QCMs is partially alleviated by the temperature controllers. The QCM temperature transient can produce temporary frequency variations as high as 100 Hz. These spikes last only several minutes and are usually easily discernable from frequency shifts caused by mass accumulation changes. However, the noise that they introduce into the data is significant in the cases of extremely small deposition rates. The liquid nitrogen fill system was, therefore, modified to eliminate these heat sink temperature variations. An intermediate

reservoir vented to the atmosphere was inserted in the inlet line to the QCM liquid nitrogen reservoir. Liquid nitrogen at 20 psig equilibrates to atmospheric pressure in this intermediate reservoir before filling the QCM reservoir. This technique essentially eliminated temperature and frequency fluctuations induced by liquid nitrogen fills.

The liquid nitrogen reservoir is suspended from a chamber mounting flange which also carries all the electrical, rotary, and liquid nitrogen feedthroughs needed to service the QCMs and the reservoir. The entire QCM assembly is carried by this flange and can be mounted to or removed from the chamber as a unit.

A two part lower shroud system is used to further thermally isolate each QCM. One of the lower shrouds consists of two intersecting perpendicular copper plates attached to the under side of the liquid nitrogen reservoir. The plates extend vertically downwards between each adjacent pair of QCMs in such a manner that the QCMs view these cooled plates and not each other. This eliminates thermal cross talk between the QCMs. The second shroud is a copper cylinder which completely surrounds the QCMs, and is suspended from the bottom of the liquid nitrogen reservoir. This shroud eliminates heat transfer to the QCMs from all peripheral sources, such as ion gauges and the mass spectrometer ionizer. Apertures are cut in the bottom end plate of the shroud so that the QCMs can view the effusion cell orifice. Instrumentation cables to the QCMs are heat sunk to the liquid nitrogen reservoir to eliminate the heat leak down the cables from the room temperature feedthroughs.

A 60-ohm evanohm wire resistance heater is wrapped around the case of each QCM. These heaters allow the QCMs to be temperature controlled above their liquid nitrogen heat sink temperature. The Mark 9 QCM sensor head used in the apparatus is constructed so that all components in the head are in good thermal contact, so the entire sensor head has to be heated to raise the crystal temperature. This means that more electrical power must be provided to the heater than would be needed if only the crystal was being heated, which, in turn, creates a greater temperature disturbance to the apparatus during QCM heating and also necessitates more frequent replenishment of the liquid nitrogen reservoir. Also, other surfaces of the QCM besides the measuring crystal may have collected some contaminant deposit so the mass spectrometer may detect species evaporating from sources other than the crystal during QTA/MS. The most complete solution to this problem is to construct the QCM so that the QCM crystal can be heated while the case is kept at the heat sink temperature. This type of construction has been incorporated into the Mark 16 QCM manufactured by QCM Research Inc. and has become available since the apparatus was built. A Mark 16 QCM has thus been purchased for the apparatus.

3.2.2 Effusion Cell

The cylindrical effusion cell is approximately 2.5 inches in diameter by 2 inches high,

and is machined from aluminum for high thermal conductivity. It has a detachable 0.125-inch-thick cover plate which carries a central 0.125-inch-diameter orifice. The cell is mounted on a plate attached to the top of the interlock insertion rod with its axis coincident with the chamber axis and with its cover plate facing upwards. The cell can be positioned so that the orifice is in the range of 4 to 11 inches from the QCMs. The insertion mechanism is indexed so that the cell can be conveniently placed at the standard distance of 6.00 inches.

The cell can be heated electrically by a 410-ohm evanohm wire resistance heater wrapped around the diameter of the cell. Two PRTs are attached to the cell for temperature control feedback and for temperature monitoring/data acquisition, respectively. Heater and PRT connections are made first via a feedthrough in the wall of the interlock chamber, and then by passing leads through the center of the tubular mounting rod up to female plug terminals integral with the mounting plate. Service connections between the effusion cell and the mounting plate terminals are made using male plug terminals in the base of the cell. An externally-operated shutter permits the effusion cell-to-QCM line of sight to be interrupted.

Prior to insertion into the main chamber, the effusion cell is normally held in the interlock chamber at ambient temperature, although a capability exists to heat or cool it in this location if so desired. After the cell has been inserted into the main chamber and placed in the selected position relative to the QCMs, it is heated as quickly as possible to the test temperature. Using a 115-Vac power supply and the 410-ohm heater, the times required for the cell to reach 75°C and 125°C are 10 minutes and 20 minutes, respectively.

If no power is provided to the effusion cell after insertion into the main chamber, it will cool to about -40°C in 1 hour by radiative heat transfer with the cold walls.

3.2.3 Temperature Control System

The temperatures of the effusion cell and the four QCMs are controlled by balancing electric resistance heating input against heat loss by conduction and radiation to the liquid nitrogen temperature reservoirs and surroundings. Temperature control and heater power are provided by programmable temperature controllers. A Doric DC7032C single-loop temperature controller is used for the effusion cell, while four Doric DC7102C ramp/soak temperature controllers are used for the QCMs. In addition to maintaining temperatures at selected specific values, the Doric DC7102C controllers can perform ramp functions in which QCM temperatures can be increased at a constant rate for the QTA test. Temperature feedback to the controllers is provided by one of the two PRTs inside the QCMs and on the effusion cell.

The Doric controllers are time-proportioning devices that output a logic voltage to external relays. These relays act as open/closed gates for constant voltage heater power

supplies. The total power delivered to a heater is determined by the power supply voltage and the duty cycle of its associated relay. The relays are solid-state and are available in configurations capable of switching either ac or dc voltage sources. At the present time, Gordos Arkansas OAC24 solid-state relays are used to switch ac power sources. The 115-Vac house lines were used as the power supplies. The relays can handle 3 A at 115 Vac, and can be quickly and independently replaced by other modules if dc voltage is preferred for the heater power supplies.

Temperature control systems using time-proportioning controllers combined with a 115 Vac power supply were selected because of their low cost and their successful use by Lockheed in the past. Time proportioning devices control temperature by providing energy pulses rather than continuous power to the object being heated. Since the frequency of a QCM is very sensitive to heat flux variations, the pulse mode of control has the potential for introducing noise into the frequency data. In the previous applications of this type of controller, the QCMs were mounted in bulky aluminum holders, and the heater wire was wound on the outside of the holders. The thermal mass of the holders and the thermal resistance of the path between heater, holder, and QCM crystal were apparently large enough to smooth out the power pulses because no controller-induced QCM frequency noise was encountered. In the present application no holder is used and the heater wire is wound directly on the QCM case, which reduces both the thermal mass and the thermal resistance between heater and crystal. As a result, the QCM crystal temperature responds more strongly to the power pulses, and the frequency data were very noisy. The noise was reduced somewhat by placing ballast resistors of 50 to 100 ohms in series with the QCM heaters, external to the vacuum chamber. These resistors serve as voltage dividers, which reduced the maximum voltage available to heat each QCM, and caused the time-proportioning controllers to supply pulses with lower average power for longer pulse durations. This modification smoothed out the power pulses considerably, but did not completely eliminate frequency noise.

Since the conclusion of this program, some tests have been performed using temperature control by dc voltage modulation and frequency stabilities of ±0.1 Hz have been achieved. The Doric controllers are now being modified to this temperature control configuration by installing internal interface cards which provide continuously variable control signal outputs and interfacing them with controllable dc power supplies.

3.2.4 Data Acquisition System

Data from the QCMs and the effusion cell are acquired, stored, and manipulated by a Hewlett Packard system consisting of a Model 310 computer with a monochrome monitor, a Hewlett Packard 9 '22D 3.5-inch dual disc drive, a Hewlett Packard 2934A impact printer,

and a Hewlett Packard 7550A plotter.

The computer aquires data from the apparatus via a Hewlett Packard 3488A switch-control unit that enables the several platinum resistance thermometers and QCM frequency measurements to be alternately read by a Hewlett Packard 3478A multimeter and a Hewlett Packard 5484A frequency counter, respectively. The multimeter can perform two-wire or four-wire resistance measurements and the counter can measure either the frequency or the period of the QCM output. Before frequency measurements are obtained, the signal from the QCM is processed by a filter/waveform conditioning circuit which produces a low-noise, consistent waveform shape of known amplitude. This reduces noise in the frequency data.

The four-wire resistance measurements are obtained using a 1-mA current and have a 10-mohm resolution with a read time of 0.05 second, which is more than adequate for resolving 0.1°C temperature changes. The desired frequency resolution of 0.1 Hz from the counter requires a gate time of 1.0 second. The time required to measure the four QCM frequencies, the four QCM temperatures, and the effusion cell temperature plus the overhead required by the computer is about 5.5 seconds.

The data from the QCMs and the effusion cell are acquired/stored and retrieved/processed using two separate computer programs. The basic software was developed for a two-QCM system by Lockheed under a prior IRAD project and was modified for four QCMs on Lockheed capital funds. The use of two separate programs means that either a second computer is needed to reduce the data or that testing has to be discontinued during data reduction. Consolidation of the two programs to provide real time output of processed data is feasible, but could not be performed during the program because of funding limitations.

3.3 MASS SPECTROMETER SYSTEM

The mass spectrometer system consists of the mass spectrometer analyzer head, an external electronics unit for supporting the analyzer, and a computer system to control the electronics unit and to acquire, store, and manipulate the data.

3.3.1 Mass Spectrometer Analyzer

The mass spectrometer analyzer was a Balzers Model QMG 511, consisting of an electron impact ionizer, a quadrupole mass filter, and a secondary electron multiplier (SEM). The electron impact ionizer permits detection of the neutral species characteristic of an outgassing flux. An ionizer configuration utilizing a grid ion source was selected because of its open structure, which allows greater sensitivity to the outgassing flux. The quadrupole mass filter was selected because it provides adequate resolution and transmission of species

over a wide mass range at relatively low expense. The filter consists of four molybdenum rods 200 mm long by 8 mm in diameter. The SEM is a CuBe discrete dynode type which provides signal gains of up to 10^8 for increased sensitivity. The analyzer has a sensitivity of 1×10^{-3} A/torr for argon and a detection limit of 1×10^{-16} torr.

3.3.2 Mass Spectrometer Electronics

The mass spectrometer electronics unit supplied with the Balzers Model QMG 511 analyzer is used for normal operational adjustments to the mass spectrometer ionizer, quadrupole filter, and electron multiplier. Internal power supplies allow adjustment of electron energy and emission in the ionizer and electron multiplier gain. The quadrupole filter can be tuned to allow only a single mass to be transmitted or to sweep over a selected mass range. The specific Balzers mass spectrometer chosen for the test apparatus has a mass range of m/e=2 to 1023, unity resolution, scan times down to 1 ms/amu and computer compatibility. The expression m/e refers to the mass-to-charge ratio of the ion being detected. The mass is usually expressed in atomic mass units (amu) and for this mass spectrometer configuration the charge is a positive integer. For singly-ionized (e = 1) argon (mass = 40 amu) the detected ion would appear at m/e = 40. For doubly-ionized argon, the ion would appear at m/e = 40/2 = 20. The level of ionization is a function of the species being detected and the ionizer parameters. With the exception of the following apparatus specifications, this report adopts the more rigorous convention of referring to detected ions by their m/e location. Where the term amu is used, it is assumed that the detected ion is singly ionized (e = 1).

For the materials test program, a mass range of m/e=10 to 500 was judged to be sufficient for characterizing outgassed species. A 0.3-amu window was sampled around each nominal mass to determine the ion intensity at that integer mass value. This helped correct for small errors in calibration and the possibility of ions with large mass defects. A 0.3-amu sweep width allowed 4 sampling points per integer amu. An integration time of 3 milliseconds per sampling point was used to determine the ion intensity, and each point was integrated twice. These values were determined by experience with the mass spectrometer in this application. These parameters, together with a small amount of overhead time in the controller, resulted in a scan time of 13.75 seconds for the m/e=10 to 500 scan.

3.3.3 Data Acquisition System

Automatic acquisition of mass spectra and control of the Balzers mass spectrometer is performed with an IBM AT personal computer, using a computer interface and software package called Microtrace, produced by Teknivent Corporation. Additional peripheral equipment supporting the IBM AT are 512-Kbyte RAM, a 1.2-Mbyte floppy disk, and a 30-Mbyte Winchester hard disk. Because of the large amount of data being collected, a

60-Mbyte Sysgen magnetic tape unit is also included in the computer system to permit occasional down-loading of the hard disk to a separate storage library. Hard copy printouts or plots can be obtained from either a Hewlett Packard LaserJet Series II printer or a Hewlett Packard 7550A plotter.

The Teknivent interface and computer software can control and monitor all mass spectrometer operating parameters. It allows simultaneous acquisition and processing of the data run being acquired or the processing of previously acquired data. The Wiley/NBS standard mass spectra library containing over 70,000 compounds has also been purchased from Teknivent by Lockheed and can be accessed by the computer for mass spectra searching and matching.

3.4 APPARATUS BASELINE PERFORMANCE

In order to determine the magnitude of the apparatus background contamination levels and the baseline apparatus performance, the isothermal outgassing and QTA test procedures of Section 4 were performed without a material sample in the effusion cell.

3.4.1 Empty Cell Isothermal Outgassing Test

The two possible sources of background contamination during the isothermal outgassing test are the chamber itself and the effusion cell. The chamber has a very clean design and the QCMs are almost totally surrounded by liquid nitrogen-cooled cold walls, so the contribution of the chamber was very small. The QCM frequencies were monitored for several days with the effusion cell removed from the chamber and the isolation valve closed. The QCM frequencies increased less than 1 Hz/day, which confirmed the low chamber background.

During an isothermal outgassing test, the QCMs will detect species outgassed by the effusion cell as well as by the sample. Although the cell is cleaned thoroughly between tests, it will inevitably regain moisture from the laboratory atmosphere when it is removed from the apparatus for exchange of samples. The magnitude of effusion cell outgassing was determined by performing the full test procedure with no sample in the cell. The test was run at 125°C since the effusion cell outgassing rate will be highest for this temperature. During this test, the 90 K QCM indicated a 60 Hz increase in frequency after 24 hours, while the three higher temperature QCMs experienced no appreciable increase in frequency. The lack of accumulation on the higher temperature QCMs indicated that the outgassing products from the cell were water vapor and/or high volatility solvents. The 60-Hz frequency increase corresponds to a 24-hour total mass loss of less than 0.0001 g. For a typical sample with a mass of 1 g and an exposed area of 5 cm^2, this mass loss is equivalent to a 24-hour percentage mass loss of less than 0.01 percent and an average outgassing rate

during the first 24 hrs of less than 2 x 10^{-10} g/cm^2 s. These values are negligibly small in comparison to typical outgassing data. We, therefore, concluded that the effect of effusion cell outgassing on the data could be neglected, and it was not necessary to perform blank tests before each material isothermal outgassing test.

3.4.2 Empty Cell QTA Test

A standard QTA test was performed on the 90 K QCM following the empty cell isothermal test of Section 3.4.1. During QTA, the QCM frequency decreased 150 Hz in the temperature range from 90 K to 150 K and decreased another 150 Hz between 300 K and 400 K. Evaporation of the collected water accounts for 60 Hz of the first frequency shift, while the remaining 90-Hz shift in the low temperature region and the entire 150-Hz shift in the high temperature region are due to the variation of QCM frequency with temperature. These frequency shifts correspond to an average thermally-induced rate of frequency change of less than 1 Hz/min. In fact, the rate of change of QCM frequency is not constant and can have values several times higher than 1 Hz/min over short temperature ranges. Because of these thermal effects on QCM frequency, QTA cannot detect deposit evaporation-induced frequency changes less than about 10 Hz/min, which corresponds to an evaporation rate of about 10^{-9} g/cm^2 s.

The QCM frequency data also show fast fluctuations as high as 50 Hz/min which are induced by high frequency changes in the heat flux through the QCM crystal produced by the on/off method of power modulation used by the temperature ramp controllers. This phenomena and a method to eliminate it were discussed in Section 3.2.3.

Section 4

TEST PROCEDURE

This section describes the standard test procedure. The procedure specifies the way in which sample preparation, data measurement, and data reduction are performed. The combination of this procedure and the apparatus described in Section 3 defines the standard test method developed on this program.

4.1 MATERIAL TEST SAMPLE PREPARATION

This section describes how the material test sample should be prepared and documented.

4.1.1 Test Sample Description

The test sample should be described as completely as possible. For standard aerospace materials, full manufacturing, procurement, and acceptance documentation is normally available and should be provided. For developmental materials, enough information should be given to clearly identify its origins. This information should include, for example, the chemical nature of the material, how the sample was prepared and who prepared it, the name of the program, organization, and/or personnel from which the material was obtained or which/who is responsible for developing it.

4.1.2 Test Sample Geometry

Because outgassing kinetics depend upon the thickness of the material and/or the surface area exposed to vacuum, the geometry of a test sample must be appropriately constrained. Where possible the test sample should have the same geometry as the material has in an actual application. For materials which are used in more than one geometry, the test sample geometry should be selected such that the outgassing rate for other material geometries can be inferred from the outgassing rate data measured for the test sample. The test sample geometry that satisfies this requirement will depend on the physical processes involved in outgassing for the specific test material.

Outgassing from materials such as adhesives and potting compounds is diffusion-controlled, so the outgassing rate depends on the distance between the interior of the sample and a free surface. For these materials, it is possible in principle to predict the outgassing rate for any arbitrary material geometry by inserting the appropriate dimensions into the diffusion equations if the diffusion coefficients of the outgassed species are known. It is possible to infer these diffusion coefficients from isothermal outgassing rate data for samples whose geometry is such that internal diffusive flow is one-dimensional

[7]. For materials for which outgassing is diffusion-controlled, the test samples should, therefore, be prepared in a geometry which results in one-dimensional internal diffusion. However, determination of diffusion coefficients from outgassing data is technically difficult, particularly if there are many outgassed species, so this determination is not part of the standard test procedure and is left to the user of the data.

Outgassing from greases and lubricants is the result of evaporation which is a surface phenomenon. The outgassing rate depends only on the surface area and is independent of the geometry or the mass of the sample. Greases and lubricants should therefore be placed in holders which maintain a constant exposed surface area as the sample is depleted.

With the above considerations in mind, samples from different material classes should be prepared as follows. The material classes identified are those used by NASA Goddard Space Flight Center for reporting ASTM E 595 data [8].

Adhesives: These materials should be prepared in a holder which causes the internal diffusion flow to the free surface to be one-dimensional.

Cable Insulation and Shrink Tubing: These materials should be tested in as-supplied geometry.

Conformal Coatings: These materials should be applied to a nonoutgassing substrate large enough to provide a representative coating sample. The substrate should then be cut into sections small enough to fit into the effusion cell.

Electrical Components: These materials should be tested in as-supplied form.

Electrical Shields: These materials should be tested in as-supplied geometry.

Film and Sheet Material: These materials should be tested in as-supplied geometry.

Foams: Where applicable these materials should be tested in as-supplied thicknesses. Sample dimensions should be selected so as to minimize edge effects.

Grease and Lubricants: These materials should be placed in dish-type holders. The holders should be shaped so that the exposed surface area remains constant as the sample mass is depleted.

Lacing Tape and Cord Tie Cables: These materials should be tested in as-supplied geometry.

Laminates and Circuit Boards: These materials should be tested in as-supplied geometry.

Marking Materials and Ink: These materials should be applied to nónoutgassing substrate such as aluminum foil.

Molding Compounds: These materials should be tested in the molded form.

Paints, Lacquers and Varnishes: These materials should be applied to a nonoutgassing substrate large enough to provide a representative coating sample. The

substrate should then be cut into sections small enough to fit into the effusion cell.

Potting Compounds: These materials should be prepared in a holder which causes the internal diffusion flow to the free surface to be one-dimensional.

Rubbers and Elastomers: These materials should be tested either in as-supplied geometry or in a typical application geometry, depending on whether the particular material is preformed or is cured after application.

Tapes: These materials should be applied to a nonoutgassing substrate. Tape samples should be long enough for outgassing from the ends to be negligible compared to outgassing perpendicular to the length.

Thermal Greases: These materials should be placed in flat dish-type holders. The holders should be shaped so that the exposed surface area remains constant as the sample mass is depleted.

4.1.3 Test Sample Mass and Size

The test sample mass should be large enough to provide a measurable accumulation of outgassed products on the QCM, but should not be so large that the QCM becomes overloaded before the end of a test. Experience with both high and low-outgassing materials has shown that these conditions can usually be met if the sample weight is between 1 and 10 g. The test sample weight should be determined before a test using a laboratory balance having a readability of 10 μg or less.

For the present apparatus, the sample dimensions should be selected such that it fits into the 2.5-inch-diameter by 2-inch-high effusion cell. The sample dimensions and surface area should be measured to an accuracy of 2 percent.

4.1.4 Test Sample Handling and Storage

Samples should be handled only with gloves or clean instruments prior to testing and should be stored in a clean area in covered glass dishes. Nominal preparation and storage conditions should be 23°C ±2°C and 40-60 percent relative humidity.

4.1.5 Effusion Cell Preparation

The effusion cell must be solvent cleaned and vacuum baked before insertion of a new sample. An initial solvent cleaning using toluene, freon, methyl ethyl ketone or acetone should be used to remove any residual sample contamination from the cell. The effusion cell should then be subjected to a second solvent cleaning with acetone.

Following cleaning, the cell should be heated to 125°C in a vacuum of less than 1×10^{-6} torr for at least 12 hours. The effusion cell bakeout should be performed in the interlock chamber. The cell should remain under vacuum until the next test is to be started. At that time, the interlock chamber should be repressurized with dry nitrogen gas before the effusion cell is removed.

4.2 MEASUREMENT PROCEDURE

The major elements of the test are an isothermal outgassing/deposition kinetics test, a QCM thermal analysis (QTA) of the collected outgassing species, and an off-line gas chromatography/mass spectrometry (GC/MS) analysis.

4.2.1 Isothermal Outgassing/Deposition Test

This section describes the isothermal outgassing/deposition test procedure, and the test parameters for the standard test method.

4.2.1.1 Test Procedure

Table 4-1 gives an outline of the isothermal outgassing/deposition test procedure.

The test sample is prepared and placed in the cleaned effusion cell using the procedures of Section 4.1. The effusion cell is placed on its holder in the interlock chamber and electrical connections to the cell are made and verified. The interlock chamber is closed to the atmosphere. The effusion cell shutter is closed so that the cell can pass through the isolation valve opening into the main chamber.

Prior to effusion cell insertion, the main chamber pressure should be in the mid to low 10^{-9} torr range, the liquid nitrogen-cooled shrouds should be cold, the QCMs should be at their designated operating temperatures, and the mass spectrometer and its electronics should be at stable operating temperatures. The position of the mass spectrometer analyzer should be adjusted using the bellows feedthrough so that its ionizer can sample the outgassing flux from the effusion cell without obstructing the line-of-sight between the cell orifice and the QCM surfaces. All QCM shutters should be closed in order to minimize the collection of chamber background contaminants when the interlock chamber isolation valve is opened for insertion of the effusion cell.

At test time zero computer acquisition of QCM frequencies and temperatures, effusion cell temperature, and mass spectrometer peak heights is initiated. The mass spectrum measured at this time is the spectrum of the empty chamber. This spectrum is assumed to be the background which obtains throughout the test, and will be subtracted from all mass spectra recorded during the test to determine the spectra due to outgassed products.

The nominal time between data points is arbitrary and is selected to be short enough to provide sufficient resolution, but not so short that the data acquisition system becomes saturated before the end of a test. The time between data points used in this program was 5 minutes.

The turbomolecular pump is turned off at exactly test time zero to allow it to slow down prior to exposing it to the atmospheric pressure of the interlock chamber. Sudden exposure of the turbomolecular pump to high pressures in order would damage the rotors

Table 4-1

Test Procedure - Isothermal Outgassing/ Deposition Test

TEST TIME	EVENT
Preset	Determine sample area and mass Place sample in effusion cell Place cell in interlock chamber Position mass spectrometer to view outgassing flux Close all shutters
0 min	Begin data acquisition at 5 minute intervals Record main chamber background mass spectrum Turn off turbomolecular pump
5 min	Record main chamber pressure
10 min	Open gate valve between turbomolecular pump and interlock chamber Turn on turbomolecular pump
15 min	Record interlock chamber pressure Open isolation valve between interlock chamber and main chamber Insert effusion cell to standard position 6.00 inches from QCMs Open QCM and effusion cell shutters Start effusion cell heating Close turbomolecular pump gate valve
20 min	Record first data point of the outgassing test Record main chamber pressure
5 days	Store computer data files Adjust effusion cell temperature to 25°C and close cell shutter Remove effusion cell to interlock chamber Close interlock chamber isolation valve and repressurize with nitrogen Remove effusion cell from interlock chamber when cooled to 25°C Remove sample from cell and weigh on laboratory balance immediately

if they were rotating at their normal operating speed of 90,000 rpm. The timing of turbomolecular pump shutdown is a function of the particular pump used and was selected on the basis of experience.

The gate valve between the turbomolecular pump and the interlock chamber is opened at a test time of 10 minutes (0.167 h). At this time, full power is restored to the turbomolecular pump to return it to full rotational speed. The interlock chamber is

evacuated initially by the mechanical pump through the slowly turning turbomolecular pump. By the time the mechanical pump has reduced the pressure to the free molecular flow regime, the turbomolecular pump has regained full operational speed and pumping capacity.

The isolation valve is opened and the effusion cell is inserted into the main chamber when the pressure in the interlock chamber has been sufficiently reduced. The time selected for effusion cell insertion is a compromise between the need to reduce the interlock chamber pressure sufficiently to minimize the pressure surge in the main chamber as the isolation valve is opened and the need to acquire data as soon as possible after the beginning of evacuation. The nominal insertion time in the standard procedure is 15 minutes (0.25 hour), by which time the interlock chamber pressure has been reduced to about 4×10^{-5} torr.

The effusion cell is positioned at a selected location relative to the QCMs by adjustment of the cell mounting rod. A nominal QCM-to-cell distance of 6.00 inches is used in the standard test procedure, so the mounting rod is indexed at this position for convenience. The QCM-to-cell distance can be reduced or increased to allow for materials with unusually low or high outgassing rates, respectively.

When the cell has been positioned, the QCM and effusion cell shutters are opened and the effusion cell is heated to the specified test temperature. The gate valve between the turbomolecular pump and the interlock chamber is closed at this time to eliminate the possibility of main chamber contamination by oil vapor backstreaming from the mechanical pump through the turbomolecular pump and interlock chamber.

After completion of the startup activities the test is almost fully automatic. The only activities required during the test are replacement of the liquid nitrogen dewars when empty and monitoring the health and status of the apparatus.

At the end of the test period, the effusion cell temperature controller is reset to 25°C, and the cell shutter is closed. The cell is then moved from the main chamber back to the interlock chamber by moving the mounting rod. The interlock chamber is isolated from the main chamber by closing the gate valve and is repressurized with dry nitrogen gas. When the cell temperature has stabilized at 25°C, the effusion cell is removed from the interlock chamber and the sample is taken out of the cell and weighed on a laboratory balance. The post test weighing should be performed as soon as possible after the sample has been reexposed to the atmosphere to minimize the amount of readsorption of water vapor.

4.2.1.2 Test Parameters

The following test parameters were selected for the isothermal outgassing/deposition test by industry consensus at the industry workshop held at Lockheed in November 1984

Sample Temperature: The material is to be tested at three temperatures. A new sample is to be used for each test. The standard test temperatures are 125°C, 75°C, and 25°C. The first two isothermal outgassing tests are performed at the standard sample temperatures of 125°C and 75°C. The temperature of the third outgassing test is selected on the basis of the results of the 75°C test. If the outgassing rate at 75°C is significant, the third test is performed at the standard 25°C temperature. If the outgassing rate at 75°C is very small and it is likely that the outgassing rate at 25°C would be negligible, the third test is performed at 100°C.

The 125°C test temperature was selected because it is a typical high space system qualification temperature and it provides correlation with the ASTM E 595 test. The 25°C test temperature was selected because it is typical of an uncooled spacecraft surface. The 75°C temperature was selected because it is midway between the first two temperatures.

QCM Collection Temperatures: The four QCMs are maintained at temperatures of 90 K or less, 150 K, 220 K, and 298 K, respectively.

The 90 K QCM collects essentially all of the outgassing flux. The data from this QCM are used to calculate total outgassing data. The specified 90 K temperature allows for a 13 K temperature difference between the QCM and the 77 K reservoir to conduct the heat generated by the QCM electronics through the thermal resistance of the attachment strut (Section 3.2.1).

The 150 K, 220 K, and 298 K QCMs are used to measure deposition data as a function of surface temperature. The 150 K QCM temperature was selected because it is high enough to prevent deposition of water vapor and most solvents. The 298 K QCM was selected because it is representative of a typical uncooled spacecraft surface. The 220 K QCM temperature was selected because it is midway between 150 K and 298 K.

Test Duration: The nominal test duration is 5 days.

The test duration is a compromise between the need for long term data to support modeling and the need to control the cost per test. The rate of change of outgassing rate diminishes rapidly with time because of kinetic considerations, so extension of the test period generates less and less useful information per unit time. On the other hand, the test should run at least several days to clearly establish trends. The 5-day test period allows a regular weekly test schedule to be established with 2 days for sample turnaround between tests. Extension of the test period to 2 weeks would increase the cost per test by a factor of two while providing minimal additional information.

Industry consensus has agreed that a test could be terminated before 5 days have elapsed if the outgassing rate becomes immeasurably small or if the outgassing rate shows negligible change with time.

4.2.2 QCM Thermal Analysis

At the end of the isothermal test, the deposits collected on all four QCMs are subjected, in turn, to QCM thermal analysis (QTA). In QTA, the QCM is heated in a controlled manner while the behavior of the deposit is measured as a function of temperature. The QTA test includes thermogravimetric analysis (QTGA), in which the mass of the deposit remaining on the crystal is measured directly by the QCM and mass spectrometer analysis (QTA/MS). In QTA/MS the molecular flux evaporating from the QCM crystal is analyzed by a mass spectrometer.

An outline of the operations performed during QTA is presented in Table 4-2. Before beginning QTA, the mass spectrometer analyzer head is repositioned to shorten the line of sight between the ionizer and the crystal of the QCM to be tested. In the Lockheed apparatus, the geometry of the linear motion mass spectrometer feedthrough allows the ionizer to be positioned directly under the 90 K or 298 K QCMs. For viewing the 150 K and 220 K QCMs, the ionizer is positioned on the apparatus center line.

The shutters of the QCMs not being heated are closed to reduce the possibility of these QCMs becoming contaminated by the flux evaporating from the QCM under test. The shutter for the test QCM is placed in the apertured position so that the ionizer views only the QCM crystal. This reduces the probability that species evaporating from surfaces other than the QCM crystal will be detected by the mass spectrometer.

After the QCM shutters have been properly positioned, the QTA test is started. The QCM temperature and frequency and the mass spectrometer peak heights are recorded at 1-minute intervals. The frequency of a QCM crystal is sensitive to heat flux through the crystal, so the heating rate must be low enough to keep heat flux-induced frequency changes within acceptable limits. However, the heating rate must not be so low that the time required for QTA becomes excessive. Published data [9] indicate that errors in frequency due to heat flux will be acceptably low if the heating rate is 1°C/min or less. The nominal maximum heating rate selected for the test method is, therefore, 1°C/min.

When the QCM has reached 125°C, the test is terminated and the QCM is allowed to cool to its operational temperature for the isothermal test. A maximum temperature of 125°C is selected for QTA because this value is equal to the maximum sample temperature. All deposited outgassed species should evaporate at or below this temperature unless they have changed chemically since deposition.

After the QTA test procedure has been repeated for all four QCMs, the mass spectrometer is returned to its position for the isothermal test.

Table 4-2

Test Procedure - QCM Thermal Analysis

- Close shutters to all QCMs except the test QCM
- Place the test QCM shutter in the apertured position
- Reposition the mass spectrometer to obtain the best possible view of the test QCM
- Start computer acquisition of QCM frequency and temperature, and mass spectrometer peak heights at 1-minute intervals
- Start heating the QCM at 1°C/min
- Terminate heating and data collection when QCM reaches 125°C
- Place the QCM shutter in closed position
- Allow the QCM to cool back to its normal operating temperature
- Repeat the procedure for all four QCMs

4.2.3 Gas Chromatography/Mass Spectrometry

In the GC/MS analysis, the material sample is heated to a selected test temperature in a 10 psig helium gas environment for about 15 minutes. The gases evolved from the sample are collected by flowing the helium through a liquid nitrogen trap. The helium flow is then turned off, the liquid nitrogen dewar is removed, and the trap is heated up. The collected species evaporate and flow through the chromatograph capillary column. Each species flows through the column at a different rate depending on the species molecular weight. The molecular stream leaving the column is monitored by a mass spectrometer, which repeatedly scans a selected mass range and records the mass spectrum and the total ion count as a function of time since the liquid nitrogen was removed from the trap.

GC/MS analyses are performed on material samples at temperatures of 125°C and 200°C. Two temperatures are selected to provide correlation with the isothermal outgassing test data. The species identified by the 125°C GC/MS test include only species which are also evolved in the highest temperature (125°C) vacuum outgassing test. However, all species evolved in the 125°C vacuum outgassing test may not be evolved in the 125°C GC/MS test because of the inhibiting effect of the helium gas pressure. The species identified by the 200°C GC/MS test will include most if not all species outgassed in vacuum at 125°C, but because of the higher sample temperature it may also detect thermal

degradation products not found in the vacuum outgassing test. The 200°C temperature was selected as a result of development testing under Phase II (Section 2.3.1.4 of Reference 6).

To ensure detection and identification of all volatiles the mass spectrometer incorporated in the GC/MS apparatus should scan a mass range of at least m/e = 2 to 1000, where m/e is the mass to charge ratio.

4.3 DATA REDUCTION

This section describes the procedures used to calculate the test output data from the experimentally-measured data.

4.3.1 Isothermal Outgassing/Deposition Data

This section presents the equations and methods used to calculate total outgassing data, total deposition kinetics data, and the contributions of each species to the total outgassing and deposition kinetics.

4.3.1.1 Total Outgassing and Deposition Data

Section 4.3.1.1.1 presents the equations used to calculate the amount of mass deposited and the rate of mass deposition on all four QCMs from measured frequency data.

Section 4.3.1.1.2 presents the equations used to calculate the QCM-to-effusion cell orifice view factor. Sections 4.3.1.1.3 and 4.3.1.1.4 present the equations used to calculate the outgassing and deposition kinetics data, respectively, from QCM mass deposition data and the QCM-to-effusion cell orifice view factor. Outgassing kinetics data are calculated from mass deposition data for the 90 K QCM, while deposition data are calculated from mass deposition data for the 150 K, 220 K, and 298 K QCMs.

4.3.1.1.1 QCM Mass Deposition Data

The mass deposition quantities of interest are the total amount deposited and the rate of deposition on a QCM as functions of time. These quantities are calculated from the measured frequency data for the four collector QCMs, which can be written in the form $f(T_q,T_s,t_i)$, where f is the frequency, T_q is the temperature of the collector QCM, T_s is the sample temperature, and t_i is the time at which a data point is acquired.

4.3.1.1.1.1 Total Mass Deposited The mass deposited on a QCM at temperature T_q from a sample at temperature T_s at time t_i is $m_d(T_q,T_s,t_i)$, calculated using Eq. (4.1)

$$m_d(T_q,T_s,t_i) = K_s\,(f(T_q,T_s,t_i) - f(T_q,T_s,0)) \qquad (4.1)$$

where $f(T_q,T_s,t_i)$ and $f(T_q,T_s,0)$ are the frequencies of the QCM at times t_i and zero,

respectively, and K_s is the QCM mass sensitivity constant. For the 10-MHz AT-cut crystals used in the Lockheed apparatus, K_s, is equal to 4.43×10^{-9} g/cm^2 Hz [2].

4.3.1.1.1.2 Mass Deposition Rate The rate of mass deposition on a QCM at temperature T_q from a sample at temperature T_s at time $(t_{i+1}+t_i)/2$ is $\dot{m}_d(T_q,T_s,(t_{i+1}+t_i)/2)$, calculated using Eq. (4.2)

$$\dot{m}_d(T_q,T_s,(t_{i+1}+t_i)/2) = K_s\,((f(T_q,T_s,t_{i+1}) - f(T_q,T_s,t_i))/(t_{i+1}-t_i)) \qquad (4.2)$$

where $f(T_q,T_s,t_i)$ and $f(T_q,T_s,t_{i+1})$ are the QCM frequencies measured at times t_i and t_{i+1}, respectively.

4.3.1.1.2 QCM-to-Effusion Cell Orifice View Factor

The QCM-to-effusion cell orifice view factor, F is calculated using Eq. (4.3)

$$F = (W_c(L/R)/B(\phi_1))\,(\pi r^2/(\cos\phi_1\cos\phi_2)) \qquad (4.3)$$

where

- r = distance between the effusion cell orifice and the QCM crystal
- ϕ_1 = angle between QCM-to-cell orifice line of sight and orifice normal
- ϕ_2 = angle between QCM-to-cell orifice line of sight and QCM normal
- L = length of the effusion cell orifice
- R = radius of the effusion cell orifice
- $W_c(L/R)$ = Clausing transmission probability for the effusion cell orifice [10]
- $B(\phi_1)$ = Clausing angular flow distribution function for the effusion cell orifice [6]

These parameters can be varied from apparatus to apparatus and from test to test without invalidating the test method, so the test procedure does not assign specific values to them. The values of the parameters that were used in the Lockheed apparatus for the tests performed on this program were as follows:

- r = 15.24 cm (6.00 in)
- ϕ_1 = 10°
- ϕ_2 = 0°
- L = 0.310 cm (0.122 in)

$$R = 0.159 \text{ cm } (0.0625 \text{ in})$$

$$W_c(L/R) = 0.52$$

$$B(\phi_1) = 0.8908$$

Substitution of these values in Eq. (4.3) gives a value for F of 432.4 cm^2.

4.3.1.1.3 Total Outgassing Data

The outgassing kinetics data of interest are the total mass loss and the total outgassing rate per unit area. These quantities are calculated from mass deposition data for the 90 K QCM and the QCM-to-effusion cell orifice view factor. In addition, the ex situ total mass loss is calculated from pre- and post-test ex situ sample weighings.

4.3.1.1.3.1 Total Mass Loss The total mass loss at time t_i from a sample at temperature T_s is $TML(T_s,t_i)$, calculated using Eq. (4.4)

$$TML(T_s,t_i) = m_d(90\,K,T_s,t_i)\,F/m_{si} \qquad (4.4)$$

where $m_d(90\,K,T_s,t_i)$ is the mass deposited on the 90 K QCM found from Eq. (4.1), F is the QCM-to-effusion cell orifice view factor given by Eq. (4.3), and m_{si} is the pre-test sample weight.

The sample total mass loss for a 125°C sample after 24 h of vacuum exposure, i.e., TML(125°C,24 h), is the QCM collection method equivalent of the TML data measured by the ASTM E 595 test.

4.3.1.1.3.2 Total Outgassing Rate The total outgassing rate at time $(t_{i+1}+t_i)/2$ is $Q_t(T_s,(t_{i+1}+t_i)/2)$, calculated using Eq. (4.5)

$$Q_t(T_s,(t_{i+1}+t_i)/2) = \dot{m}_d(90\,K,T_s,(t_{i+1}+t_i)/2)\,F/A_s \qquad (4.5)$$

where $\dot{m}_d(90\,K,T_s,(t_{i+1}+t_i)/2)$ is the rate of mass deposition on the 90 K QCM found from Eq. (4.2), F is the QCM-to-effusion cell orifice view factor given by Eq. (4.3), and A_s is the area of the sample exposed to vacuum.

4.3.1.1.3.3 Ex Situ Mass Loss The ex situ total mass loss, $XTML(T_s,t_e)$, is calculated using Eq. (4.6)

$$XTML(T_s,t_e) = (m_{si}-m_{sf})/m_{si} \qquad (4.6)$$

where m_{si} and m_{sf} are the pre- and post-test sample mass measured by ex situ weighing, T_s is the sample temperature, and t_e is the test duration. $XTML(T_s,t_e)$ is the ex situ equivalent of the total mass loss at the end of the test determined in situ by QCM collection. $TML(T_s,t_e)$.

4.3.1.1.4 Deposition Data

It has been customary in the industry to express the deposition characteristics of material outgassing products expressed in terms of the volatile condensable material (VCM). VCM is the fraction of the mass of a test sample at a specified temperature which will condense on a surface at a specified temperature over a specified period of time. The ASTM E 595 measures the VCM on a 25°C surface over a 24-hour period from a 125°C test sample but refers to this fraction of condensed mass as the collected volatile condensable material (CVCM). VCM, however, is not a unique property of the material sample and collector surface types and temperatures. The net deposition rate of an outgassing flux on a surface is the difference between the impingement rate multiplied by a sticking or condensation coefficient and the surface desorption or evaporation rate. For a given source outgassing rate the impingement rate on the collector surface depends on the distance between the outgassing source and the surface. Hence deposition rate and VCM depend on the geometry of the apparatus as well as the sample material and surface types and temperatures. The kinetic interpretation of the QTA data is discussed in more detail in Section 5.1.2.2.2.

It is desirable to present deposition data in a form which is independent of apparatus geometry, but to do this we need to assume a model for the kinetic processes occurring at the deposition surface. Since there is currently no industry consensus on how deposition kinetics should be modeled it is inappropriate to propose a standard method for removing the effect of apparatus geometry from the deposition data at this time. The issue of presentation of deposition data has therefore been addressed as follows:

(i) The standard data reduction procedure specified in this section calls for deposition data to be presented in terms of VCM.

(ii) A method for removing the effect of apparatus geometry from the deposition data is proposed in Section 5.

The volatile condensable material, $VCM(T_q,T_s,t_j)$, defined as the fraction of the mass of a sample at temperature T_s which has condensed on a QCM at temperature T_q at time t_j, is calculated using Eq. (4.7)

$$VCM(T_q,T_s,t_j) = m_d(T_q,T_s,t_j)\ F/m_{si} \qquad (4.7)$$

where $m_q(T_q,T_s,t_i)$ is the mass deposited on the QCM at T_q found from Eq. (4.1), F is the QCM-to-effusion cell orifice view factor, defined by Eq. (4.3), and m_{si} is the pre-test sample weight.

The volatile condensable material from a sample at 125°C on the 298 K QCM after 24 hours of exposure, i.e., VCM(298 K,125°C,24h), is the QCM collection method equivalent of the CVCM data measured by the ASTM E 595 test.

4.3.1.2 Individual Species Outgassing Rates

The data reduction procedure approach proposed for the fully developed test method for determining the outgassing rates of each outgassed species requires that the QTA/MS test, Section 4.3.2.1, is able to separate the individual species in the collected outgassed flux with sufficient resolution to permit the mass fragmentation patterns of the individual species in the deposit to be obtained. The individual mass fragmentation patterns are then input with the isothermal test mass spectrometer data to a deconvolution algorithm to resolve the relative contributions of each species. However, at the outset of the Phase II Extension, the separation capability of QTA/MS had not yet been proven and remained to be evaluated during the course of the database measurement program. The results of this evaluation, described in detail in Section 5.2, show that while the QTA/MS technique is clearly practical, it does not have sufficient species separation capability in its present state of development to permit the individual species mass fragmentation patterns to be determined by routine computerized data reduction procedures. Consequently, it was necessary to use manual procedures to perform both the QTA/MS and individual species outgassing data analysis in the current program. Section 4.3.1.2.1 describes the computerized data analysis procedure which is proposed for the fully developed test method. Section 4.3.1.2.2 describes the manual procedures which were used in the Phase II Extension to work around the current QTA/MS species separation issues. These issues and the manual data analysis procedure are described in more detail in Sections 5.2 and 5.3.

4.3.1.2.1 Computerized Data Analysis

If the QTA/MS procedure, Section 4.3.2.2, is able to adequately separate the individual species in the outgassing species condensed on the 90 K QCM the isothermal outgassing test mass spectrometer data are processed as follows:

(i) The mass fragmentation patterns for the individual species are obtained from the QTA/MS test in an appropriate format, to be determined.

(ii) The mass spectrometer data for a particular measurement time in the isothermal outgassing test plus the mass fragmentation patterns for each species are entered

into a deconvolution algorithm and the relative fractions of each species in the outgassing flux at that measurement time are calculated.

(iii) The previous step is repeated for as many measurement times in the outgassing test as are necessary to define the variation of the fraction of each species with measurement time.

(iv) The absolute outgassing rate of each species at each measurement time is calculated by multiplying the total outgassing rate at that measurement time by the fraction of each species in the total flux at that measurement time.

Note: The above procedure assumes that the ionization constant is the same for each species. The Phase II report, Reference 6, describes a procedure for calculating the ionization constant for each species from the QTA/MS test data. Addition of the procedure for calculating the different ionization constants will be reconsidered after the separation capability of the QTA/MS test has become better developed.

4.3.1.2.2 Manual Data Analysis

If the QTA/MS procedure, Section 4.3.2.2, is not able to adequately separate the individual species in the outgassing species condensed on the 90 K QCM, the isothermal outgassing test mass spectrometer data are processed as follows:

(i) The QTA/MS ion count data for all species peaks are inspected to select ions which are unique for that species. Where unique ions cannot be identified, ions which are due predominantly to one species are selected. These ions, whether unique or merely predominant, are designated as tracking ions.

(ii) The isothermal outgassing test mass spectrometer ion count data for all values of m/e are printed out in tabular form for as many measurement times as are necessary to define the variation of the fraction of each species with measurement time. (In the data analysis of Section 5.3 the selected times were 0.333 hour, which was the first data point measured in the test; 1 hour; 5 hours; and every 10 hours thereafter.)

(iii) For each species, the time-dependent ion count data are extracted from the total data tabulation for all tracking ion m/e values selected for that species.

(iv) After visual inspection to correct anomalies the ion counts for the tracking m/e values are summed at each point in time to determine a total tracking ion count characteristic for the species, $I_j(t)$.

(v) The absolute outgassing rate for the j^{th} species at time t, $OGR_j(t)$, is related to the total tracking ion count, $I_j(t)$, by Eq. (4.8)

$$OGR_j(t) = P_j \times I_j(t) \qquad (4.8)$$

where P_j is a proportionality constant. The proportionality constant can also be expressed by Eq. (4.9), which is the integral of Eq. (4.8).

$$P_j = \int^t OGR_j(t)\,dt + \int^t I_j(t)\,dt \qquad (4.9)$$

The outgassing rate integral, $\int^t OGR_j(t)\,dt$, is related to the total sample mass loss by Eq. (4.10)

$$\int^t OGR_j(t)\,dt = (TML(T_s,t_i)) \times m_{si} \times f_j) \;/\; A_s \qquad (4.10)$$

where f_j is the fraction of the j^{th} species in the outgassing products, calculated using the QTA/MS data of Section 4.3.2.2.2, $TML(T_s,t_i)$ is the total mass loss at time t_i from a sample at temperature T_s, m_{si} is the initial sample mass, and A_s is the surface area of the sample. The ion count integral, $\int^t I_j(t)\,dt$, is related to the area under the plot of the total tracking ion count versus time for the j^{th} species, A_j, by Eq. (4.11).

$$\int^t I_j(t)\,dt = A_j \times 3600 \qquad (4.11)$$

The factor of 3600 in Eq. (4.11) accounts for the fact that the abscissa of the ion count plots are presented in hours rather than seconds. A_j can be calculated from the ion count plots using numerical integration techniques.

4.3.2 QCM Thermal Analysis

This section presents the equations and methods used to reduce and present the QTGA and QTA/MS data.

4.3.2.1 QTGA Data

The output data from QTGA are the fraction of the initial deposit mass remaining on the QCM and the evaporation rate of the deposit as functions of QCM temperature. The methods used to calculate these quantities from the measured data are described in Sections 4.3.2.1.1 and 4.3.2.1.2, respectively. The measured data are QCM frequency, $f(t_i)$, and QCM temperature, $T_q(t_i)$, as functions of time t_i. The QCM is heated at a constant rate of 1°C/min during QTA and the QCM frequency-time data, $f(t_i)$, can be converted directly to frequency-temperature data, $f(T_q(t_i))$.

4.3.2.1.1 Deposit Mass versus Temperature

As the QCM temperature is increased and the deposit evaporates the QCM frequency decreases from an initial value corresponding to the mass deposited at the end of the isothermal test, to a final value corresponding to a clean QCM surface. The mass on the QCM at the beginning of heating is m_{qo}, given by Eq. (4.12)

$$m_{qo} = K_s (f(T_q(0)) - f(125°C)) \quad (4.12)$$

where $f(T_q(0))$ and $f(125°C)$ are the QCM frequencies at the beginning of heating, $t_i = 0$, and at 125°C, respectively, and K_s is the QCM mass sensitivity constant. $T_q(0)$ will be equal to 90 K, 150 K, 220 K, or 298 K, depending on which set of QTGA data is being reduced.

The mass on a QCM at time t_i and temperature $T_q(t_i)$ is $m_q(T_q(t_i))$, given by Eq. (4.13).

$$m_q(T_q(t_i)) = K_s (f(T_q(t_i)) - f(125°C)) \quad (4.13)$$

The fraction of the total deposit mass remaining on the QCM at temperature $T_q(t_i)$ is the fractional condensable material, $FCM(T_q)$. $FCM(T_q)$ is given by Eq. (4.14), which is obtained by dividing Eq. (4.13) by Eq. (4.12).

$$\begin{aligned} FCM(T_q) &= m_q(T_q(t_i)) / m_{qo} \\ &= (f(T_q(t_i)) - f(125°C)) / (f(T_q(0)) - f(125°C)) \end{aligned} \quad (4.14)$$

4.3.2.1.2 Evaporation Rate versus Temperature

The evaporation rate of the deposit at temperature $(T_q(t_{i+1}) + T_q(t_i))/2$ is $m_q((T_q(t_{i+1}) + T_q(t_i))/2)$, given by Eq. (4.15)

$$m_q((T_q(t_{i+1}) + T_q(t_i))/2) = K_s((f(t_{i+1}) - f(t_i)) / (t_{i+1} - t_i)) (1/\omega_q) \quad (4.15)$$

where ω_q is the Clausing transmission probability [10] for the aperture in the QCM case through which the crystal views the surroundings and through which evaporation takes place. ω_q is 0.89 for the QCM Research, Inc. Mark 9 QCMs currently used in the Lockheed apparatus.

4.3.2.2 QTA/MS Data

The QTA/MS data reduction procedure approach proposed for the fully-developed test method assumes that the QTA/MS test is able to separate the individual species in a condensed deposit of outgassed species with sufficient resolution to permit the mass spectra of the individual species in the deposit to be obtained with sufficient qualitative and quantitative accuracy to:

(a) Support the proposed data reduction procedure for deconvoluting the isothermal test mass spectrometer data, Section 4.3.1.2.

(b) Permit the chemical identity of the outgassed species to be determined by comparing the mass spectra with a standard library.

In fact, the separation capability of QTA/MS had not been proven by the outset of the Phase II Extension and remained to be evaluated in parallel with the database measurement program. The results of this evaluation, described in detail in Section 5.2, show that while this technique is clearly practical, it does not have sufficient species separation capability in its present state of development to permit the individual species mass fragmentation patterns to be determined by routine computerized data reduction procedures. Consequently, it was necessary to use a manual procedure to perform the analysis in the current program. Section 4.3.2.2.1 describes the procedure that will be used when QTA/MS is sufficiently developed to permit using completely computerized data analysis. Section 4.3.2.2.2 describes the manual procedures which were used in the Phase II Extension to work around the current QTA/MS species separation issues. These issues and the manual data analysis procedure are described in detail in Section 5.2.

4.3.2.2.1 Computerized Data Analysis

If the QTA/MS procedure is able to adequately separate the individual species in the outgassing species condensed on the 90 K QCM the QTA/MS data is processed as follows:

(i) The average ion count (AIC) plot as a function of QCM temperature is printed out by the mass spectrometer data system.

(ii) The QCM temperatures at which the species peaks in the AIC data plot occur are recorded.

(iii) The mass spectra corresponding to the QCM temperature peak locations are obtained from the mass spectrometer data system in the following forms:

- A hard copy table.
- A format, to be determined, suitable for entering into the computerized isothermal test mass spectrometer data deconvolution algorithm of Section 4.3.1.2.
- A format, to be determined, suitable for entering into the computerized NBS

mass spectra library for determination of the chemical identity of the outgassed species.

4.3.2.2.2 Manual Data Analysis

If the QTA/MS procedure is not able to adequately separate the individual species in the outgassing species condensed on the 90 K QCM the QTA/MS data is processed as follows:

(i) Hard copy plots of mass spectrometer ion count data versus QCM temperature are made for each m/e value monitored.

(ii) The plots of ion count versus QCM temperature for all m/e values are inspected to identify the QCM temperatures at which peaks in ion count occur. These peaks correspond to the evaporation of specific species from the QCM. The species are then referenced by their evaporation temperatures.

(iii) The value of the ion count for each peak in the plot of ion count versus QCM temperature are entered into a table for each m/e value, in columns corresponding to the species at whose reference temperature the peak occurred.

(iv) The fraction of the j^{th} species, f_j, in the mixture of outgassing products is calculated by dividing the sum of the tabulated ion counts for all m/e values for the j^{th} species by the sum of the tabulated ion counts for all m/e values for all of the species.

(v) The mass fragmentation pattern and/or unique m/e values are determined for each species from the ion count versus m/e data contained in its appropriate table column.

(vi) The species are identified chemically by manual comparison of the fragmentation pattern data in their table columns with the fragmentation patterns provided by GC/MS.

4.3.3 GC/MS Test

The primary data acquired in the GC/MS test are mass spectra as a function of scan time. The GC/MS system software processes these data to provide total ion count (TIC) as a function of scan time, relative proportions, and the chemical identity of the individual species.

The TIC is calculated by summing the individual mass peak intensities in the measured mass spectra for each time in the scan. A chromatogram is created by plotting TIC against the scan time. The detection of a particular species is indicated by a peak in the chromatogram.

The amount of a particular species in the evolved gases is approximately proportional to the area of the TIC peak recorded for that species, which is equal to the height of the

peak integrated over the width of the peak. The approximate fraction of a given species in the total gases evolved is defined as the ratio of the area of the peak for that species to the sum of the areas of the peaks of all species

The mass fragmentation pattern measured at a chromatogram peak is the unique pattern of a particular evolved species. The chemical identity of the species is determined by comparing the measured mass fragmentation pattern with a computer-based fragmentation pattern library. Because species identification is not an exact science, the library search will frequently suggest more than one possible identity for each species, and final identification is made by an experienced analytical chemist.

Section 5

DATA ANALYSIS

The objectives of the Phase II Extension were to exercise and evaluate the test method by performing the database measurement program described in Section 6. The evaluation task covered the apparatus performance, the test procedure effectiveness, and the data analysis methodology. The apparatus performance evaluation involved mainly operational issues and is presented in Section 3. The test procedures presented in Section 4 were very satisfactory and were followed successfully throughout the measurement program. The major aspect of the test method requiring detailed evaluation was the data analysis methodology, which includes data reduction, interpretation, and presentation.

This section presents a detailed evaluation of the test method data analysis methodology. Since the same approach was used to analyze the data from all material tests, a convenient way to describe the data analysis methodology is to select a typical material test and follow the data from this test through all steps of data analysis. The example selected is the 125°C test on R-2560 adhesive.

The overall data analysis methodology, Fig. 2-2, shows that the isothermal test total outgassing and deposition data can be reduced directly using the procedures of Section 4.3.1. However, the isothermal test mass spectrometer data cannot be analyzed without information on the different outgassed species generated by the QCM thermal analysis (QTA) test, which is performed following the isothermal outgassing/deposition test. These three major steps in the data analysis are therefore discussed in this order.

Section 5.1 presents the analysis of the total outgassing and deposition data, which consists of simple and straightforward algebraic processing of the QCM data.

Section 5.2 presents the analysis of the QTA test data, which includes both QCM thermogravimetric analysis (QTGA) and mass spectrometer analysis of the outgassed species (QTA/MS). The QTA/MS test is included in the test method to determine the mass fragmentation patterns of the individual species, which are then used to determine the contributions of the individual outgassed species to the total outgassing/deposition behavior. The QTA/MS test technique is a novel form of in situ gas chromatography which has many potential benefits. However, the QTA/MS test technique is relatively complex, and this database measurement program is the first time that its capability has been investigated in any depth. Section 5.2, therefore, presents a very detailed analysis of the QTA/MS data.

Because of the undeveloped, high risk nature of the QTA/MS test, preliminary ex situ

gas chromatography/mass spectrometry (GC/MS) tests were included in the test method to provide additional supporting data on the type, abundances, and mass fragmentation patterns of the volatile species. The GC/MS data are analyzed in Section 5.2 in conjunction with the QTA/MS data.

Section 5.3 presents the analysis of the isothermal outgassing test mass spectrometry data to resolve the outgassing rates of the different outgassed species.

5.1 ISOTHERMAL OUTGASSING/DEPOSITION TEST

This section describes the test sample used in the outgassing test, analysis of the total outgassing and deposition data measured in situ by QCM collection, and the mass loss data obtained by ex situ weighing.

5.1.1 Test Sample Preparation

The material sample used in the example test is R-2560, which is a two-part, flowable, red, room temperature vulcanizing silicone used in bonding, potting, and sealing applications. R-2560 is made by McGhan-NuSil Corporation and is nominally equivalent to RTV 560 made by General Electric Company. The adhesive is prepared by mixing 0.5 percent of the dibutyl tin dilaurate catalyst to R-2560 base, and curing for 24 hours at 25°C. Since outgassing from this material is diffusion-controlled, the test sample was prepared in a tubular holder, causing outgassing to take place by one-dimensional diffusion along the axis of the tube to the free end faces. The sample holder was an open-ended aluminum tube 1.00 inch long by 0.375 inch inside diameter. The tube was filled by completely submerging it in a dish of uncured R-2560. After the adhesive had cured the tube was cut from the dish and the ends of the sample were trimmed flush with the ends of the tube. This method of preparation ensured that the sample was homogeneous. The exposed sample area was 1.43 cm^2 and the initial sample weight was 2.40841 g.

5.1.2 Isothermal Total Outgassing and Deposition Data

This section discusses how the experimental QCM data are used to calculate total outgassing and deposition data, and ex situ percent total mass loss.

5.1.2.1 Isothermal Total Outgassing Data

The outgassing data of most interest are the sample total mass loss, $TML(T_s,t)$, and total outgassing rate, $Q_t(T_s,t)$, where T_s is the temperature of the sample and t is the time since the beginning of evacuation. These quantities have been calculated using the measured frequency data for the 90 K QCM using Eqs. (4.4) and (4.5), respectively, and are plotted in Fig. 5-1(a) and 5-1(b).

Figure 5-1(a) shows the total mass loss, $TML(T_s,t)$, as a function of time. This plot is

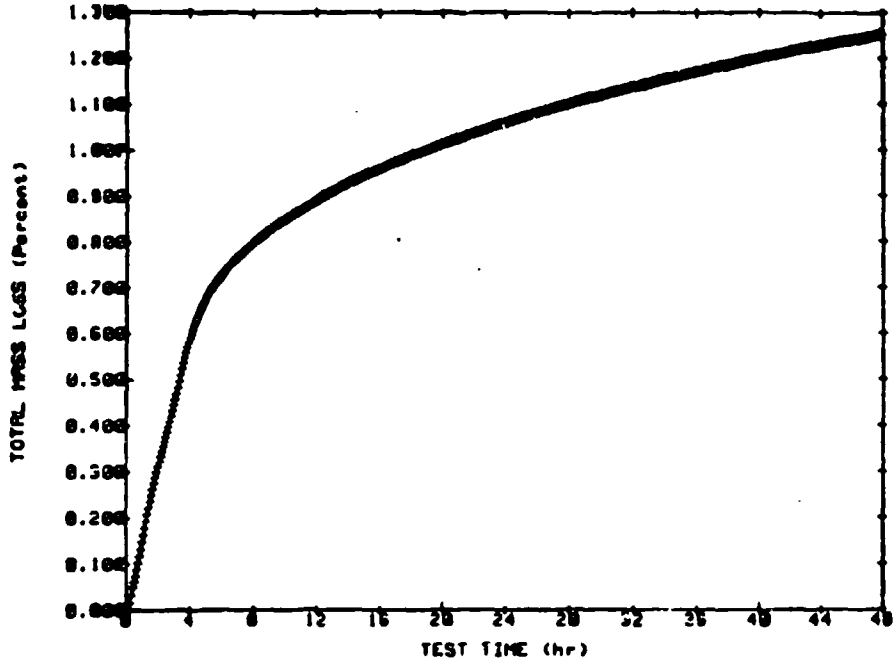
equivalent to a plot of measured QCM frequency versus time, multiplied by a constant, and so is a direct representation of the experimental data. The curve shows the usual outgassing characteristic of high initial mass loss, followed by a tendency towards an asymptotic value corresponding to depletion of volatile material components.

Figure 5-1(b) is a plot of total outgassing rate versus time, calculated from the 90 K QCM frequency data using Eq. (4.5). The major features are a very short duration spike in the rate right at the beginning of the test, followed by two additional longer duration peaks during the first 4 hours. Comparison with the mass spectrometry data, Section 5.3, indicates that the initial spike and the double peaks are real and not an artifact of the measurement system. The auxiliary chamber pressure is not reduced to the same level as the main chamber at the time the auxiliary valve is opened, so the initial spike is almost certainly due to the collection of residual atmospheric gases from the auxiliary chamber when its valve is opened. The peak at about 1 hour is the balance point between the increase of outgassing rate due to the initial heating of the sample and the usual decrease of outgassing rate with time. The peak at about 4 hours is unusual and was unexpected. The most probable explanation is that the sample was initially incompletely cured and that heating to the 125°C test temperature completed the cure. The peak at 4 hours would then be due to the outgassing of the additional reaction products produced by the completion of the R-2560 adhesive cure. This explanation is supported by the mass spectrometry data of Section 5.3, which also appear to indicate that curing continues throughout the outgassing test.

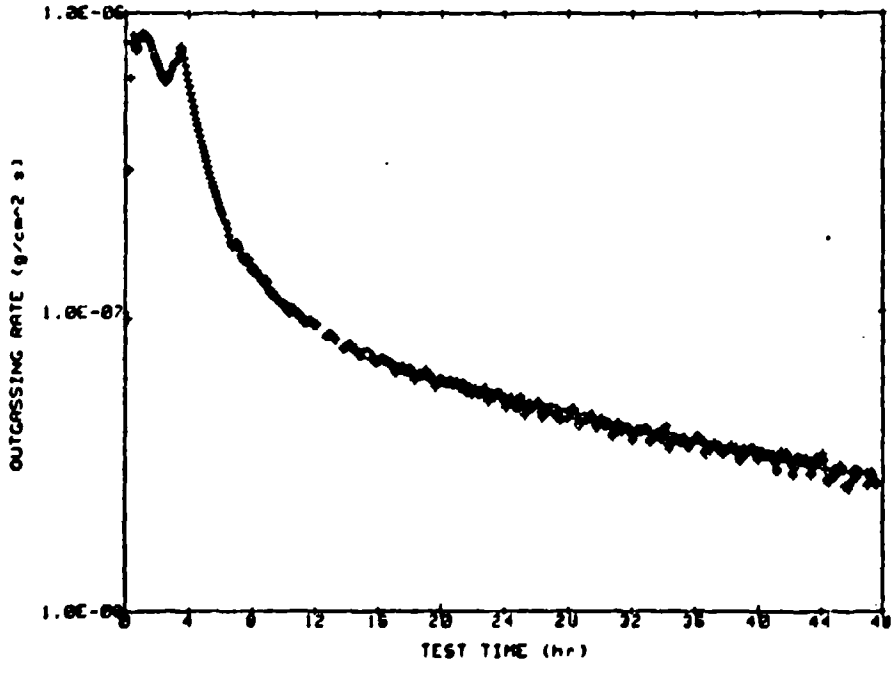
The noise in the outgassing rate data is due to a combination of the method used to calculate the rate from the measured QCM frequency data and changes induced in the QCM frequency by cycling of the QCM temperature over a small range between liquid nitrogen reservoir fills. The outgassing rate is calculated using a finite difference method to calculate the outgassing rate from difference in measured QCM frequency data points spaced 5 minutes apart. This method will tend to amplify irregularities in the raw data, especially at the longer test times for which the mass accumulation between the 5 minute data points is very small. Many sophisticated software techniques exist for filtering and smoothing data but the scope of the program did not allow these techniques to be fully explored. Instead, several relatively simple smoothing approaches were evaluated.

Figure 5-2(a) shows the outgassing rate calculated the same as Fig. 5-1(b), i.e., using 5 minute intervals, but the outgassing data are printed out every 25 minutes rather than every 5 minutes. This approach is not strictly a smoothing technique, but it does produce a less confusing plot.

Figure 5-2(b) shows outgassing rate calculated using Eq. (4.5) but using frequency

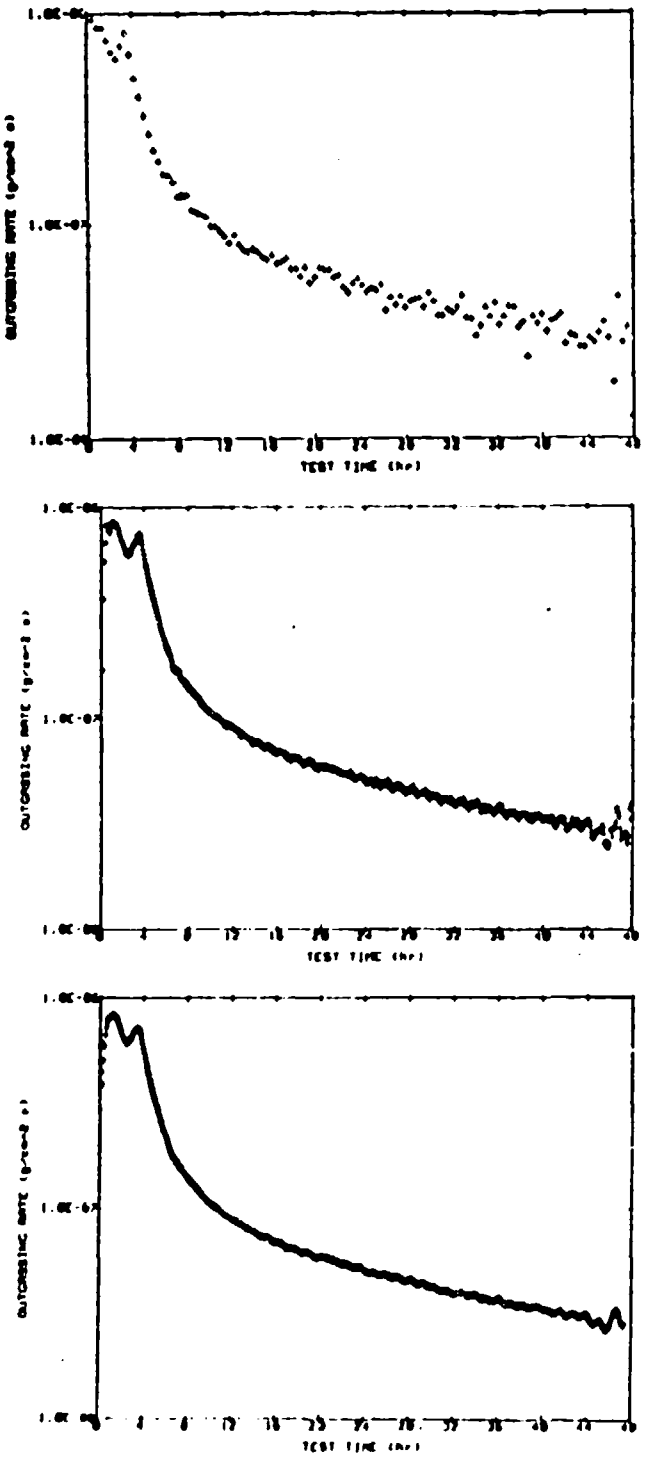


(a)



(b)

Fig. 5-1 Total Mass Loss (a) and Outgassing Rate (b) as Functions of Time for an R-2560 sample at 125°C.



(a)

(b)

(c)

Fig. 5-2 Outgassing Rate Data for R-2560 at 125°C Calculated using Various Smoothing Techniques: (a) Plot Every Fifth Point, (b) Average Over 25 Minutes, and (c) Average Over 25 Minutes, Repeated Four Times.

data points separated by 25 minutes rather than 5 minutes. This technique smoothes by determining the outgassing rate over a longer period. The figure shows that the technique removes most of the random noise, leaving only the cyclic effect of the QCM frequency variations with temperature. It also removes the initial spike and rounds off the two peaks.

A third technique is to apply the smoothing technique of averaging over a larger time interval several times in succession. This approach can eventually remove all variation from the data if used a very large number of times, and so must be used judiciously. Figure 5-2(c) shows the effect of repeating the 25 minutes averaging technique four successive times. The additional averaging clearly removes all of the random noise and further highlights the effect of QCM temperature cycling.

The most appropriate way to smooth a given set of data is a strong function of the properties of the data set. All three of the above techniques were used in reducing the outgassing data for the materials in the database of Section 6. The techniques were applied and modified as appropriate for each material.

5.1.2.2 Deposition Data

An accepted practice in the industry has been to present deposition data in the form of volatile condensable material (VCM). The VCM of a material at a specified temperature is the fraction of the original mass of an outgassing test sample that will deposit on a collector surface held at that temperature. The VCM of a material is a function of the sample temperature, the collector temperature, and the duration of exposure. However, VCM is also dependent on apparatus geometry and so it is not a basic material property. Use of VCM data is therefore not a rigorous way to characterize the deposition characteristics of material outgassing products.

Because of the limitations of expressing deposition characteristics of the VCM, we should develop a data reduction approach which removes the effect of apparatus geometry. However, the effect of geometry cannot be removed without making some assumptions about the kinetics of deposition. Since no standard deposition kinetics model has been adopted by industry, any further processing of the deposition data would have to be based on Lockheed's understanding of the deposition kinetics, and it would be presumptuous and costly to present the deposition data in a manner that has not been generally accepted. This dilemma has been resolved here by presenting the main deposition database in the form of VCM, while proposing a method for removing the effect of apparatus geometry from the VCM data. It is then left to the user to decide whether or not to use this method. The method proposed for removing the effect of apparatus geometry is presented in Section 5.1.2.2.2.

5.1.2.2.1 Volatile Condensable Material (VCM)

The VCM has been calculated for each QCM temperature using Eq. (4.7), and has been plotted in Figs. 5-3(a), (b), and (c). The form of these plots is very similar to the TML data of Fig. 5-1(a), and indeed, the VCM for a 90 K surface is, by definition, equal to the TML.

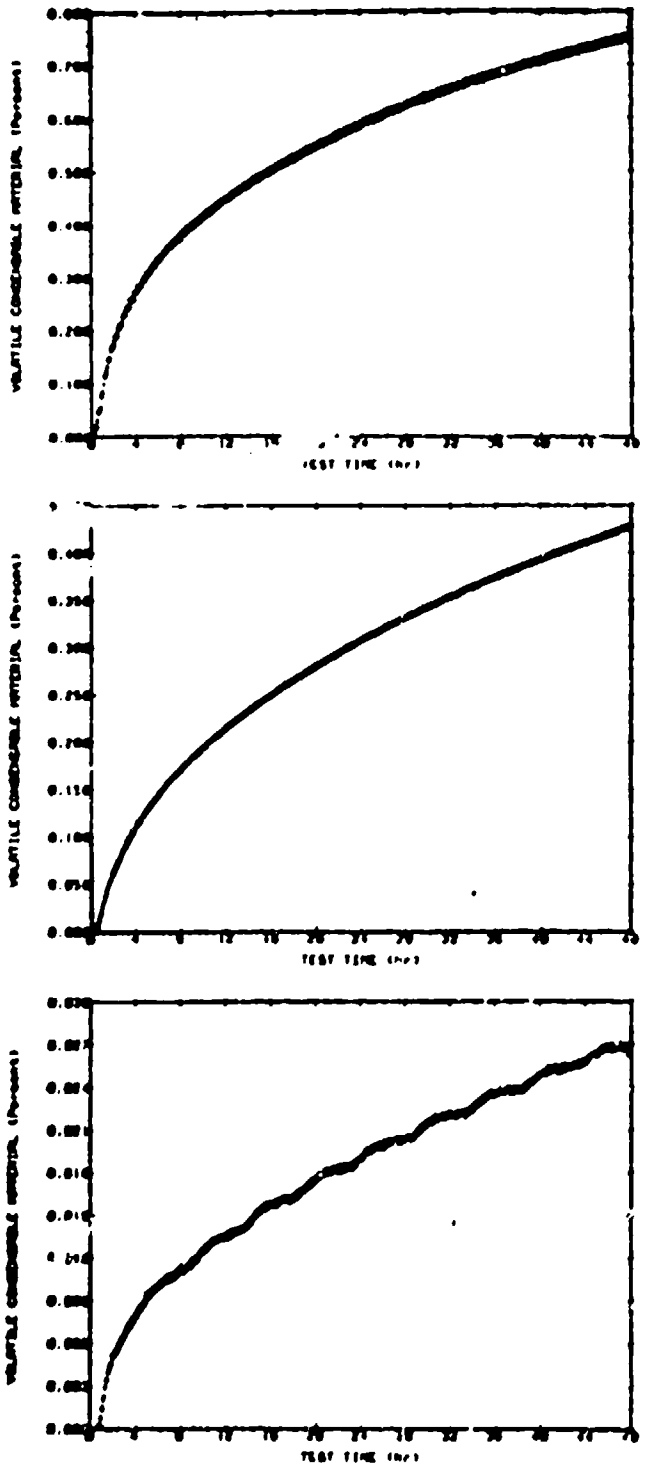
The data of Fig. 5-3 can be used to make a rough estimate of the fraction of the total outgassing flux which is condensable at the three collection temperatures as a function of time. Table 5-1 shows TML data taken from Fig. 5-1(a) and VCM data taken from Fig. 5-3 for various exposure times. The ratios of VCM to TML, calculated for each temperature and time, are plotted in Fig. 5-4. The figure shows that the more volatile components are outgassed in the first 10 to 20 hours, after which time the ratios do not change much with time. This figure can be used to quickly estimate the fraction of the total outgassing flux which will condense on a surface at one of these temperatures. However, we must remember that these data are a function of the apparatus geometry.

5.1.2.2.2 Kinetic Interpretation of the Deposition Data

This section proposes a simple model for representing the deposition process. Deposition is a kinetic process in which the net deposition rate is the difference between the impingement rate multiplied by a sticking or condensation coefficient and the surface desorption or evaporation rate. This relationship is expressed by Eq. (5.1).

$$\dot{m}_d = (\dot{m}_i \times C) - \dot{m}_e \qquad (5.1)$$

where $\dot{m}_d$ is the net deposition rate, $\dot{m}_i$ is the impinging flux, C is the condensation or sticking coefficient, depending on whether deposition is in the bulk condensation or adsorption regimes, respectively, and $\dot{m}_e$ is the evaporation rate from the surface. Because the impingement rate will vary with the distance between the outgassing source and the collector, the net deposition rate is geometry-dependent. On the other hand, the desorption or evaporation rate is a property of the surface/contaminant system, and for low impingement rates is independent of the impingement rate. It is therefore more useful to present the deposition data in the form of the desorption/evaporation rate, $\dot{m}_e$, rather than in the form of the net deposition rate, $\dot{m}_d$. Given the desorption/evaporation rate and an estimated value of C, the modeler could then estimate the net deposition rate for an arbitrary impinging flux. Experimental evidence suggests that for a species impinging on its own condensed phase, C is close to unity. Assuming that C is unity Eq. (5.1) can be rearranged



(a)

150 K QCM

(b)

220 K QCM

(c)

298 K QCM

Fig. 5-3 Volatile Condensable Material for R-2560 at 125°C for Three QCM Collector Temperatures: (a) 150 K, (b) 220 K, and (c) 298 K.

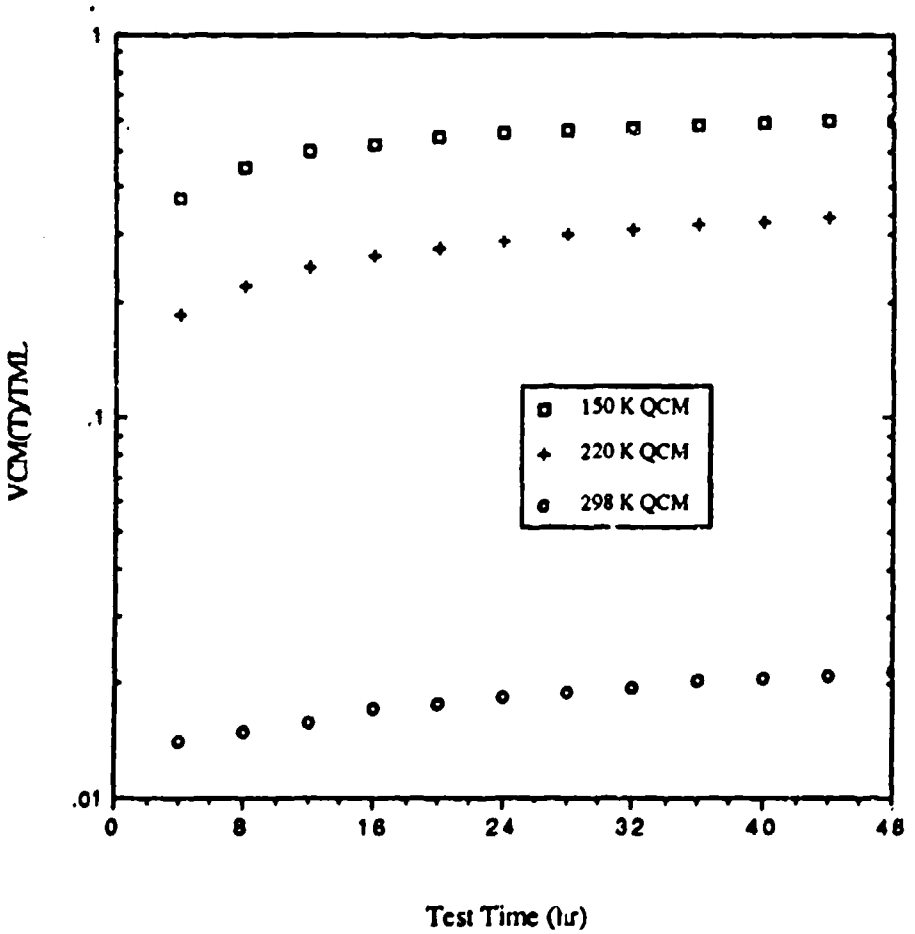


Fig. 5-4 VCM/TML for R-2560 at 125°C for Three QCM Collector Temperatures.

Table 5-1

Fraction of Total Outgassed Products Condensable at Three Surface Temperatures

Time (hrs)	TML(90)	VCM(150)	VCM(150) / TML(90)	VCM(220)	VCM(220) / TML(90)	VCM(298)	VCM(298) / TML(90)
4	0.565	0.21	0.371	0.105	0.186	0.008	0.01416
8	0.775	0.35	0.452	0.17	0.219	0.0115	0.0148
12	0.89	0.445	0.5	0.22	0.247	0.014	0.0157
16	0.96	0.5	0.521	0.255	0.266	0.0164	0.0171
20	1.015	0.55	0.542	0.282	0.278	0.018	0.0177
24	1.058	0.59	0.558	0.305	0.288	0.0195	0.0184
28	1.1	0.622	0.565	0.33	0.3	0.021	0.0191
32	1.135	0.655	0.577	0.355	0.313	0.0223	0.0196
36	1.17	0.685	0.585	0.375	0.321	0.0238	0.0203
40	1.21	0.71	0.587	0.39	0.322	0.025	0.0207
44	1.235	0.735	0.595	0.41	0.332	0.026	0.0211
48	1.255	0.755	0.602	0.425	0.339	0.027	0.0215

to give the following expression for the evaporation rate

$$\dot{m}_e = \dot{m}_i - \dot{m}_d \qquad (5.2)$$

The impingement rate, $\dot{m}_i$, is the same on all QCMs because of the symmetrical apparatus geometry. It is equal to the deposition rate on the 90 K QCM, which can be estimated from the slope of the TML data, Fig. 5-1(a). The deposition rates on the 150 K, 220 K, and 298 K QCMs can be estimated from the slopes of the VCM data plots, Fig. 5-3. Since the TML and VCM data are expressed as a fraction of sample mass the slopes of both the TML and VCM plots are converted to deposition rates on the QCMs by multiplying by the factor (m_{si} / F), where m_{si} is the sample initial mass and F is the effusion cell orifice-to-QCM view factor (Section 4.3.1.1.2). The evaporation rate is then found from Eq. (5.3), which is obtained by substituting the TML and VCM slope data into Eq. (5.2).

$$\dot{m}_e = (\text{(slope of TML data)} - \text{(slope of VCM data)})\ m_{si} / F \qquad (5.3)$$

Evaporation rates have been calculated for the 125°C R-2560 test using Eq. (5.3) and

the TML and VCM data of Figs. 5-1(a) and 5-3, respectively, and are plotted in Figs. 5-5(a) and 5-5(b). The linear plot of Fig. 5-5(a) shows that at all three surface temperatures, the deposit evaporation rate is much higher in the earlier stages of outgassing when the more volatile, lower molecular weight species are being released. The evaporation rate falls rapidly with time as the more volatile species are completely outgassed. There is a marked change in the rate of decline at about 10 hours as the most volatile species are almost completely depleted.

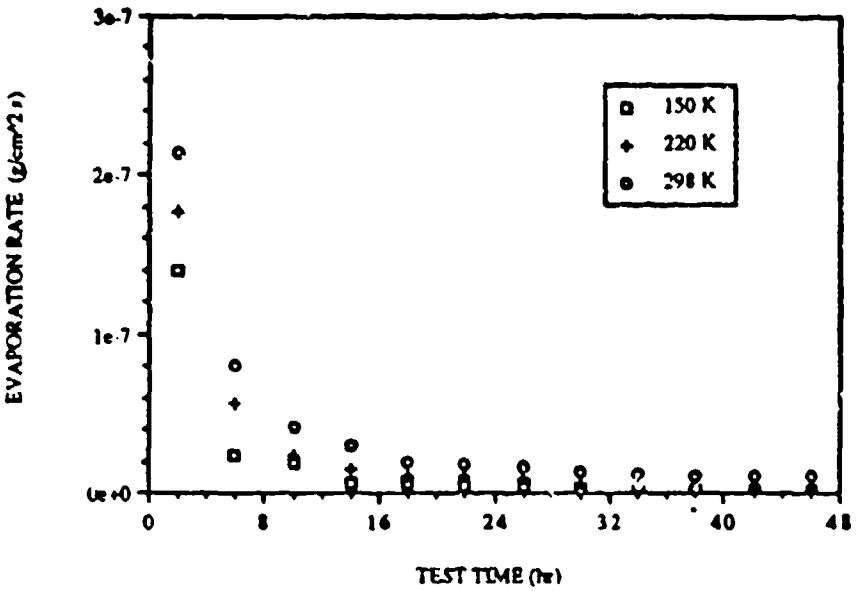
The log plot of Fig 5-5(b) shows the evaporation rate at longer test times more clearly. The net deposition rate for an arbitrary impingement rate can be calculated by substituting the impingement rate and an evaporation rate taken from Fig. 5-5(b) into Eq. (5.1). Note that the values of $\dot{m}_e$ given in Fig. 5-5 are not unique functions of the surface temperature and time. The effective evaporation rate at a given time also depends strongly on the amount of mass deposited and the types and proportions of species in the deposit at that time.

5.1.2.3 Ex Situ Total Mass Loss

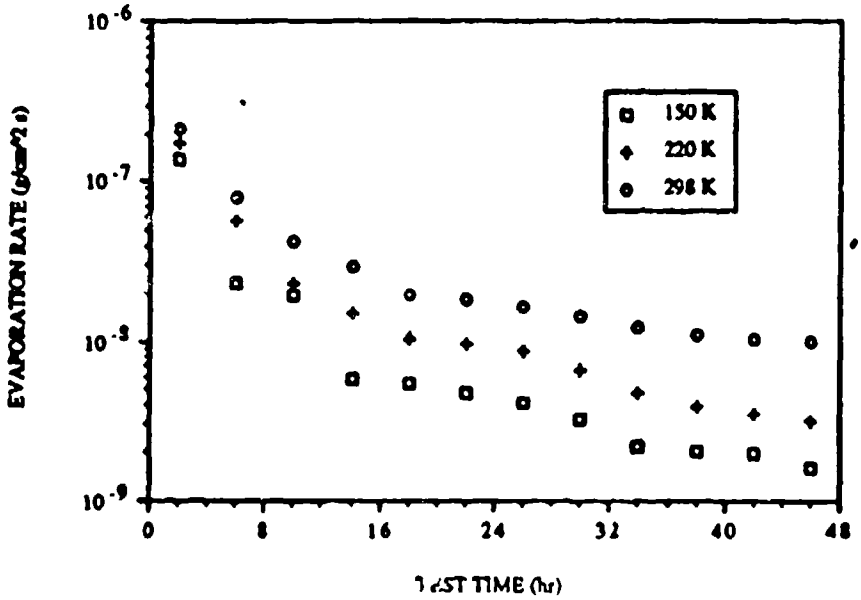
The initial and final sample masses determined by ex situ weighing were 2.40841 g and 2.37165 g, respectively, which corresponds to an ex situ TML of 1.53 percent. This is about 20 percent higher than the TML of 1.25 percent determined by QCM collection. The level of agreement obtained in Phase II for similar comparisons was much better - about ±2 percent. The lower level of agreement obtained in the Phase II Extension is believed to be due to weighing errors; in Phase II sample weighings were made with greater care because of the need to determine absolute accuracy of the test method. In the Phase II Extension sample weights were determined by single routine weighings.

5.2 QCM THERMAL ANALYSIS

This section discusses the results of the QCM thermal analysis (QTA) test on the outgassing products deposited on the QCMs at the end of an isothermal outgassing test. The QTA test includes QCM thermogravimetric analysis (QTGA), in which the QCM deposit mass is measured as a function of temperature, and QCM thermal analysis plus mass spectrometry (QTA/MS), in which the outgassing products evaporating from a QCM are analyzed with a mass spectrometer. The QTGA test is relatively simple to execute and interpret and has been used routinely at Lockheed since the mid 1970's. The QTA/MS test is a new development, and to the authors' knowledge has not been described previously. Although the validity of the concept had not been verified previously, the QTA/MS test was included in the test method because it offered the only conceptually straightforward means for determining the mass fragmentation patterns of the individual outgassed species.



(a)



(b)

Fig. 5-5 Apparent Evaporation Rate of Outgassing Products from R-2560 at 125°C from the Collector QCrys at 150 K, 220 K, and 298 K as a Function of Time: (a) Linear-Linear Plot and (b) Log-Linear Plot.

It is thus a key element in the ambitious strategy of Fig. 2-2 for resolving the outgassing rates of the individual species from the total outgassing flux. Since the QTA/MS test is such a key element in the overall test method while also being its most complex and highest risk component, this section analyzes QTA/MS in a relatively detailed manner.

5.2.1 QCM Thermogravimetric Analysis

In a QTGA test a QCM is heated from its base collector temperature to 125°C at a rate of 1°C/min, and its frequency and temperature are recorded as functions of time. These data are reduced using Eqs. (4.10) and (4.11) to determine the fraction of the initial deposit mass remaining on the QCM, FCM, and the evaporation rate, m_e, as functions of temperature.

5.2.1.1 Fraction of Initial Deposit Mass Remaining on the QCM (FCM)

Figures 5-6 and 5-7 show FCM as a function of temperature during the QTGA test on the R-2560 outgassed species deposited on the 90 K, 150 K, 220 K, and 298 K QCMs. The FCM data for all four QCMs have been normalized to the 90 K data by expressing them as fractions of the mass on the 90 K QCM at the beginning of QTA.

The form of Fig. 5-6(a) implies the evaporation of four different major species, or groups of species, evaporating in the temperature regimes of 158 K, 198 K, 238 K, and 290 K respectively. The results of the GC/MS and QTA/MS tests, presented later, show that the 158 K and 198 K groups consist mainly of a single species, but the 238K and 290 K groups include several species.

The relative mass fractions of each species or species group can be readily estimated from Fig. 5-6(a). The 158 K, 198 K, 238 K, and 290 K species have mass fractions of about 0.43, 0.22, 0.17, and 0.18, respectively.

If the QTGA test were to be performed using a heating rate slow enough for the deposit mass to equilibrate at each QCM temperature, then the FCM data at 150 K, 220 K, and 298 K should be equal to the value of VCM/TML for each of these temperatures recorded at the end of the outgassing test. The FCM at 150 K in Fig. 5-6(a) is falling rapidly to an equilibrium value of about 0.57, which compares with a VCM/TML at 150 K from Table 5-1 of 0.60. The FCMs at 220 K and 298 K from Fig. 5-6(a) are about 0.33 and 0.02, respectively, which compare with VCM/TML figures of 0.34 and 0.02, respectively, from Table 5-1. The FCM data at a given temperature thus do indeed agree well with the VCM/TML data. The data can therefore be used to estimate VCM/TML and hence VCM for temperatures in between the standard isothermal test VCM measurement temperatures of 90 K, 150 K, 220 K, and 298 K.

Since the impingement rate of each outgassing species and the relative amounts of

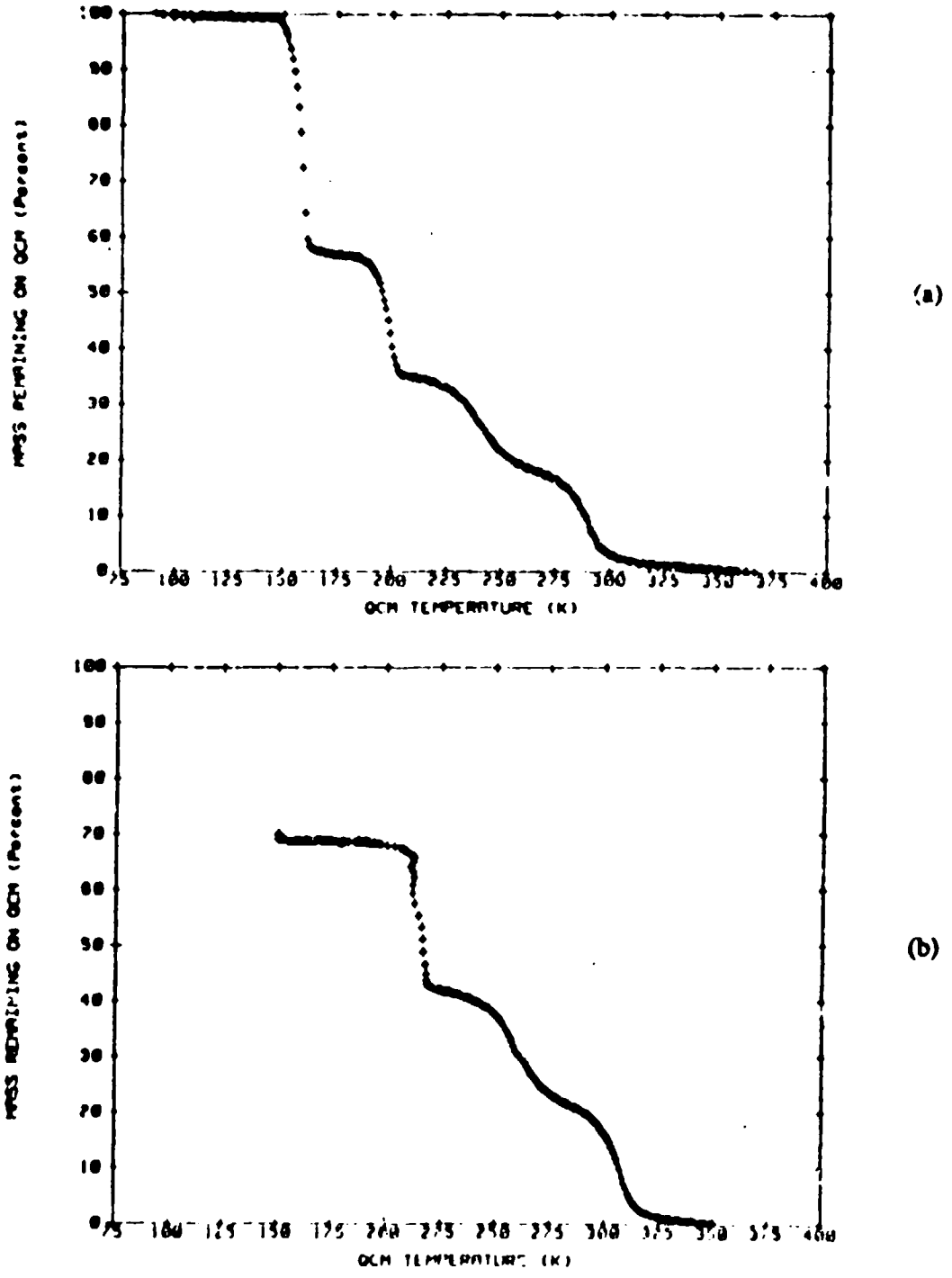
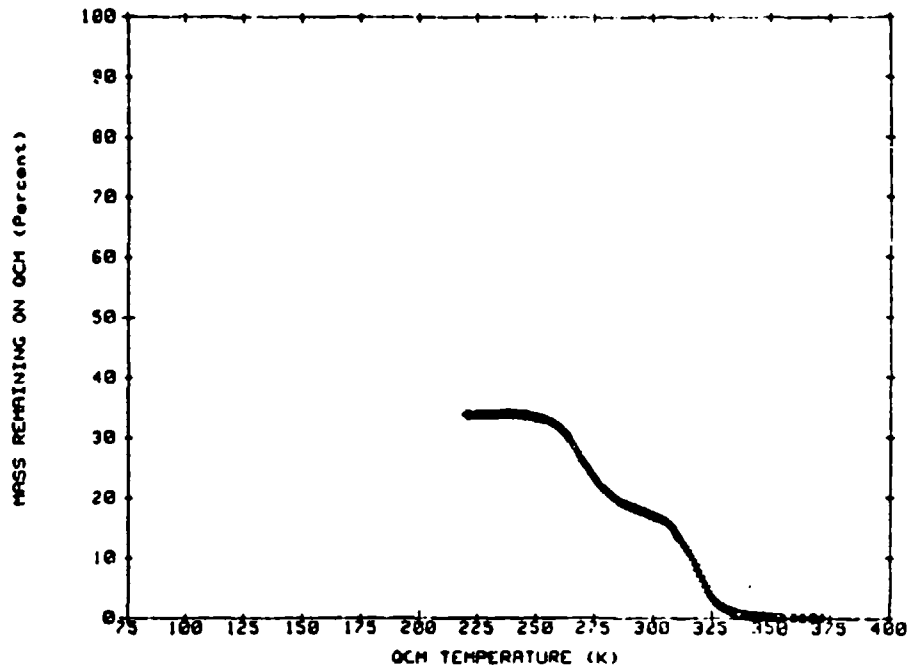
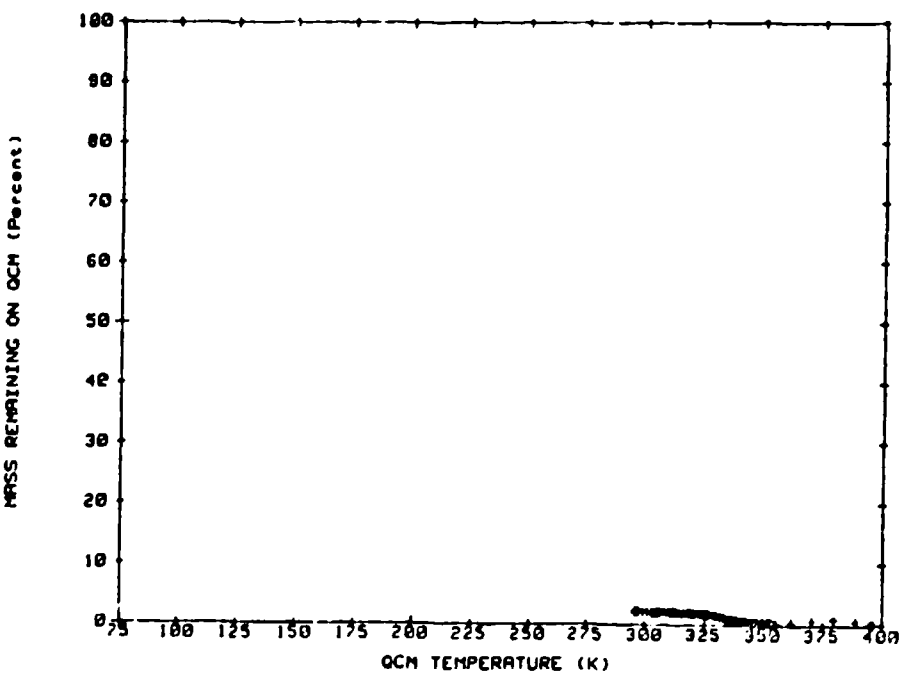


Fig. 5-6 QCM Thermogravimetry Data (TGA) for Outgassing Products Collected on the (a) 90 K and (b) 150 K QCMs from R-2500 at 125°C. Mass of Collected Products Remaining on the QCMs as a Function of Temperature.



(a)



(b)

Fig. 5-7 QCM Thermogravimetry Data (FCM) for Outgassing Products Collected on the (a) 220 K and (b) 298 K QCMs from R-2560 at 125°C. Mass of Collected Products Remaining on the QCMs as a Function of Temperature.

each species in the outgassing flux is the same on all four QCMs, the same amount of a given species should condense on all QCMs, as long as the QCM is operating below the evaporation temperature of that species. The QTGA plots for all four QCMs could, therefore, be expected to be qualitatively and quantitatively similar in form. The only difference expected between these four QTGA plots was that for the higher temperature QCMs there will be no data for the temperature range between 90 K and the normal operating temperature of that QCM. The qualitative nature of the four QTGA characteristics and the relative fractions of each component implied by the plots do agree well. However, the temperature at which a particular species or group evaporates is higher for the higher collection temperature QCMs. The differences in evaporation temperature are too large and too systematic to be explained as random measurement errors.

Section 2.2.1.3.1 discusses the performance of QTGA and lists several factors which could produce a temperature displacement of the evaporation characteristic. The effect of most of these factors is to displace the evaporation characteristic to a higher temperature for larger initial deposit masses. This is the opposite of what is observed in Figs. 5-6 and 5-7, since the higher collector temperature QCMs have smaller initial deposits.

Another way of viewing the QTGA data is that the lower collector temperature QCMs appear to have their evaporation characteristics shifted to lower temperatures. The only major systematic factor which could explain the displacement of a temperature characteristic to lower temperatures for higher initial deposit masses is a mixture effect such as the formation of azeotropes. For example, consider the hypothetical case of two species A and B whose evaporation properties are very similar but are such that A alone will not condense on the 150 K QCM but B alone will. The deposit on the 150 K QCM will contain no species A, so as the QCM is heated, B will evaporate in its normal characteristic temperature regime. However, the 90 K QCM will carry a mixture of B and A ,and if these two species form an azeotrope, species B may evaporate at a lower temperature than normal due to the influence of A.

The precise cause of the temperature displacement phenomenon could be investigated further with the help of the QTA/MS data because the mass spectrometer is able to resolve the different species. Since it is not necessary to identify the evaporation temperature of each species accurately in the present test methodology and since funding was limited the issue was not pursued further in this program. However, this phenomenon is deserving of a more rigorous explanation in the interests of improving our understanding of QTGA.

5.2.1.2 QTA Evaporation Rate Data

Additional information can be obtained from the QTGA data by plotting the differential of the mass data, i.e., the rate of evaporation from the QCM, $\dot{m}_q$, versus

temperature. A plot of evaporation rate versus temperature is analogous to a conventional differential thermogravimetric analysis (DTGA) characteristic and hence by analogy can be referred to as DQTGA. Two types of DQTGA plot are presented here. First, it is shown that the latent heat of an evaporating species can be deduced from a log-linear plot, so this type of plot is useful to the modeler who wishes to obtain more information about the properties of the outgassed species from the data. However, the log-linear plot gives background noise the same degree of prominence as real mass changes, and does not show the qualitative nature of the differential evaporation process very clearly. The different evaporation regimes of the different species are more dramatically highlighted on a linear-linear plot. The log-linear and linear-linear plots are presented and discussed in Sections 5.2.1.2.1 and 5.2.1.2.2, respectively.

5.2.1.2.1 The Log-Linear Plot

The evaporation rate of a species can be expressed by the Langmuir relationship:

$$\dot{m}_q = \alpha P_v (M/2\pi RT)^{1/2} \qquad (5.4)$$

where

- $\dot{m}_q$ = evaporation rate, g/cm^{2}s
- α = evaporation coefficient
- P_v = vapor pressure, dynes/cm^2
- M = molecular weight
- T = temperature, K
- R = universal gas constant, 8.31 x 10^7 dyne cm/g mol K

For most species, the relationship between the vapor pressure and temperature can be expressed by an equation of the form of Eq. (5.5)

$$P_v = P_o \exp(-H_l/RT) \qquad (5.5)$$

where

- P_o = a constant, dynes/cm^2
- H_l = latent heat of evaporation, cals/mol
- R = universal gas constant, 1.98 cals/mol K

Equations (5.4) and (5.5) can be combined to give the following relationship between evaporation rate and temperature.

$$\ln(\dot{m}_q\sqrt{T}) = \ln(\alpha P_o(M/2\pi R)^{1/2}) - H_t/RT \qquad (5.6)$$

Equation (5.6) indicates that if $\ln(\dot{m}_q\sqrt{T})$ is plotted against $1/T$, a straight line should be obtained whose slope is H_t/R. In a QTGA test on the evaporation of water ice [11] it was demonstrated that the latent heat determined from the slope of the evaporation rate data agreed very well with published latent heat data for water. The absolute value of the measured evaporation rate also agreed well with the rate calculated from Eq. (5.6) using published vapor pressure data for water.

Figure 5-8 shows the DQTGA data for the test following the 125°C outgassing test on R-2560 plotted in the form of $\ln(\dot{m}_q\sqrt{T})$ vs $1/T$. The prominence given to the noise in this type of plot is quite apparent.

For the two species which evaporate in the temperature regimes of 158 K and 198 K, the evaporation data produce distinct straight lines. These lines have been further analyzed using Eq. (5.6). Figure 5-9(a) shows the data from Fig. 5-8 on an expanded scale which covers the evaporation temperature regime near 158 K. The experimental data in this regime fall on a straight line whose slope is found from the linear curvefit equation given on the graph to be 5,669.4 K, which implies a heat of sublimation of 11,225 cals/mol. Analysis of the mass spectrometer data later in the report indicates that the 158 K species is 1-propanol, for which the CRC Handbook gives the following equation for vapor pressure.

$$\log_{10}P = 9.518 - 2469/T \qquad (5.7)$$

Equation (5.7) implies a latent heat of 11,256 cals/mol, which is very close to that determined by QTGA from Fig. 5-9(a).

The theoretical evaporation rate of 1-propanol has been calculated by substituting Eq. (5.7) into Eq. (5.4), with the assumption that the evaporation coefficient is equal to unity, and has been plotted in Figure 5-9(a). The temperature used in the calculation is the temperature indicated by the QCM platinum resistance thermometer (PRT). The theoretical evaporation rate has the same slope as the measured data, but the theoretical line lies above the measured data. There are several possible explanations for the difference between these two characteristics. If the temperature distribution in the QCM is such that the temperature

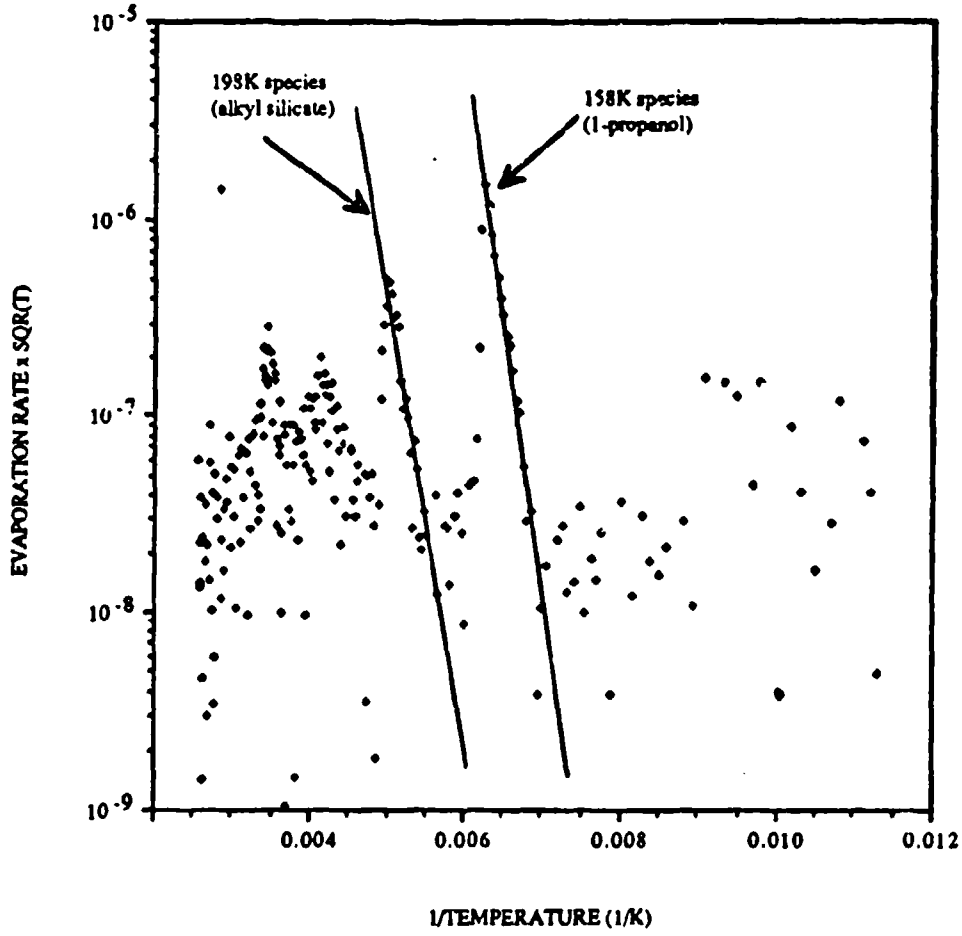
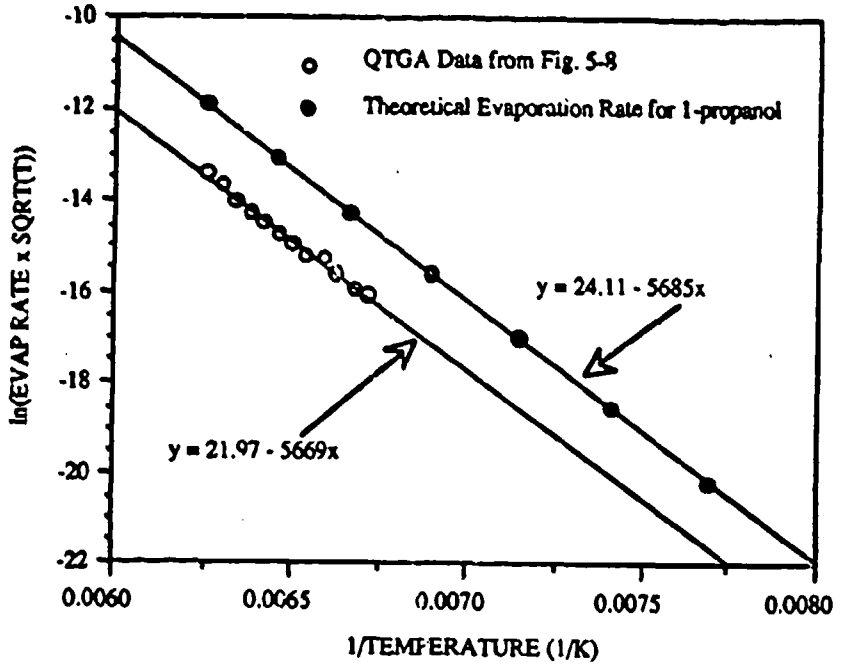
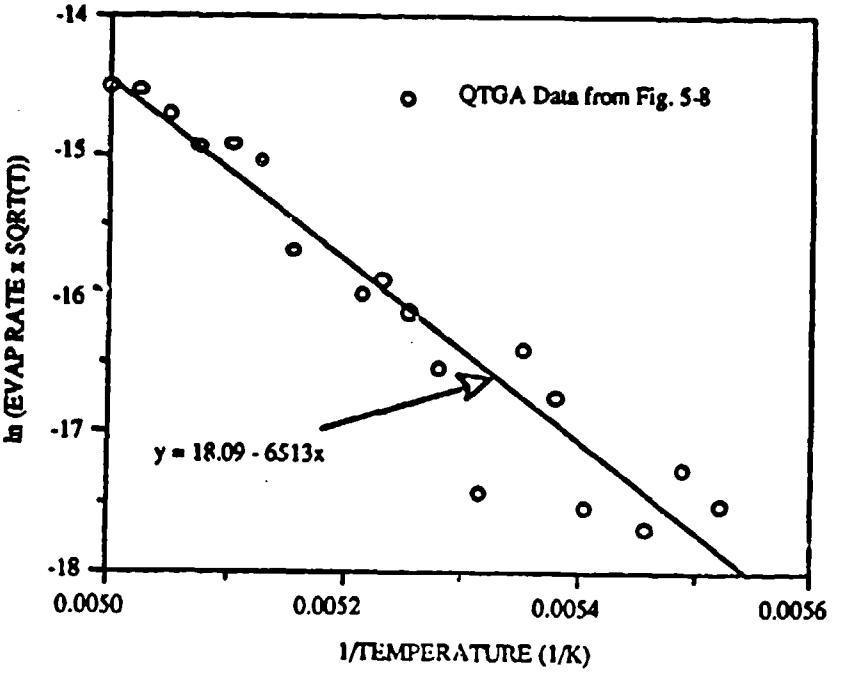


Fig. 5-8 Differential QCM Thermogravimetry Data for Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C ($\dot{m}_g\sqrt{T}$ versus 1/T).



(a)



(b)

Fig. 5-9 Evaporation Rate Plots ($\dot{m}_q\sqrt{T}$ versus $1/T$) of the 158 K and 198 K Species: (a) Comparison of Measured and Theoretical Evaporation Rates for the 158 K Species (1-propanol) and (b) Measured Evaporation Rate for the 198 K Species.

of the QCM crystal is less than the temperature of the PRT then the measured evaporation rate will be systematically less than the theoretical rate. The crystal will in fact always be cooler than the PRT because of surface cooling caused by evaporation and radiative cooling by the cold walls. The crystal temperature would have to be about 4.5 K less than the PRT temperature in order to explain the observed difference. Alternatively, if it is assumed that the crystal is at the same temperature as the PRT, the difference implies that the measured evaporation rate is a factor of 4.4 times lower than theoretical. This could be caused by the reduction in evaporation rate that occurs when a high volatility species, which will be deposited nearer the QCM surface because it is outgassed earlier, has to diffuse through a lower volatility deposit to reach the free surface. Finally, the published data for the latent heat of 1-propanol may not be valid in this temperature regime. Previous experience suggests that the most probable explanation for the difference between the characteristics is a combination of a difference in PRT and crystal temperatures of one or two degrees, combined with a reduced evaporation rate due to diffusion effects.

The measured data for the 198 K species have been plotted on an expanded scale in Fig. 5-9(b). These data have more scatter than the 1-propanol data, but are still clearly linear. The curve fit gives a slope of 6513.3 K, which corresponds to a latent heat of 12,896 cals/mol. Since the exact nature of this chemical species is not known, it is not possible to calculate a theoretical curve in the same manner as for the 1-propanol.

The slopes of the evaporation characteristics of the species evaporating near 238 K and 290 K are much lower than that those of the lower temperature species, when in fact it would be expected that these species would have higher molecular weights and hence higher latent heats. The smaller slopes are probably the result of the evaporation of a group of species with a range of molecular weights over a range of temperatures, and so cannot be used to determine latent heats. The log-linear plot is thus seen to be useful for determining the latent heats of well separated species. When the evaporation temperatures are not well separated, the log-linear plot is of limited value.

5.2.1.2.2 The Linear-Linear Plot

Figure 5-10(a) shows the DTGA data on a linear-linear plot of $\dot{m}_q$ vs temperature. This plot suppresses the noise evident in the log-linear plot, and distinguishes the evaporation temperatures of the different species in a much more dramatic manner. Also, the linear DQTGA plot reveals the evaporation of a fifth species near 95 K, which is not apparent in the QTGA plot of Fig. 5-6(a), or the log-linear DQTGA plot of Fig. 5-8.

To enhance clarity, the linear DQTGA data have been smoothed by calculating the average evaporation rate over time intervals of several minutes rather than the 1 minute intervals used for the data in Figs. 5-8 and 5-10(a). Figures 5-10(b), 5-11(a), and 5-11(b)

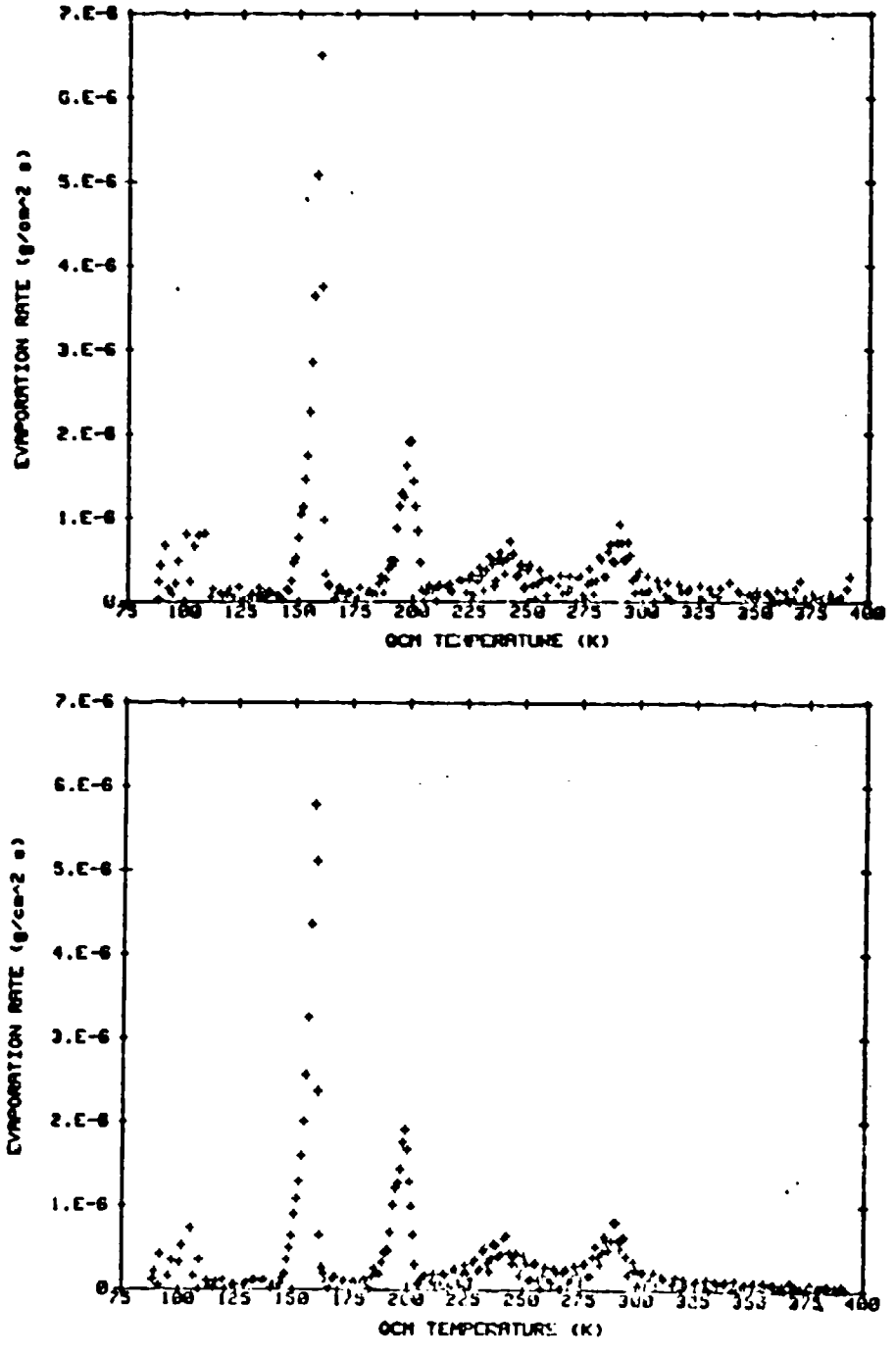
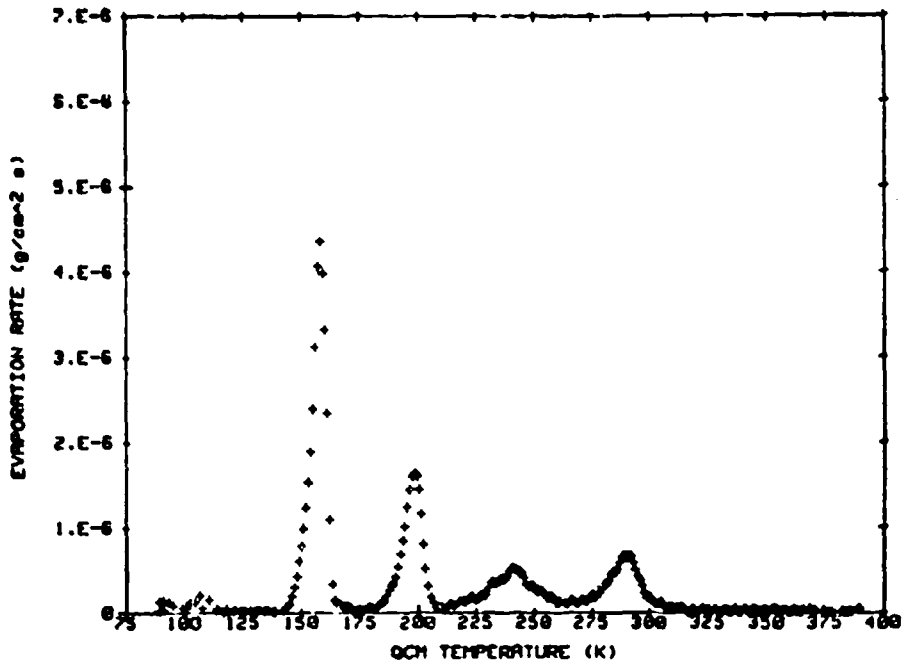
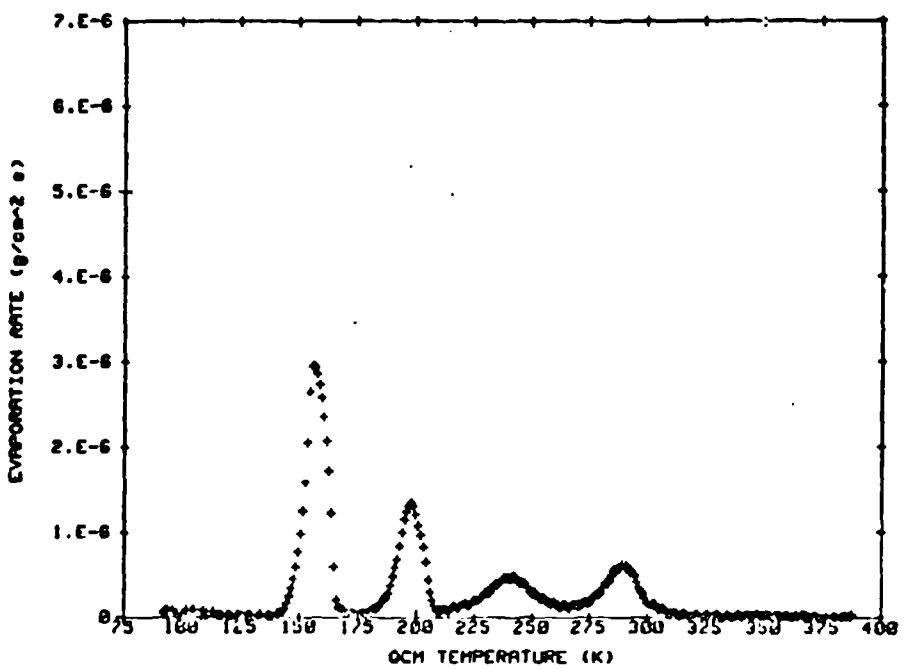


Fig. 5-10 Differential QCM Thermogravimetry Data for Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C (m_q versus T): Data Averaged Over (a) 1-Minute Intervals and (b) 2-Minute Intervals.



(a)



(b)

Fig. 5-11 Differential QCM Thermogravimetry Data for Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C (m_q versus T): Data Averaged Over (a) 5-Minute Intervals and (b) 10-Minute Intervals.

are plots of m_e calculated from the measured frequency changes over time intervals of 2, 5, and 10 minutes, respectively. Averaging over progressively longer time intervals clearly further smoothes the data, but conceals more and more of the fine structure and reduces the absolute magnitude of the evaporation rate. For the 10-minute interval, the evaporation peak for the 95 K species has been almost entirely suppressed. The figures suggest that, for this example, an averaging interval of between 2 and 5 minutes appears to strike a reasonable balance between smoothness and definition.

5.2.2 QCM Thermal Analysis Plus Mass Spectrometry (QTA/MS)

The QCM thermal analysis plus mass spectrometry (QTA/MS) test consists of heating the QCM in a controlled manner and measuring the mass spectrum of the evaporating species at 1-minute intervals. The major objective of the QTA/MS test was to separate the different components in the outgassed flux and to tag them so that they could be tracked during the isothermal outgassing test. A secondary objective was to identify the species chemically using their mass fragmentation patterns.

The concept of QTA/MS was explored in a preliminary manner in Phase II of this contract using single species, but its ability to analyze the more complex deposits produced by real materials with multiple outgassed species was not evaluated at that time. Since the Phase II Extension database measurement program provides the first opportunity to critically examine the chromatographic capability of QTA/MS this section will, therefore, assess this capability as well as present the data. The capability will be judged against two criteria. The first criterion is the ability to separate the major individual outgassed species sufficiently for their mass fragmentation patterns and/or unique fragments to be identified. The second criterion is its ability to identify the individual species chemically, which will be evaluated by comparing the QTA/MS data with GC/MS data.

5.2.2.1 QTA/MS Species Separation Capability

The mass spectrometer system can provide several types of data output in both tabular and graphical formats. The data of interest to the present tests were the mass spectra over a selected m/e scan range, the ion count for each m/e value in this range, and the average ion count (AIC) at each point in time during the QTA/MS test. Since the heating rate was constant at 1°C/min the QCM temperature-time relationship is linear, so the mass spectrometer data can be plotted interchangeably as functions of QCM temperature or time. In this section, all QTA/MS data are plotted versus QCM temperature to facilitate comparison with the QTGA data. Even though the mass spectrometer was capable of a m/e scan range of 2-1023, the scan range was limited to 10-500 in the isothermal outgassing tests to restrict the amount of data to be handled. This same m/e scan range was, therefore, also used during QTA/MS.

The average ion count (AIC) at each point in time is calculated by summing the total ion count (TIC) in a mass spectrum taken at that time and dividing by the total number of mass peaks. The AIC and the TIC are thus the same except for a scaling factor equal to the number of mass peaks being monitored. A plot of the AIC or the TIC versus time or QCM temperature during QCM heating constitutes a chromatogram, analogous to chromatograms generated by other techniques such as GC/MS. If the QTA/MS is able to separate the species adequately, the chromatogram will display peaks corresponding to the evaporation of discrete species. The mass spectra corresponding to the chromatogram peaks can be used to determine the chemical identity of the species evaporating at that time.

Figure 5-12 shows the QTA/MS AIC chromatogram for the outgassing products collected from R-2560 at 125°C. The ordinate of the chromatogram has been normalized to the highest AIC value. Since the evaporation of a discrete species from the QCM deposit should be indicated by a peak in the QTA/MS chromatogram, the QTA/MS chromatogram should be very similar in form to the DQTGA plots, Figs. 5-8 and 5-10. Comparison of the DQTGA and AIC plots shows that the AIC plot does indeed have four peaks corresponding to the four main DQTGA peaks but it also has at least two additional peaks near 140 K and 170 K that do not correspond to evaporation of mass from the QCM. An analysis of the data presented in Section 5.2.2.1.1 shows that the 140 K and 170 K peaks were spurious and due to detection of species evaporating from surfaces other than the QCM crystal. The spurious AIC peaks from the 238 K and 290 K species groups do not appear in Fig. 5-12 because they coincide with the real peaks at 198 K and 238 K, respectively.

Because the mass spectrometer may detect species evaporating from more than one surface at more than one temperature, the AIC at any point in the QTA/MS scan can include contributions from more than one species. The mass fragmentation patterns of the different species in the deposit on the QCM could thus not be determined by simply recording the mass spectra corresponding to the AIC peaks, and the more intensive manual analysis described in Section 5.2.2.1.2. had to be performed.

5.2.2.1.1 Analysis of the Spurious Peaks

A more detailed analysis of the QTA/MS was made to confirm that the additional peaks in the AIC chromatogram were, indeed, spurious and to find a way to work around this problem in analyzing the present data. In the GC/MS tests the fragment with m/e=151 was detected for only one species - an alkyl silicate - and this species was one of the most abundant. This species could therefore be expected to be a major component of the outgassed species, and during QTA/MS the fragment at m/e=151 should be very strong and ideally should be detected only once, as the alkyl silicate evaporates from the QCM. The

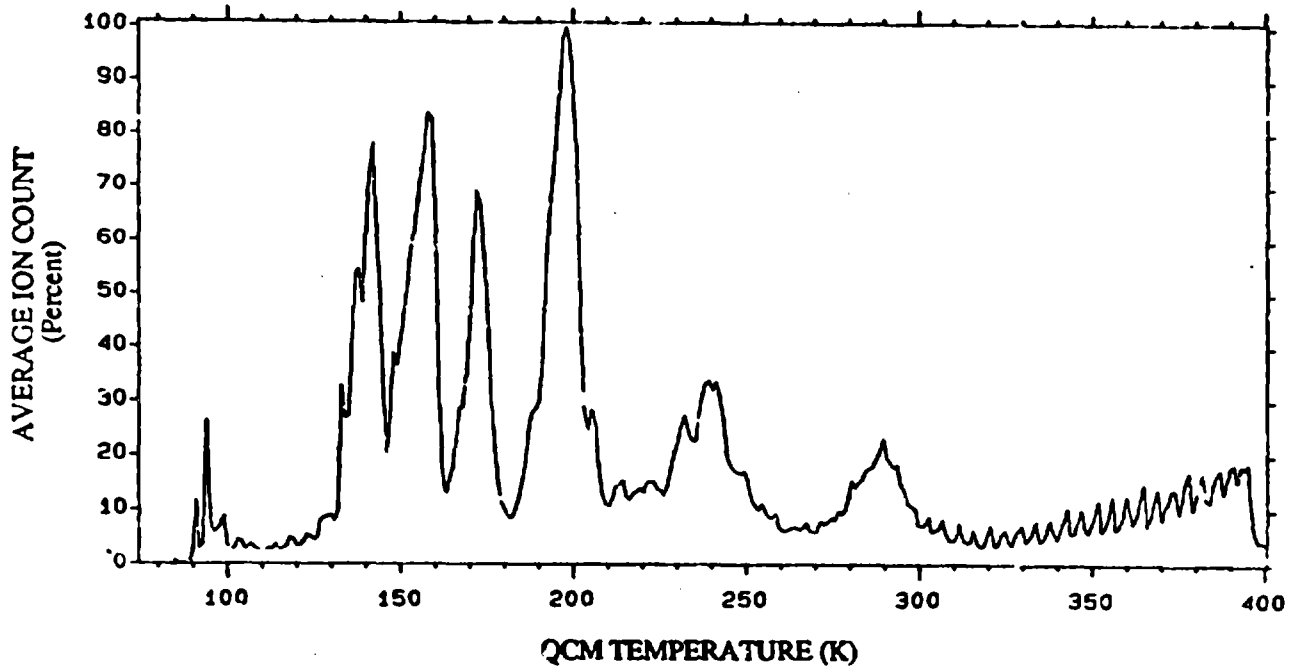


Fig. 5-12 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Average Ion Count as a Function of QCM Temperature.

m/e=151 fragment was, therefore, used to analyze the spurious peak problem further.

Figure 5-13 is a plot of the QTA/MS m/e=151 data versus temperature. The plot shows two distinct peaks, at 198 K and 172 K, so the ionizer must be seeing two evaporation sources for species with a 151 fragment. Comparison of Figs. 5-11(a) and 5-13 shows that the 198 K peak in Fig. 5-13 corresponds to evaporation of a major species from the QCM, whereas the 172 K peak does not. It is concluded therefore that the 198 K peak is due to species evaporating from the QCM crystal and is the peak of interest to the test method. The 172 K peak is due to detection of species evaporating from other surfaces of the apparatus which heat up as the QCM is heated and is, therefore, spurious.

Analysis of the QTA/MS peak height data at other m/e values with relatively simple peak patterns unambiguously confirms the above conclusions.

The spurious m/e=151 peak produced by evaporation of alkyl silicate from surfaces other than the QCM crystal occurs when these surfaces reach 198 K. Figure 5-13 implies that these surfaces reach 198 K before the QCM crystal does. The surfaces whose temperatures are higher than the QCM crystal temperature during transient heating are the electrical leads, the heater windings, and the QCM case. The major spurious evaporation source is probably the case because of its area and orientation. It is noted that the temperature separation between the spurious and real peaks on the QCM crystal temperature scale increases as the QCM temperature increases. This is because the heat input to the QCM heater is higher at higher QCM temperatures. The temperature difference between the QCM case on which the heater is wound and the QCM crystal must also be higher at higher temperatures in order to conduct this higher heat flux through the QCM.

The problem of the dual peaks due to evaporation from the case was encountered and addressed in Phase II, and is referenced in Section 2.3.1.3.2. At that time the problem was eliminated in the development test apparatus by placing an aperture plate between the QCM and the mass spectrometer ionizer so that the ionizer had no view of the case and could see only the QCM measuring crystal. It was hoped to incorporate this feature into the new apparatus by providing apertured shutters. The data indicate that this was apparently not an effective way to incorporate this feature in the new apparatus.

The spurious peak in Fig. 5-13 shows several smaller associated shoulders which indicates that the spurious peak is due to species evaporating from several other apparatus surfaces besides the QCM case. These surfaces could include the electrical heater and other service wiring.

It should be possible to eliminate the dual peak problem entirely by using a QCM design in which only the QCM crystal has to be heated during QTA/MS. This feature is now available commercially in units such as the QCM Research, Inc. Mark 16. As

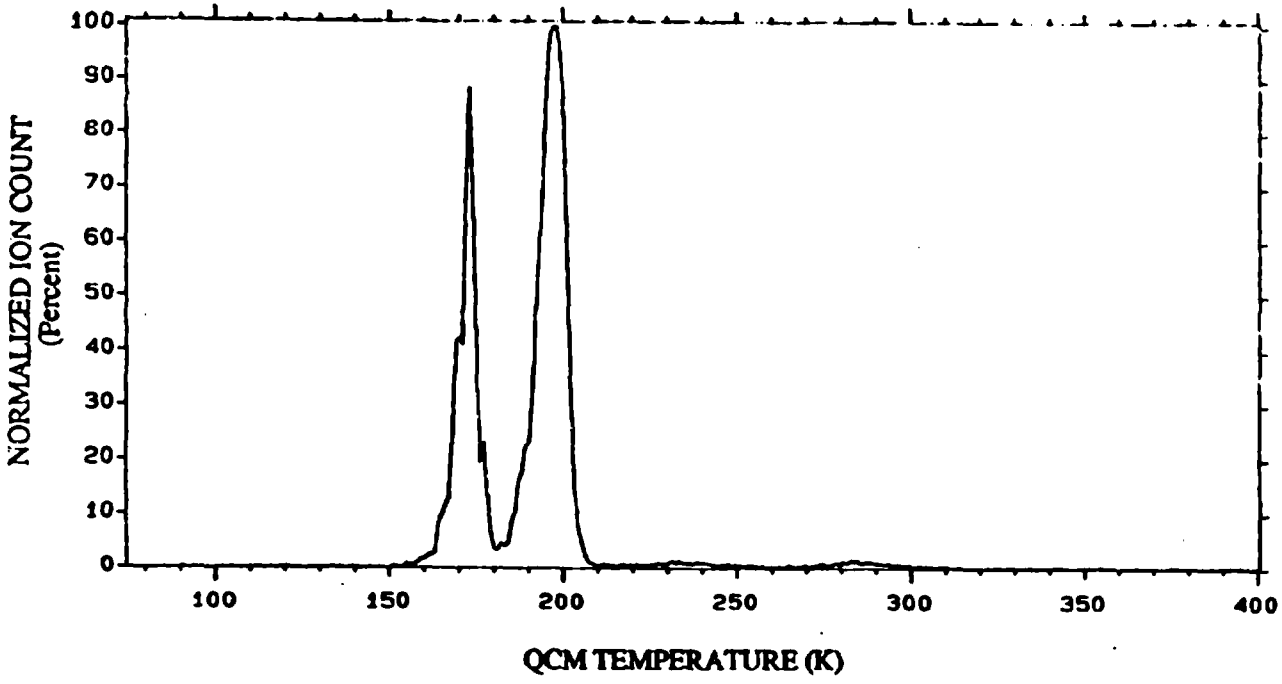


Fig. 5-13 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count for m/e = 151 as a Function of QCM Temperature.

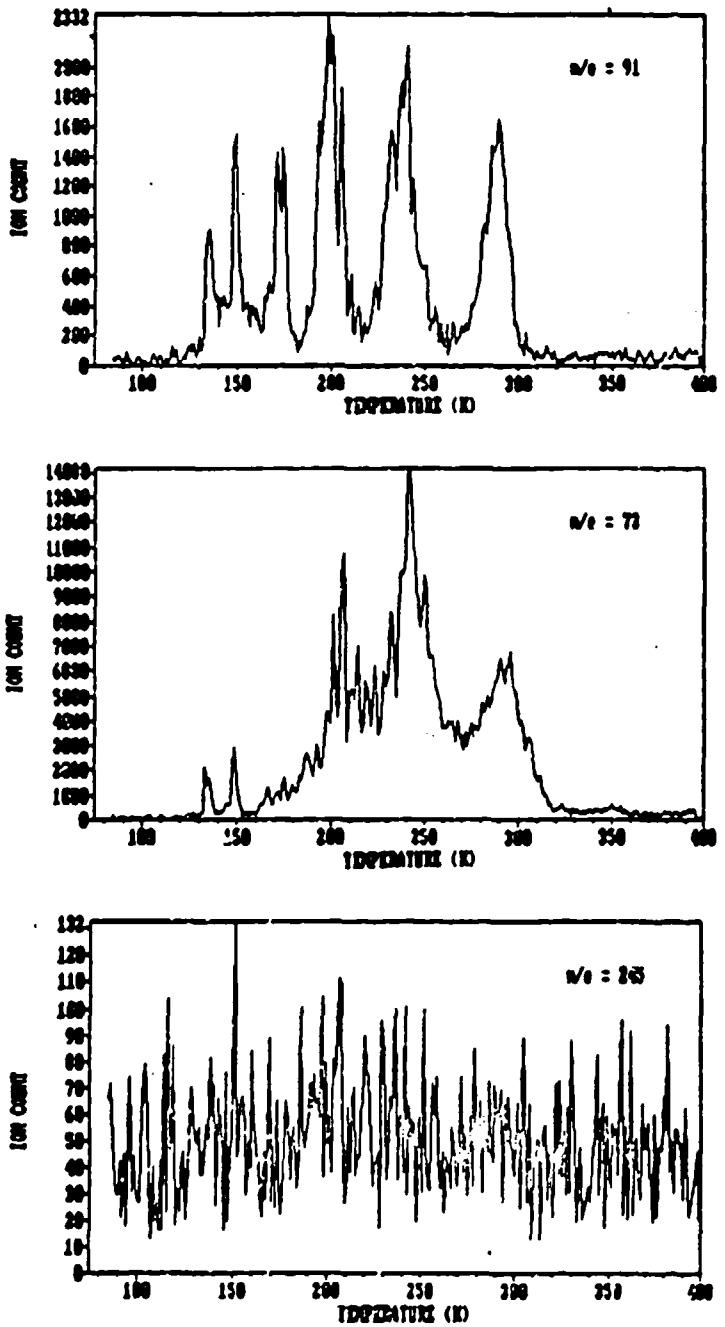
noted in Section 3.2.1 a Mark 16 QCM has been purchased and will be added to the apparatus in the near future.

5.2.2.1.2 Analysis of QTA/MS Mass Fragment Data

The basic QTA/MS data acquired were the mass spectra for m/e values from 10 to 500 taken at one degree temperature intervals from 90 K to 400 K. This creates a total of about 152,000 data points per test. The mass spectrometer software can provide the total mass spectrum at each temperature step or the variation of the ion count for each m/e value with QCM temperature. All data can be provided in terms of actual ion count or normalized as a percentage of the highest peak. These data can be presented in either graphical or tabular form. The software can determine the difference between a measured spectrum and a reference spectrum. This capability was used to subtract the vacuum chamber background spectrum, measured immediately before starting QTA/MS, from the spectra measured during the test.

If there were no spurious peaks and QTA/MS were able to separate the species adequately, then the normalized ion counts as a function of m/e, i.e., a mass spectrum, for a temperature in the test corresponding to a peak in the AIC data, Fig. 5-12, would be the mass fragmentation pattern for the species responsible for that peak. In this case the fragmentation pattern data for each species could be entered directly into a deconvolution algorithm to resolve the outgassing rates of each species from the total isothermal outgassing rate. The fragmentation patterns could also be entered directly into the computerized NBS library to identify the species. It was not possible to obtain individual species fragmentation pattern data simply by printing out a table at a given QCM temperature because the spurious peaks discussed earlier excessively confused the patterns at a given temperature. The body of QTA/MS data could, therefore, not be analyzed using the mass spectrometer system software and the data analysis had to be made manually.

The manual analysis began by printing out the plots of ion counts versus QCM temperature for all m/e values between 10 and 500. A typical plot for a given m/e showed ion count peaks corresponding to the evaporation of each species which had a mass fragment at that m/e value. If there was only one species with a particular m/e, a plot similar to Fig. 5-13 was obtained. If there was a small number of species with the m/e value a plot of the form of Fig. 5-14(a) was obtained. The ion count for m/e=91 in Fig. 5-14(a) reveals several distinct species as well as their associated spurious peaks. If a particular m/e value was common to many species, such as m/e = 73, 135, and 147 for silicone species, the plot would show a high output continuum of peaks similar to Fig. 5-14(b). For many m/e values there were no associated fragments of outgassed species and a plot similar to Fig. 5-14(c) for m/e=245 showing random background was obtained.



(a)

(b)

(c)

Fig. 5-14 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Plots of Ion Counts Versus QCM Temperature: (a) m/e= 91, Common to a Few Species, (b) m/e=73, Common to Many Species, (c) m/e= 245, Present in No Species.

The temperatures at which peaks occur in an ion count plot for a given m/e corresponds to the evaporation of specific species from the deposit on the QCM. Since the number of species is finite, all the peaks in the ion count plots for all m/e values should occur at specific temperatures corresponding to the evaporation of one or other of these species. The QTA/MS data can thus be extracted from the plots and placed in a table whose columns correspond to specific species, identified in the first instance by their evaporation temperatures, and whose rows correspond to specific m/e values. The heights of the ion count peaks in the plots are then entered into the table at the location corresponding to the m/e value of the plot and the QCM temperature at which the peak appears.

The ion count peak data for R-2560 were extracted from the plots of ion count versus temperature and entered into Table 5-2. Section 5.2.2.1.2.1 describes how the number of resolvable species listed in Table 5-2 was determined. Section 5.2.2.1.2.2 describes how the table was completed.

5.2.2.1.2.1 Resolvable Species

The plots of ion count versus QCM temperature for all m/e values from 10 to 500 were printed out. The plots were surveyed manually to determine the approximate number of resolvable species. It proved to be possible to separate species with evaporation temperatures as close as about 5 K. Separation of species with evaporation characteristics closer than 5 K was hampered in part by the spurious peak problem and in part by the basic resolution limitations of the QTA/MS technique. It was concluded that distinguishable ion count peaks could be found at about 20 different temperature locations, each of which corresponded to the evaporation of a specific species. Some of these species were not very abundant, and it proved to be difficult to resolve them consistently, so the number of species categories was finalized at 15. The specific evaporation temperatures at which separable species could be identified and which are used to reference these species are given in the column headings in Table 5-2.

For each of the separable species, a specific m/e plot which clearly showed the temperature location of the ion count peak was selected as a reference. The selected reference plots are shown in Figs. 5-15 through 5-29. The plots have all been normalized to the highest peak.

Figure 5-15 is the plot for m/e equal to 45, which was used to locate the 95 K species. This is the best defined of all the reference peaks. There is no spurious peak associated with this peak because it occurs right at the beginning of heating, at which time the temperature differentials in the QCM are very small.

Figure 5-16 is the plot for m/e equal to 49, which was used to locate the 145 K species. The peak is very clean, narrow, and well defined, and suggests that it may

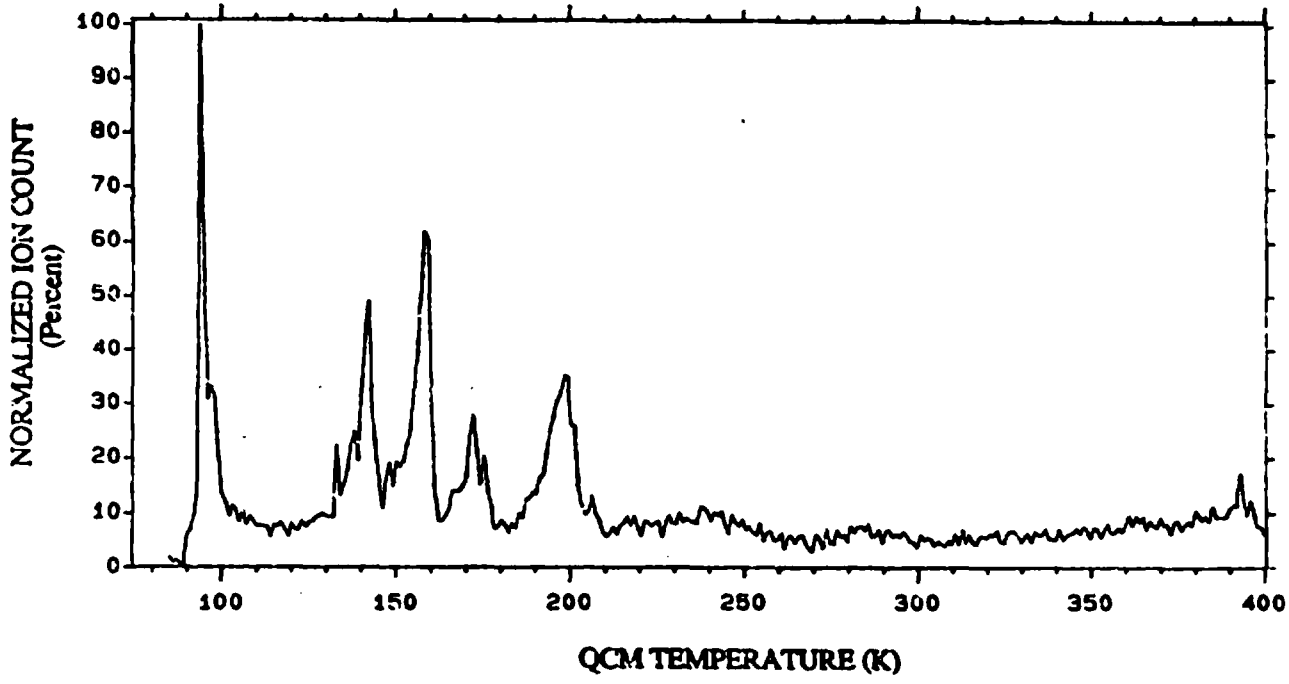


Fig. 5-15 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 45, Used to Locate the 95 K Species.

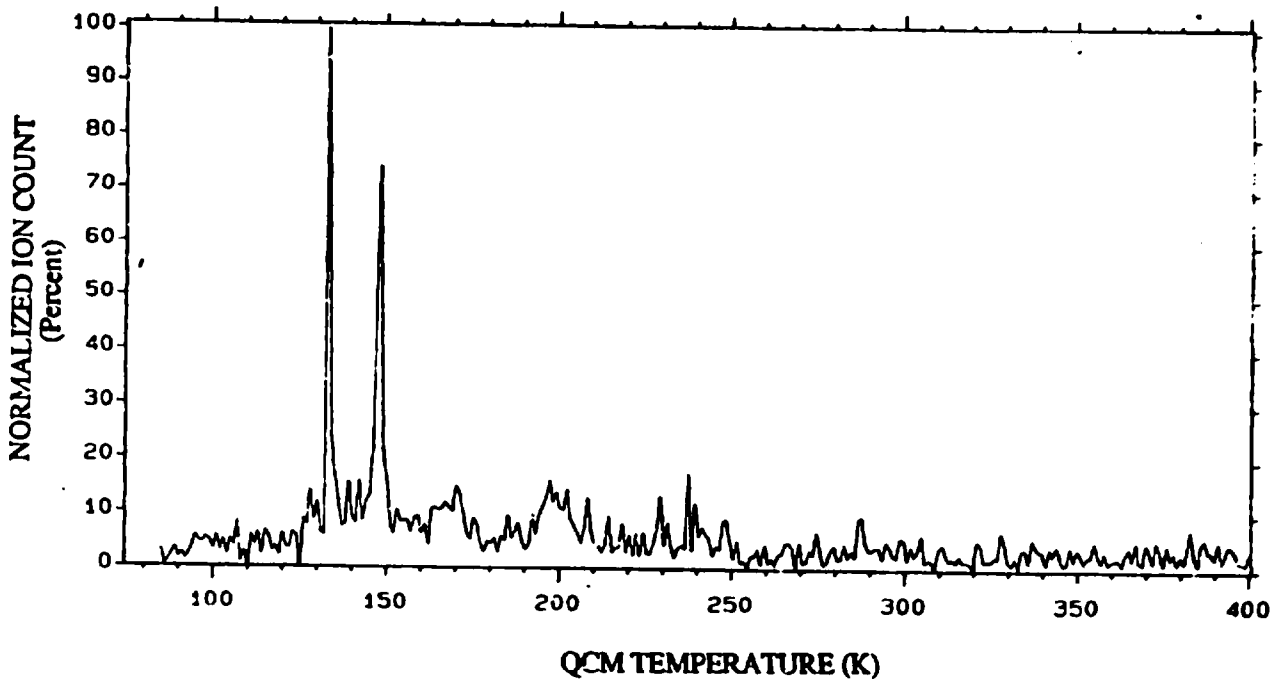


Fig. 5-16 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 49, Used to Locate the 145 K Species.

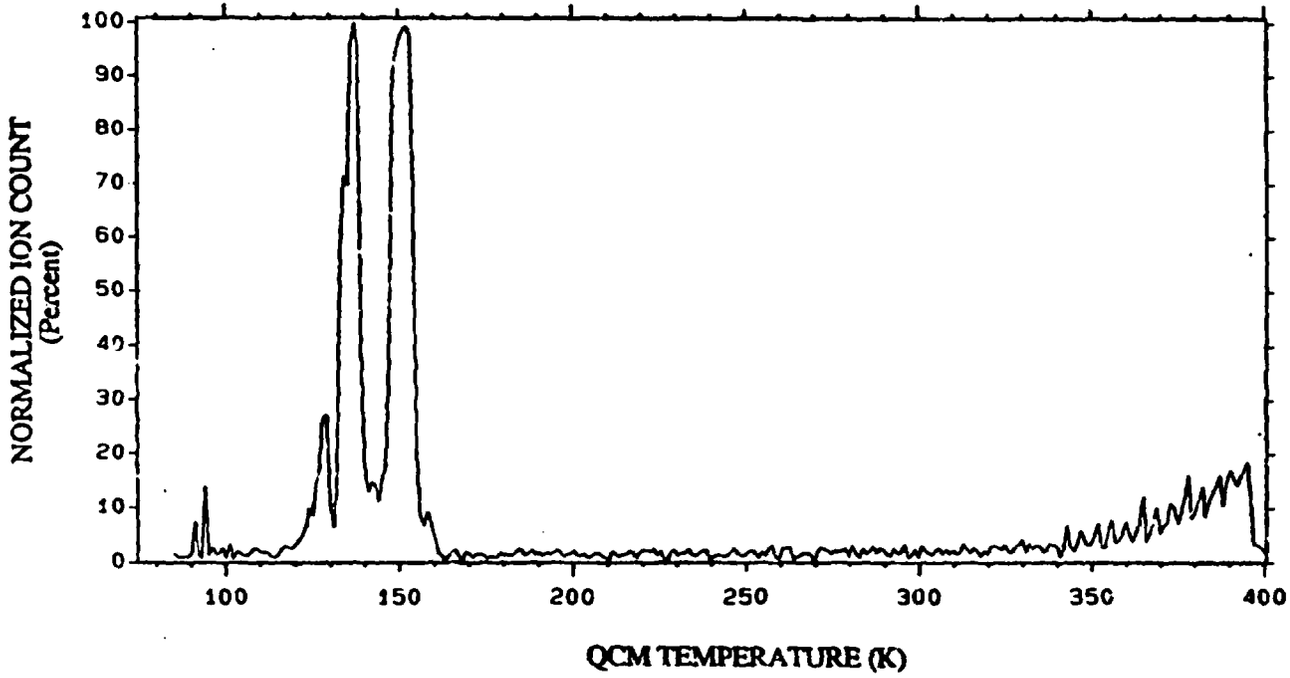


Fig. 5-17 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 18, Used to Locate the 150 K Species.

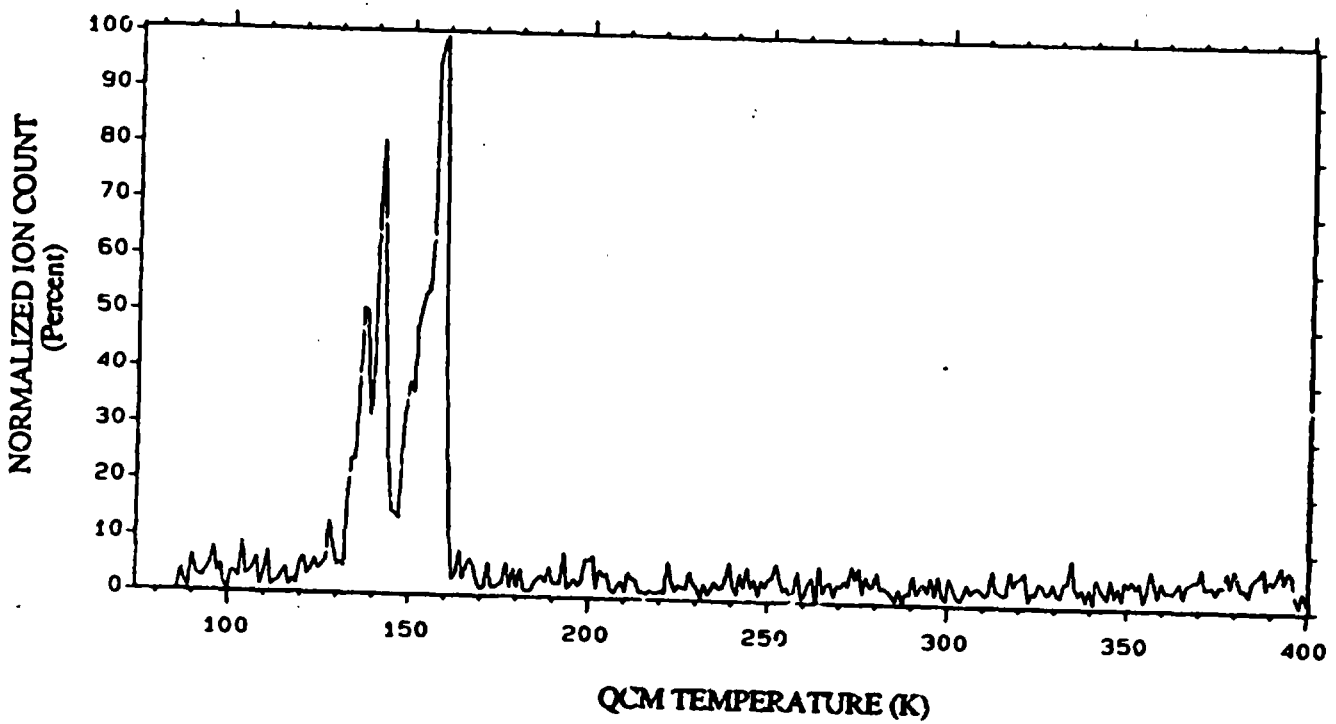


Fig. 5-18 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 21, Used to Locate the 158 K Species.

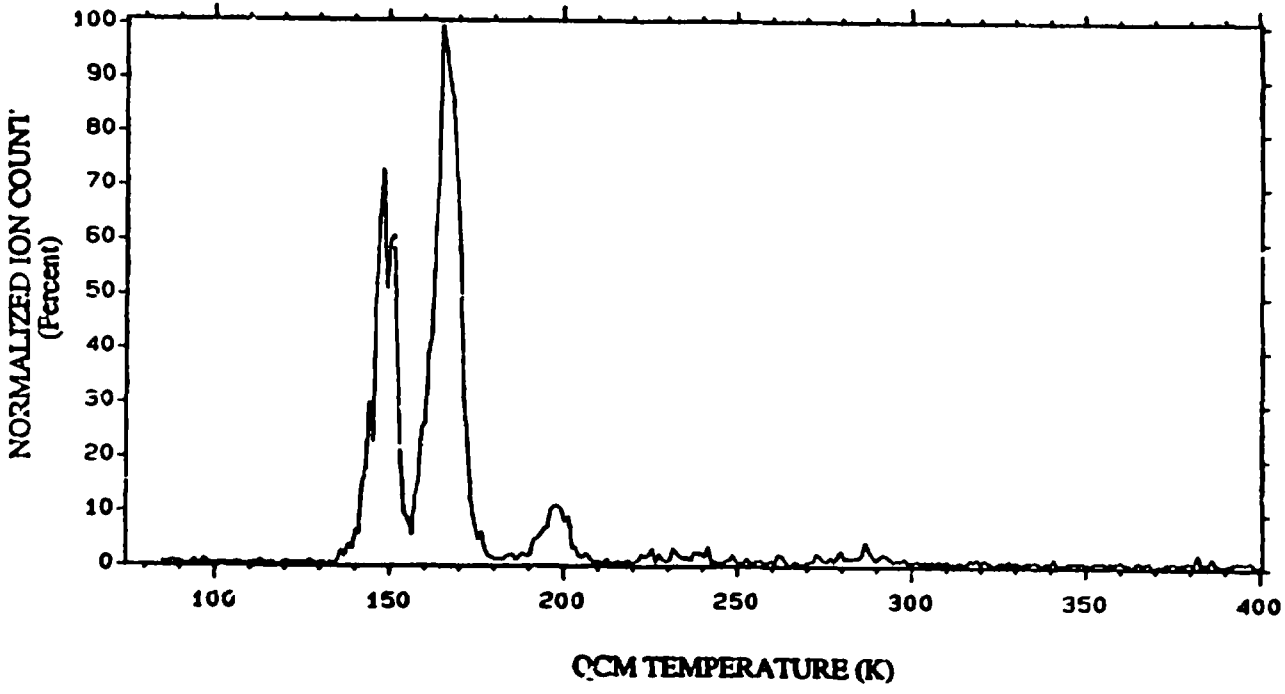


Fig. 5-19 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 161, Used to Locate the 170 K Species.

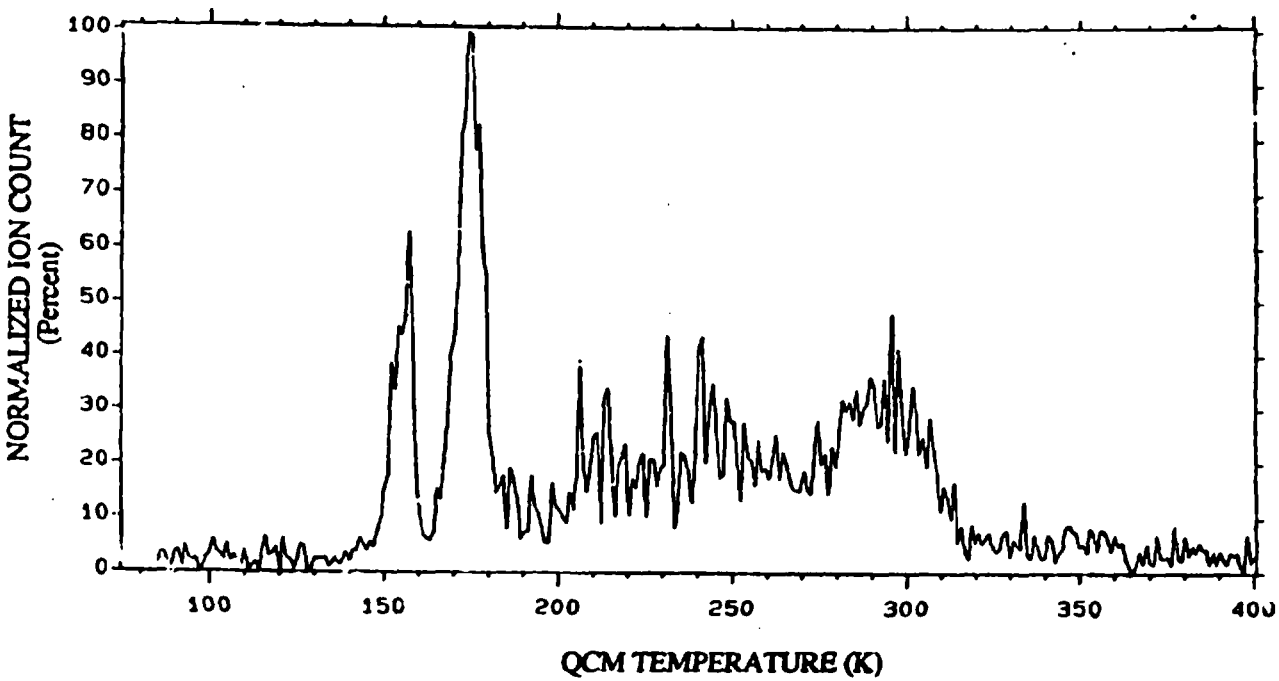


Fig. 5-20 . Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 281, Used to Locate the 175 K Species.

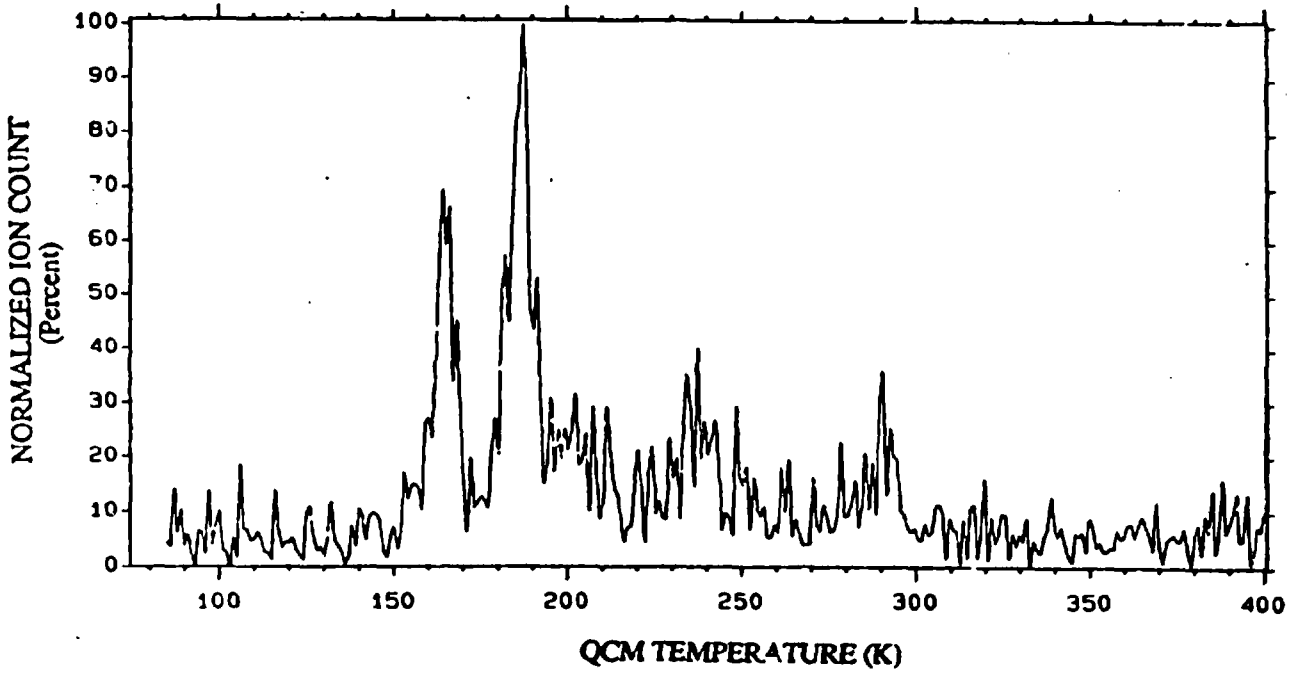


Fig. 5-21 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 170, Used to Locate the 185 K Species.

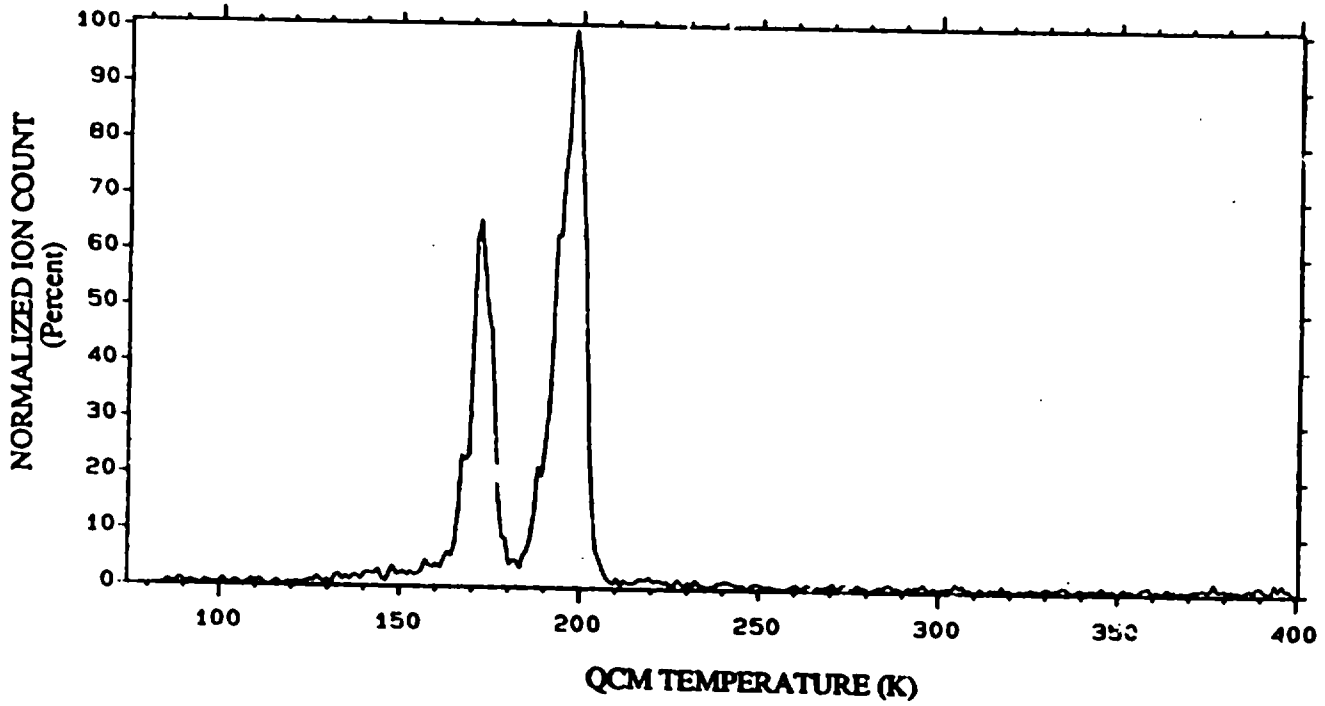


Fig. 5-22 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 64, Used to Locate the 198 K Species.

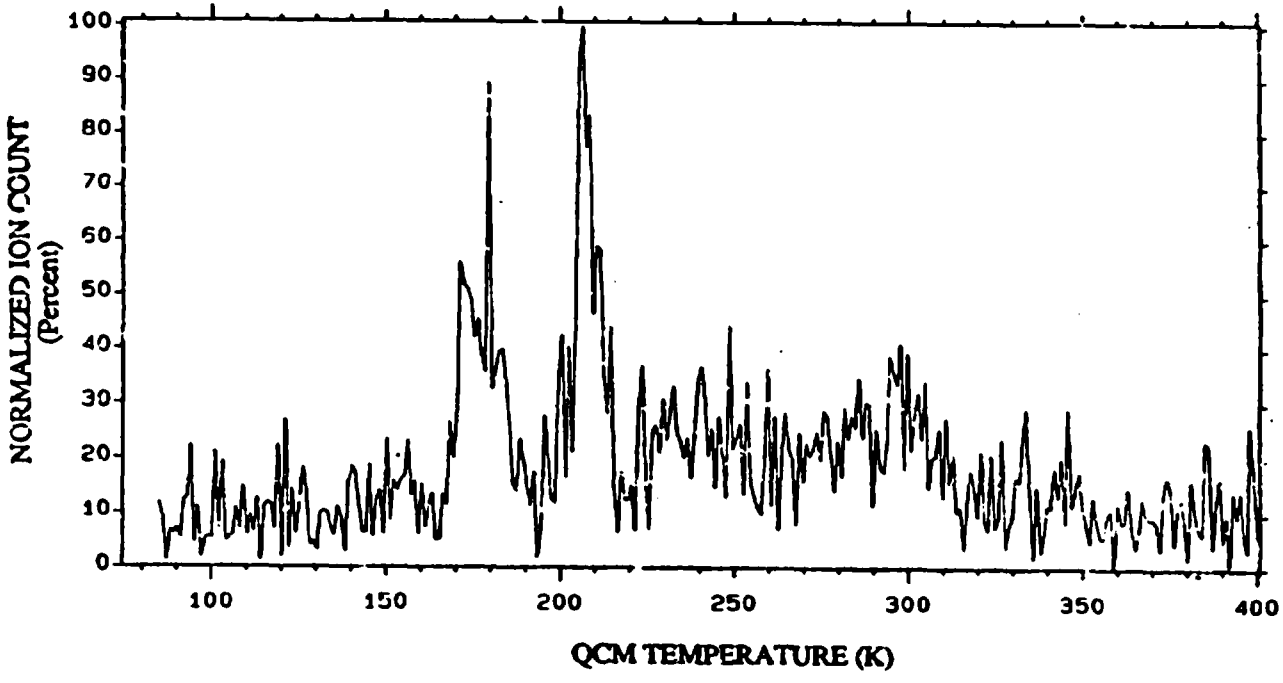


Fig. 5-23 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 280, Used to Locate the 210 K Species.

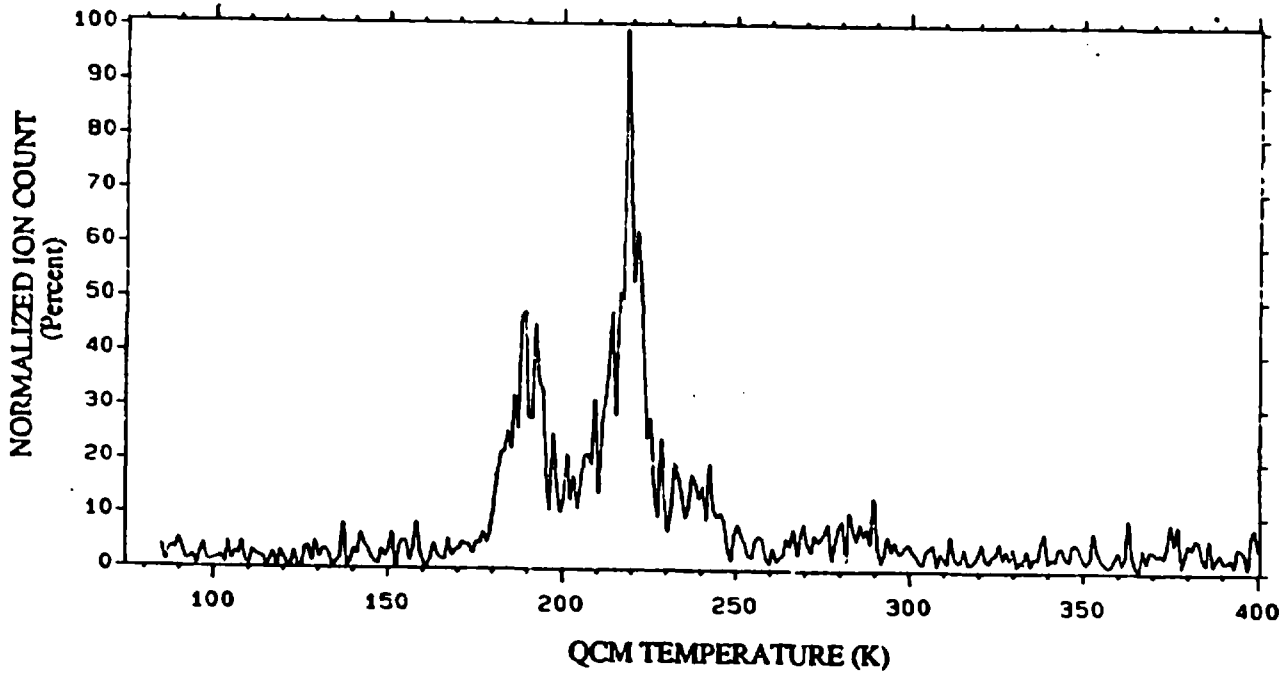


Fig. 5-24 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 242, Used to Locate the 220 K Species.

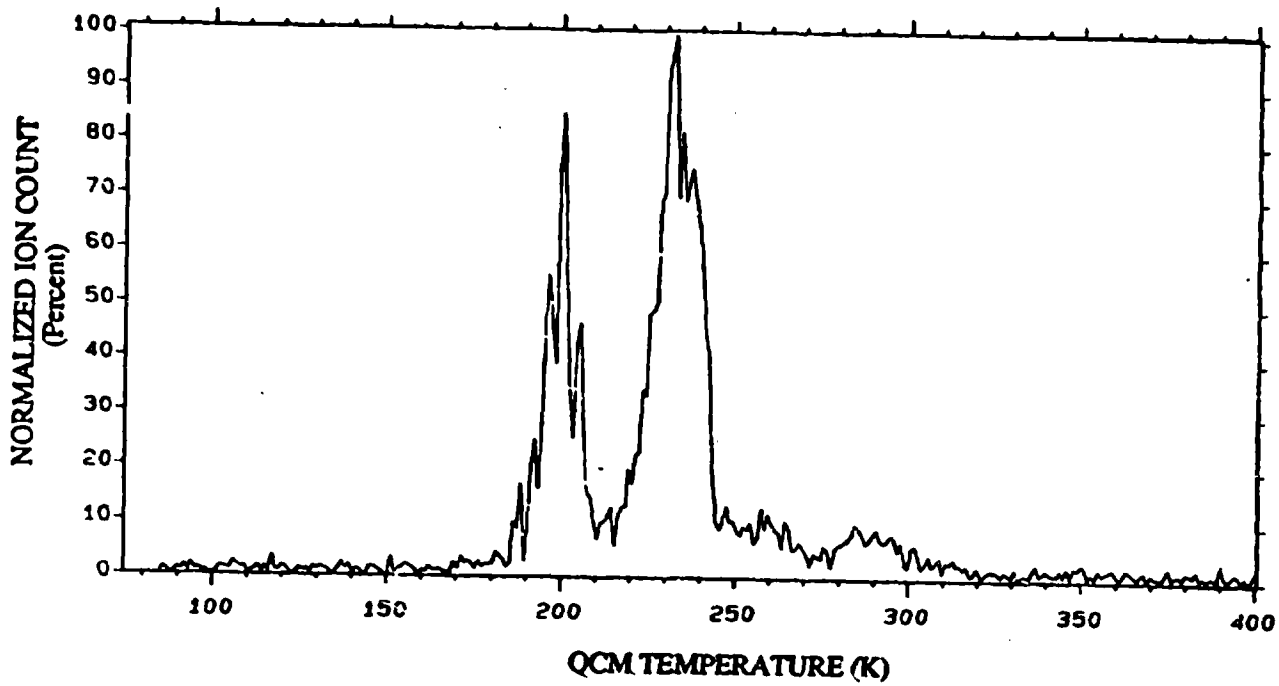


Fig. 5-25 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 327, Used to Locate the 230 K Species.

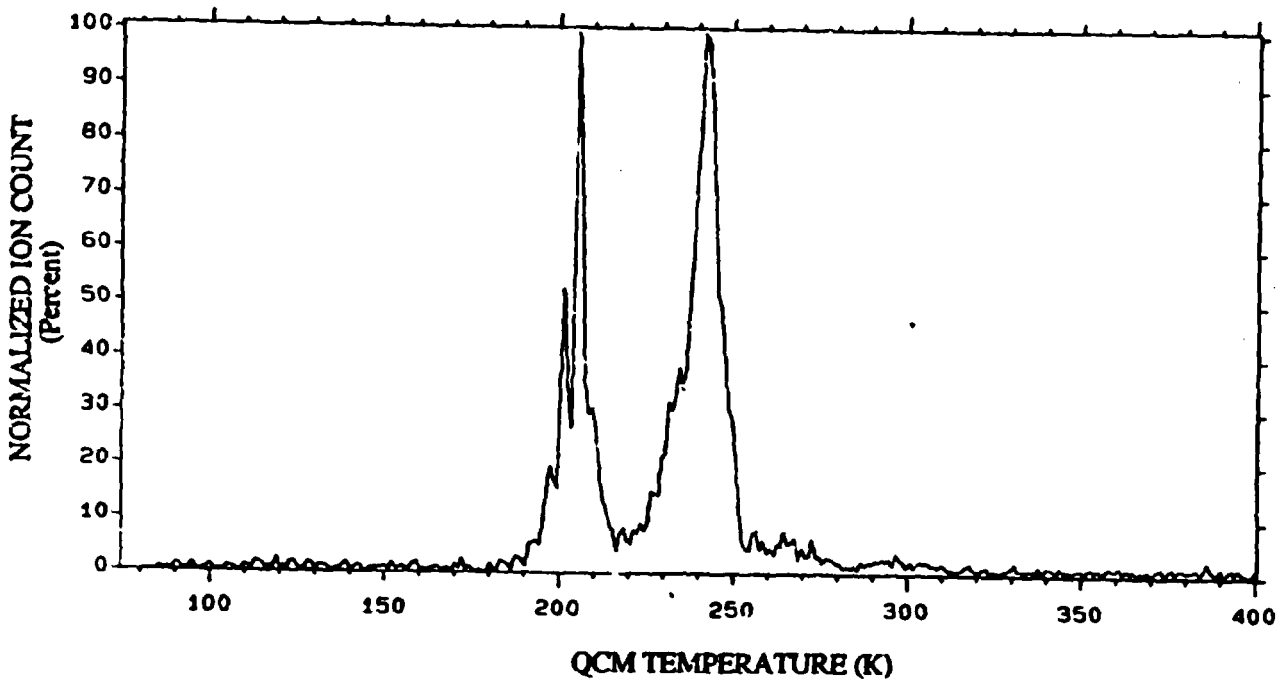


Fig. 5-26 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 479, Used to Locate the 238 K Species.

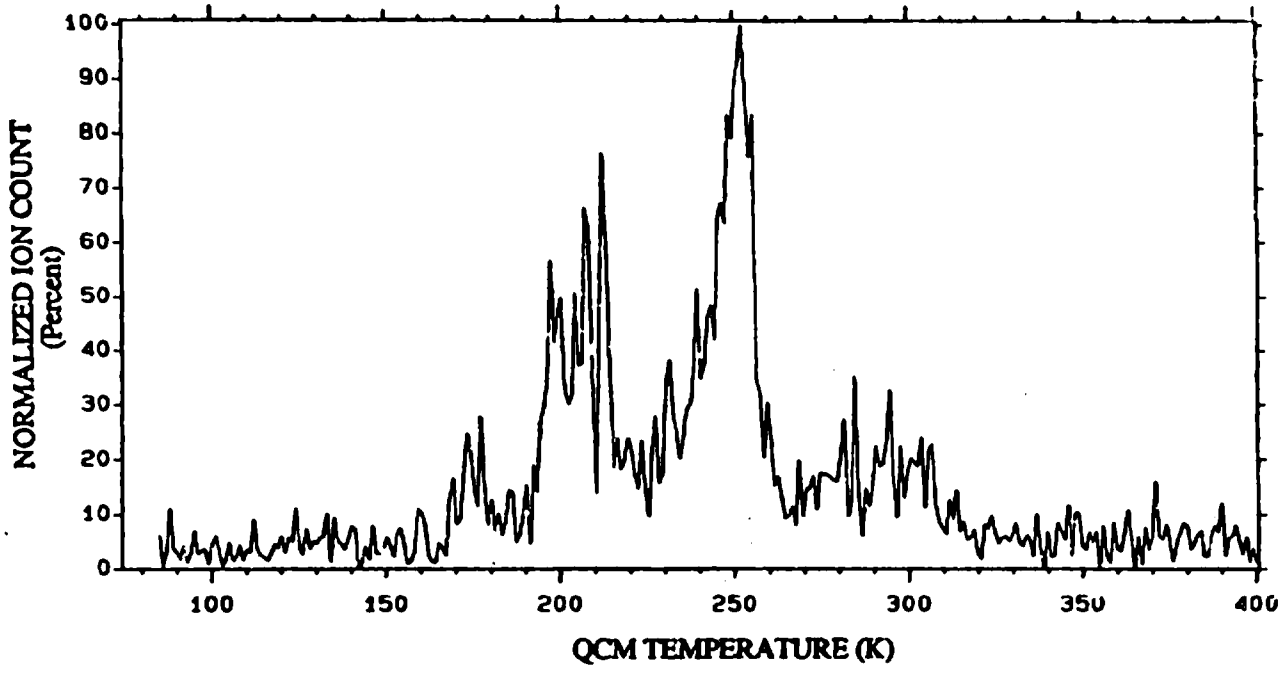


Fig. 5-27 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 341, Used to Locate the 250 K Species.

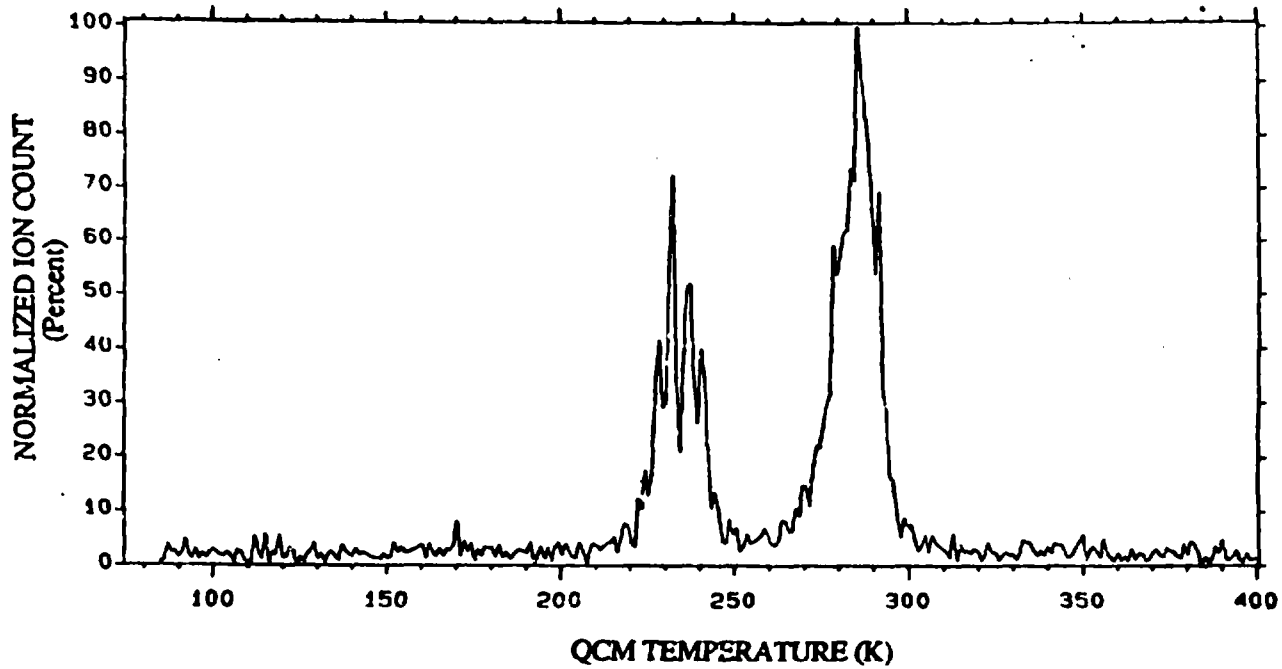


Fig. 5-28 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 452, Used to Locate the 285 K Species.

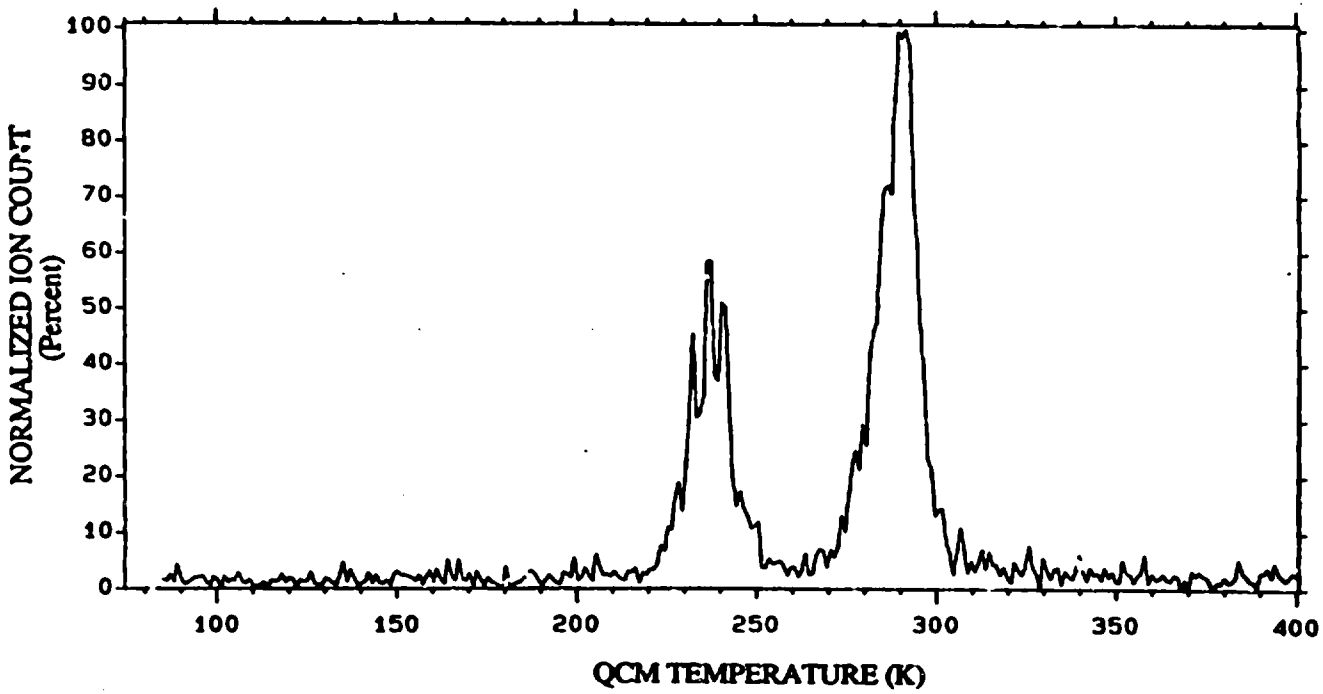


Fig. 5-29 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Normalized Ion Count Versus QCM Temperature for m/e = 259, Used to Locate the 290 K Species.

eventually be possible to resolve species with evaporation temperatures as close as one or two degrees with QTA/MS. The spurious peak is also very clean, which suggests that it was caused mainly by a single spurious source.

Figure 5-17 is the plot for m/e equal to 18, which was used to locate the 150 K species. The peak is very strong and reached the saturation level of 30120. This peak is not unique to the 150 K species since there is also a small peak at 93 K.

Figure 5-18 is the plot for the m/e equal to 21, which was used to locate the 158 K species. The peak also includes contributions from species evaporating at about 150 K and 153 K. The presence of these two lesser species is shown more clearly in the shape of the spurious peak.

Figure 5-19 is the plot for m/e equal to 161, which was used to locate the 170 K species. The main peak appears to include contributions from the spurious peak for the 198 K species, as well as two species at about 168 K and 161 K. Again, the presence of adjacent species is more evident from the spurious peaks than from the main peaks.

Figure 5-20 is the plot for m/e equal to 281, which was used to locate the 175 K species. The main peak includes contributions from closely adjacent species. Peaks also appear for many other higher temperature species, although the number cannot be estimated because of the spurious peak problem.

Figure 5-21 is a plot for m/e equal to 170, which was used to locate the 185 K species. This is a relatively weak peak and it appears also in many adjacent and higher temperature species.

Figure 5-22 is a plot for m/e equal to 64, which was used to locate the 198 K species. This is a very clear and almost unique peak, but there appears to be significant contributions from closely adjacent species.

Figure 5-23 is a plot for m/e equal to 280, which was used to locate the 210 K species. This is a very weak peak and is surrounded by a relatively high background. It is noted that the m/e of 280 is adjacent to the m/e of 281 which was used to locate the 145 K peak (Fig. 5-16).

Figure 5-24 is the plot for m/e equal to 242, which was used to locate the 220 K peak. The 220 K peak itself is very clearly defined and is surrounded by peaks from adjacent species.

Figure 5-25 is the plot used for m/e equal to 327, which was used to locate the 230 K species. The 230 K species appears to be but one of a number of species evaporating in this general temperature regime. At least seven shoulders can be seen on the main peak, and the presence of other species can be seen more clearly in the spurious peaks.

Figure 5-26 is the plot for m/e equal to 479, which was used to locate the 238 K

peak. The main peak is very well defined but is broad and clearly includes several adjacent species as well as the 238 K species.

Figure 5-27 is the plot for m/e equal to 341, which was used to locate the 250 K species. Although the 250 K peak is quite distinct, it is broad and includes a number of adjacent species.

Figures 5-28 and 5-29 are the plots for m/e equal to 452 and 253, respectively, which were used to locate the 285 K and 290 K species, respectively. The plots are very similar in shape, in that they have a central peak but also show a significant number of adjacent species. In this temperature regime, there are clearly more than just two species, but QTA/MS is not able to resolve them and they must be lumped in with the 285 K and 290 K species.

In order to show the discrimination capability of QTA/MS more graphically, the major peaks from Figs. 5-15 through 5-29 have been plotted in Figs. 5-30 and 5-31. Figure 5-30 is a superimposition of all of the normalized peaks from Figs. 5-15 through 5-29 and shows the ability of QTA/MS to identify 15 species in the outgassed products, whereas only four major species groups could be identified by the QTGA mass measurements. It is possible that several more species could be identified from the QTA/MS data with more intensive analysis, but 15 is probably already more than can be usefully accounted for in system contamination modeling studies.

Figure 5-31 is also a superimposition of the peak data from Figs. 5-15 through 5-29 but plotted using true rather than normalized peak height data. Since this plot presents only one mass peak for each species, it does not give a reliable quantitative indication of the relative amounts of each species. However, it does show quite clearly that use of the mass spectrometer greatly increases the ability of QTA to detect species with very low concentrations. The most dramatic example in Fig. 5-31 is the ability to separate the 145 K species from the 150 K species. Using the mass-only measurement capability of QTGA alone, the evaporation of the 145 K species would be completely masked by the evaporation of the 150 K species.

5.2.2.1.2.2 QTA/MS Peak Height Inventory

The entire body of QTA/MS data was analyzed manually, and the ion count peak height data were entered into Table 5-2. The plots of ion counts versus temperature for every m/e value between 10 and 500 were compared with the reference plots, Figs. 5-15 through 5-29, by holding them up to the light. In more than 98 percent of the cases, we found that the peaks could be unambiguously matched with one of the reference temperatures. Those that could not be matched were confined to minor species. The height of the peak was read from the ordinate and was entered into the table in the appropriate

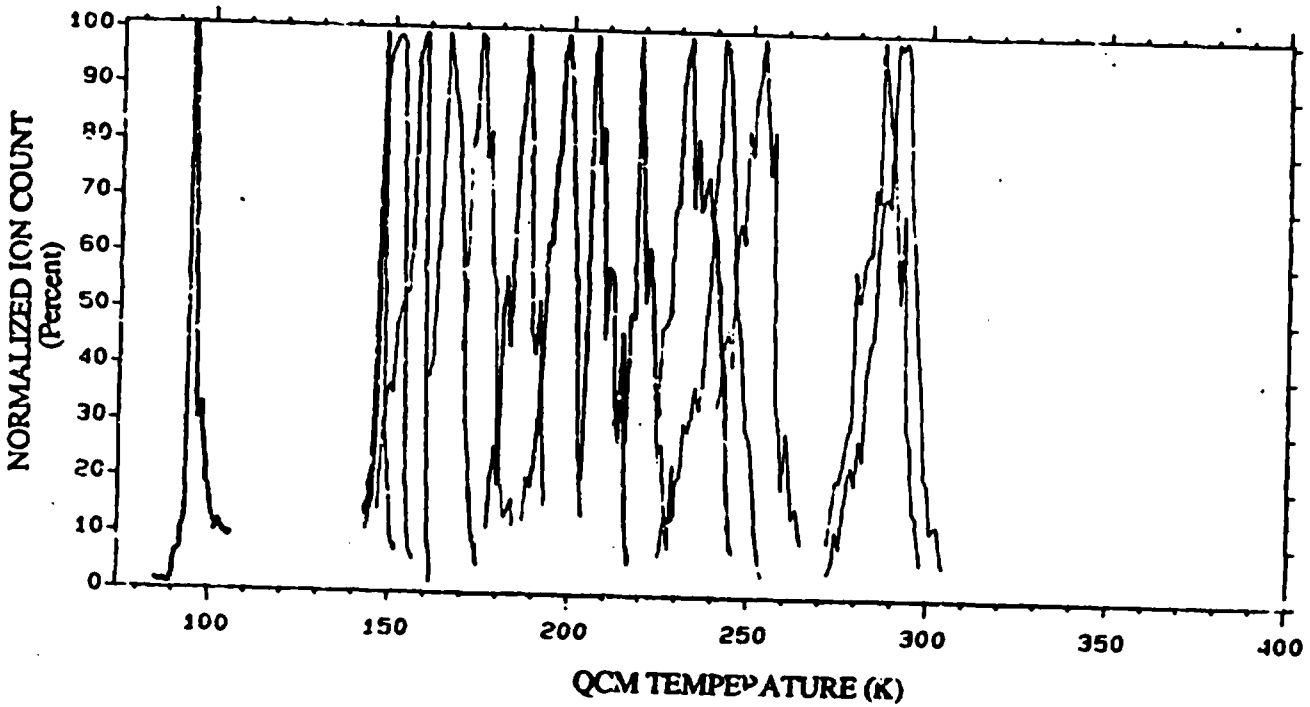


Fig. 5-30 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Superimposition of Locator m/e Peaks for All Species Separated in QTA/MS: All Peaks Normalized to 100 Percent.

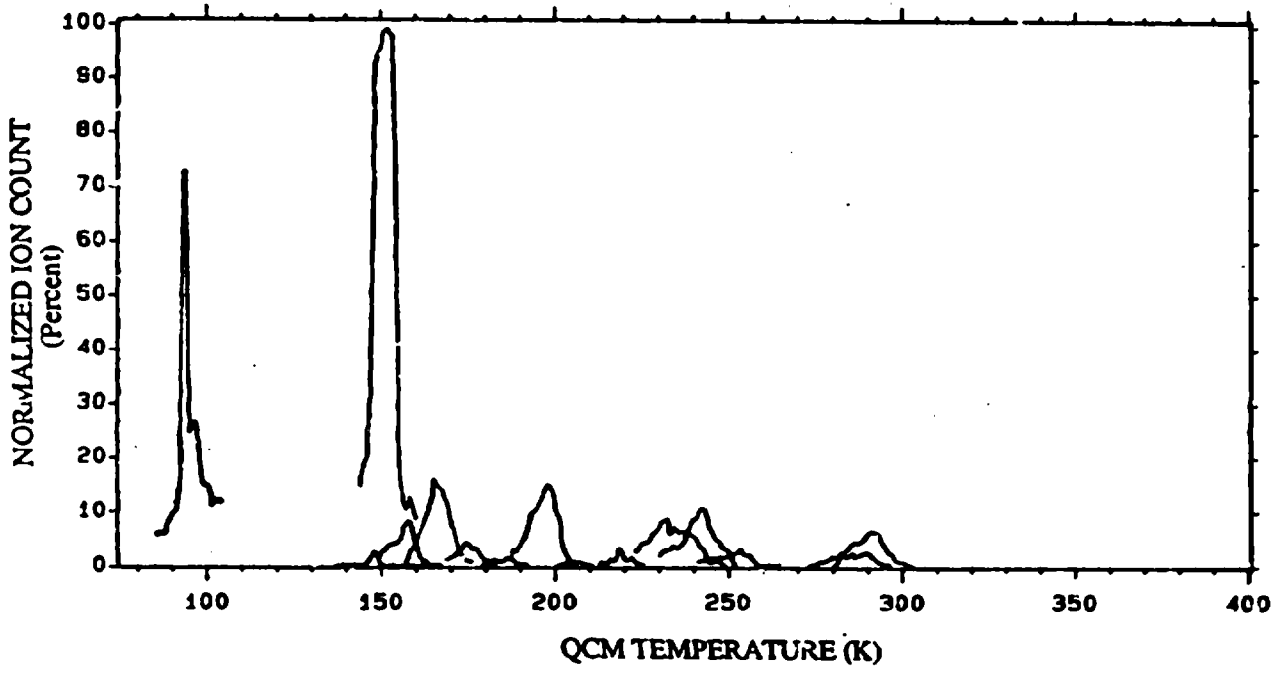


Fig. 5-31 Mass Spectrometer Monitoring During QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Superimposition of Locator m/e Peaks for All Species Separated in QTA/MS: Peaks Plotted with True Relative Heights.

temperature column and m/e row. In determining ion count peak heights, the two-peak phenomenon was noted and the heights were recorded only for the higher temperature of each pair of peaks. The peak heights were recorded in terms of ion count.

The table entries fall into the following categories:

(i) If there was a clear peak in the m/e versus temperature plot, the peak temperature location was correlated with one of the species identified in Figs. 5-15 through 5-29, and its height was read from the ordinate and entered into the table in the appropriate species column and m/e row.

(ii) If the ion peak height was less than twice the background and the signal was small (less than about 100 ion counts), no entry was made in the table.

(iii) Certain m/e values were common to a homologous series of materials and although the signal was large, the ion count data appeared more as a continuum with temperature rather than as discrete peaks because of the large number of species with these fragments. In these cases, the table shows the same peak height for the entire range of temperatures for which this phenomenon occurred.

(iv) The table shows many entries with the value 30120. This was the highest value that the mass spectrometer could indicate before saturating. An entry of this value means that the mass spectrometer was saturated and that the true ion count was higher than 30120.

The mass fractions of each species were determined by adding up the total ion count for each species and expressing it as a fraction of the total ion count for all species. These fractions are shown at the bottom of Table 5-2. These numbers are not quantitatively reliable because the ion counts recorded for some species peaks included contributions from the spurious peaks from other species which happen to coincide. Also, for those species which saturated the mass spectrometer, the recorded ion count is less than the true ion count. Quantitative interpretation must also take into account that the ionization constants of the different species will be different.

The cumulative total of the mass fraction detected by the mass spectrometer and calculated from the ion count at any QCM temperature should be quantitatively very similar to the fraction of the initial QCM deposit that has evaporated by that temperature. Consequently, the quantity (1 - cumulative ion count total) should be similar to the QTGA plot, Fig. 5-6(a), which shows mass fraction remaining on the QCM as a function of QCM temperature. The quantity (1 - cumulative ion count total) has been plotted as a function of QCM temperature in Fig. 5-32. It does strongly resemble the QTGA plot, with the notable exception that Fig. 5-6(a) does not show the presence of a 95 K species. The 95 K species is apparent in the DQTGA data of Fig. 5-10, and so is not an artifact of the QTA/MS data.

Table 5-2

Inventory of Mass Spectrometer Ion Count Data from the QTA/MS Test

MOL.	<-------- EVAPORATION TEMPERATURE -------->														
WT.	95 K	145 K	150 K	158 K	170 K	175 K	185 K	193 K	210 K	220 K	230 K	238 K	250 K	265 K	290 K
12	5400			2400											
13	9800			5090											
14	10800			17300											
15	29000			30040											
16	30120			28000											
17	28360		15000	8000											
18	5000	5000	30120												
19		11000	28180	13500											
20			7000	12920											
21			1400	2612											
22	628			500											
23	396														
24				1232											
25				6980											
26				28400				2000							
27	4800			30120				19000							
28	28000			30120				25000	18000	18000	18000	19000	18000	19000	19000
29	25000			30120				25000	17600	17300	17000	17000	17000	17000	17000
30	7000			30120				21000	5000	5000	5000	5000	4000	4000	4000
31				30120				4000							
32	13000			30120											
33	11000			28780			6000	6000	6000	6300	6000	6000	7000	7000	7000
34				12800											
35				2130											
36				1744											
37				8360											
38				15620				500							
39				29980				4000							
40				29120				4000							
41				30120				16500				4000			
42				30120				14500				4000			
43	8000			30120				17000		5000		6000			
44	27340	8500		27430				15000		5000		6000			
45	22240	5000		14000				8500	2500	2500	2500	2500	2500	2500	2500
46	3700	3000		9780				6400		1100		1800			
47	690	1100		1804				1700		250		400			
48	150	760		430	784			784							
49		900													
50		1220						252				300			300
51		1500		420					380			500			400
52		1220		1600				350				400			250
53		650		2054	200	200	200	500	300	300	300	500	50		
54				2500				3860		1700		2250	250		
55				2612				5080		1900		2700			400
56				6400				3300		1800		2400	500		
57		2400		7380				3500		2100		2500	500		
58				27760				1900				1000			
59				30120				2200		1500		3000			
60				30120				3500		4000		4000			
61				14400				4500		3500		2100			
62				2700				19000		800					
63								1800							
64								4500							
65								1954							
66								1034							
67								1192							
68								1074				450			
69					400	400	400	1014	400	950	400	1300	200	100	400
70					200	200	600	1165	400	850	500	1100	300	200	300

Table 5-2 (continued)

MOL.	<-------- EVAPORATION TEMPERATURE -------->														
WT.	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	270 K	230 K	238 K	250 K	285 K	290 K
71					300	300	1880	1850	400	700	300	1250	200	200	200
72					200	200	1652	1500	300	700	300	1050	200	200	200
73		3000			1000	1000	1500	10500	2000	5000	2000	14080	2000	2000	2000
74		3000				500	1000	9500	1500	5000	1500	12840	1500	1500	5500
75		6980			2700			500	2:00	2400	500	3300	500	500	1500
76		6340			2300			1800				1200			500
77		3520			2900			3520				600			650
78		4220			2600			3400				600			500
79		3500						27600							
80		500						26440							
81								6400							
82								3394							
83								4620				800			
84								4180				800			
85								1802	200	200	200	1150	200	200	100
86					600			1456	100	500	150	1000		100	100
87								1748		500		650			
88					800			1474				700			
89		1200			1300			2414							
90		900			1300			2200							
91		1500						2332				2200			1600
92		1500			2000			3156				1600			1200
93		1000			5000			8400				600			800
94								6940							
95								1812							
96								942				300			
97								2494				650			
98								2372				600			
99								884				600			
100								892				300			
101								2296		400		600			
102		400						2630		1300		600			
103		1300						4920		1400					
104		1100						3960		700					
105								5180				600			600
106								3980				600			400
107								2526				900			700
108								1970				800			500
109								3046				400			400
110								2100				300			1000
111								1530				400			
112								1032				400	100	100	100
113								516				250	80	80	80
114								690				450	80	80	80
115								1392		800		850	100	100	100
116		2004			1250			2200		500		600			
117		5400			2300			3000							
118		4260			1900			3100				300			250
119		2000			2500			3880				500			500
120		800						9900				400			300
121								12060				400			200
122								6420				300			150
123								4440				250			
124								1834				350			
125								760			80	300	80	80	
126															
127															
128															
129												1270			
130												1160			
131								956				400			280
132		750						934				3.0			250
133		600			500			3640	100	100	100	600	100	100	300
134								3224				600			300
135								11000				20460			11000

Table 5-2 (continued)

MOL. WT.	EVAPORATION TEMPERATUPE														
	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	290 K
136								9000				18520			11000
137								6780				5000			3000
138								6340				1500			1000
139								2788				600			200
140								2550				300			200
141															
142															
143															
144															
145								1676				300			290
146								1376				300			250
147					2200			2856	500	600	700	1700	700	700	1400
148					2200			2966	400	500	600	1600	600	600	1300
149					1300			2090				1200			1000
150								1818				1100			1000
151								26900							
152								24700							
153								6400							
154								2298				500		<<<<<	300
155								726	100	100	100	726	100	150	500
156								3000				4460		2000	>>>>>
157								3000				4280		2000	>>>>>
158								1500				1960		700	>>>>>
159															
160															
161					4780			500							
162					4300			600							
163					5500			6600							
164								5900							
165								2664				600			800
166								2016				600			600
167								636				340			340
168															
169															
170					574							260			200
171							650	150	150	150	150	500	20		50
172															
173															
174															
175								578							
176					900			2272				200			100
177								10340							
178								8660				500			500
179								3940				900			1000
180								2598				800			900
181								2342				550			600
182								1760				350			350
183								500		822		220			210
184										664		280			180
185												822			370
186												800			940
187												850			1394
188												800			974
189												250			386
190															
191															
192															
193								15540				1500			800
194								14500				1500			500
195								4340				1500			1500
196								1870				1600			1600
197												5730		<<<<	11460
198												5280		<<<<<	10560
199												3620			3620
200												2294			1100

Table 5-2 (continued)

MOL.	<-------- EVAPORATION TEMPERATURE -------->														
WT.	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	290 K
201										1200		2178			300
202									200	1224	200	600	200		
203															
204															
205								8900							
206								8181							
207				1000				2604				800			500
208				1000				1210	200	200	200	700	200	200	500
209				320				300	300	300	300	812	300	300	812
210															
211															
212															
213															
214															
215															
216														<<<<<	1362
217														<<<<<	1356
218														<<<<<	2174
219															1930
220															846
221								4560				800	>>>>>	<<<<<	600
222								4620				600	>>>>>	<<<<<	700
223								4720				300	>>>>>	<<<<<	300
224								4460				300	>>>>>	<<<<<	300
225								1400				350	>>>>>	<<<<<	300
226								502				250	>>>>>	<<<<<	200
227															
228															
229															
230															
231															
232															
233								576							
234								1824							
235								27460							
236								28260							
237								13260							
238								4840							
239								1058				450			200
240								340				450			150
241															
242										1058					
243										890					
244										254					
245															
246															
247															
248															
249															
250															
251															
252															
253															
254															
255															
256															
257															
258															
259															2020
260															1760
261															636
262															256
263								2216							
264								15260							
265								14100							

Table 5-2 (continued)

MOL.	<-------- EVAPORATION TEMPERATURE -------->														
WT.	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	293 K
266								4860							
267								1594				700			400
268								600				756			300
269															
270															
271															
272															
273															
274															
275															
276															
277															
278															
279									344						
280									354						
281						1326				200	200	200	200	200	200
282						1266				200	200	200	200	200	200
283						490				150	150	150	150	150	150
284						250				100	100	250	150	150	250
285															
286															
287															
288															
289															
290															
291															
292															
293															
294															
295															
296															
297															
298															
299															
300															
301															
302															
303															
304															
305															
306															
307															
308															
309															
310											<<<<<	562		<<<<<	280
311											<<<<<	600		<<<<<	400
312											<<<<<	600		<<<<<	700
313											<<<<<	700		<<<<<	680
314											<<<<<	450		<<<<<	420
315											<<<<<	280		<<<<<	380
316											<<<<<	356		<<<<<	250
317											<<<<<	200		<<<<<	240
318															
319															
320															
321															
322															
323															
324															
325															
326															
327											2626	>>>>>			
328											2534	>>>>>			
329											1506	>>>>>			400
330												1400			400

Table 5-2 (continued)

MOL. WT.	EVAPORATION TEMPERATURE															
	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	290 K
331												628			200
332												504			
333															
334															
335															
336															
337															
338															
339															
340															
341													790		
342													714		
343												330			
344												872			
345												434			
346															
347															
348															
349															
350															
351															
352															
353															
354															
355							686			150	150	150	150	150	150
356							624			150	150	150	150	150	150
357							382			100	100	100	100	100	100
358							261			140	140	140	140	140	140
359															
360															
361															
362															
363															
364															
365															
366															
367											492				
368											464				
369											295				
370															
371															
372														710	
373														906	
374														762	
375														610	
376														508	
377														312	
378														199	
379															
380															
381															
382															
383															
384															
385															
386															
387												358		250	>>>>>
388												326		250	>>>>>
389														1040	>>>>>
390														1008	>>>>>
391														<<<<<	950
392												550		<<<<<	792
393												200		364	>>>>>
394												288		280	>>>>>
395															

Table 5-2 (continued)

MOL.	<-------- EVAPORATION TEMPERATURE --------														
WT.	95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	290 K
396															
397															
398															
399															
400															
401												590			
402												506			
403												850	1122		350
404													990		350
405											2906				350
406											2580				
407											1520				
408											852				
409											280				
410															
411															
412															
413															
414															
415															
416															
417												1590			
418												1400			
419												900			
420											872				
421											816				
422											462				
423											259				
424															
425															
426															
427															
428															
429								468				450			340
430								474				150			150
431								300				364			325
432															
433															
434															
435															
436															
437															
438															
439															
440															
441															
442															
443															
444															
445															
446															
447															
448															
449															
450															
451														1452	
452														1570	
453														948	>>>>>
454														608	>>>>>
455														282	>>>>>
456															
457															
458															
459															
460															

Table 5-2 (continued)

MOL. WT.	EVAPORATION TEMPERATURE 95 K	145 K	150 K	158 K	170 K	175 K	185 K	198 K	210 K	220 K	230 K	238 K	250 K	285 K	290 K
461															
462															
463												350		<<<<<<	200
464												330		<<<<<<	250
465												350		<<<<<<	650
466														<<<<<<	712
467														<<<<<<	970
468														<<<<<<	840
469														<<<<<<	544
470														<<<<<<	250
471														<<<<<<	178
472															
473															
474															
475															
476															
477															
478															
479															
480												3780			
481												2200			
482												1300			
483												568			
484												252			
485															
486															
487															
488															
489															
490															
491													358		
492													293		
493													227		
494												520			
495												458			
496												300			
497															
498															
499															
500															
PERCENT OF EACH SPECIES IN THE MIXTURE:-															
	8.89	3.31	2.73	24.69	1.83	0.20	0.52	29.31	1.99	3.62	2.56	9.80	2.11	2.49	5.95

NOTE: In certain instances a mass peak could not be unequivocably associated with a single temperature because of its breadth. In these instances the entire height of the peak has been entered in the table in the column corresponding to the closest temperature match. The possibility that a portion of the ion count associated with this peak could be due to an adjacent species has been indicated by entering the arrows "<<<<<<" or ">>>>>>" in the column for the adjacent species.

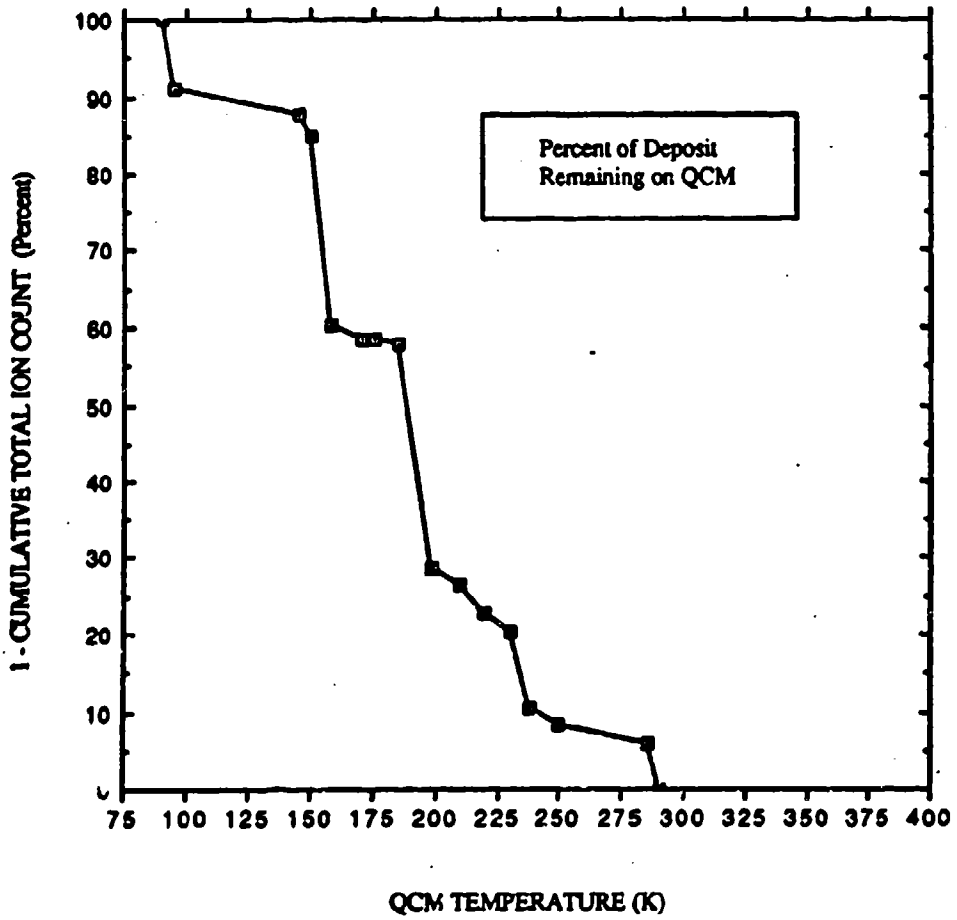


Fig. 5-32 QCM Thermal Analysis of the Outgassing Products Collected on the 90 K QCM from R-2560 at 125°C. Fraction of Initial QCM Deposit Remaining on the QCM as Determined from the Mass Spectrometer (1 - Cumulative Total Ion Count) Data as a Function of QCM Temperature.

The general qualitative agreement between Figs. 5-6(a) and 5-32 provides a useful check on the internal consistency of the data.

Table 5-2 summarizes all of the information contained in the plots of 490 m/e values as a function of QCM temperature. The vertical columns are the best estimate of the mass fragmentation patterns of each of the separated species that can be obtained from the QTA/MS data from the current tests. The use of the vertical column mass fragmentation pattern data to identify the species chemically is discussed in Section 5.2.2.2. The horizontal column data can be used to determine m/e values that are unique or nearly unique to a given species. The use of these unique m/e values to track the outgassing of that species during the isothermal outgassing test is explored in Section 5.3.

5.2.2.2 Chemical Identification of Outgassed Species

It is not necessary to know the chemical identity of the outgassing products in order to model the contamination environment of a satellite system, so chemical identification of the outgassed species is not an essential part of the test method. However, this information is clearly desirable if it can be obtained at reasonable cost. It can be of help in diagnosing sources of contaminants in thermal vacuum tests and providing insights into how outgassing problems could be minimized by changing material application processes such as cure cycles time and temperature. Also, knowledge of the chemical family to which a contaminant belongs gives insight into its probable infrared absorption bands. Hence, one of the goals of this test method was to obtain as much chemical identity data as possible within the restrictions of a routine test.

Since the QTA/MS technique is a form of chromatography it is possible, in principle, to determine the chemical identities of the outgassed species by entering the mass fragmentation pattern data measured for each species as it leaves the QCM into a mass fragmentation pattern library. However, the ability of QTA/MS to separate species efficiently had not been demonstrated by the beginning of the Phase II Extension, so it was decided to include a preliminary GC/MS test as part of the test method to support the species identification task and help evaluate the QTA/MS technique. To this end Section 5.2.2.2.1 analyzes the results of the preliminary GC/MS tests. Section 5.2.2.2.2 evaluates the species identification capability of QTA/MS by comparing its performance with the GC/MS data.

5.2.2.2.1 Analysis of the Gas Chromatography/Mass Spectrometry Data

5.2.2.2.1.1 Basic GC/MS Data Output

The GC/MS test separates the individual species evolved from a heated material sample by collecting them in a liquid nitrogen trap, passing them through a capillary column, generating a chromatogram by detecting the emerging species with a mass

spectrometer, and identifying the species by comparing the measured mass fragmentation pattern with a fragmentation pattern library. The relative amounts of each species in the mixture are estimated using the total ion count detected for each species.

Figures 5-33 and 5-34 show GC/MS chromatograms for R-2560 samples tested at 125°C and 200°C. The figures are plots of total ion count detected by the mass spectrometer versus the time at which a species was detected. Each peak in the chromatogram corresponds to detection of a specific chemical species.

Species are identified by comparing their mass spectra measured by the GC/MS system with a standard library of mass fragmentation patterns. Mass spectra are a function of the instrument as well as the species, so it is rarely possible to obtain a perfect match between a measured spectrum and a library spectrum. Because of this uncertainty the library search presents a number of possible matches, and although it selects a preferred first choice, the final identification is made by an experienced analytical chemist. For example, Fig. 5-35 shows the mass fragmentation pattern detected at a scan time of 768 s during the 200°C test, while Fig. 5-36 shows the library search data for this pattern. The upper plot is the fragmentation pattern detected during the test. The lower three patterns are the closest three matches selected by the library search, presented in descending order of preference. In this case, the search has identified the species as dodecanoic acid and the analytical chemist has concurred.

The species identified by GC/MS are listed in Tables 5-3 and 5-4. The chemical identifications are given exactly as provided by the Analytical Chemistry Department at Lockheed. In cases where identification was difficult, the tables indicate only the family name, such as phenyl methyl siloxane, while some species could not be identified at all.

The major groups of volatile species identified were as follows:

(i) Low molecular weight species such as 1-propanol, benzene, toluene, butane, and xylene which may be present as solvents or as reaction by-products.

(ii) A series of methyl cyclosiloxanes and phenyl methyl siloxanes homologues.

(iii) A number of unidentified species which appear to be closely related to the linear and cyclic siloxanes by virtue of their peaks at m/e=73, 135, and 147.

(iv) A series of straight chain saturated carboxylic acids.

(v) A number of minor silicate and silicone oddments.

(vi) A major alkyl silicate species and an aromatic acid which appear in the 200°C test but not in the 125°C test.

The total amount of each species in the collected volatiles is roughly proportional to the area of the corresponding peak in the chromatogram. The GC/MS system calculates these areas and determines the percentages of each species found in the total collected

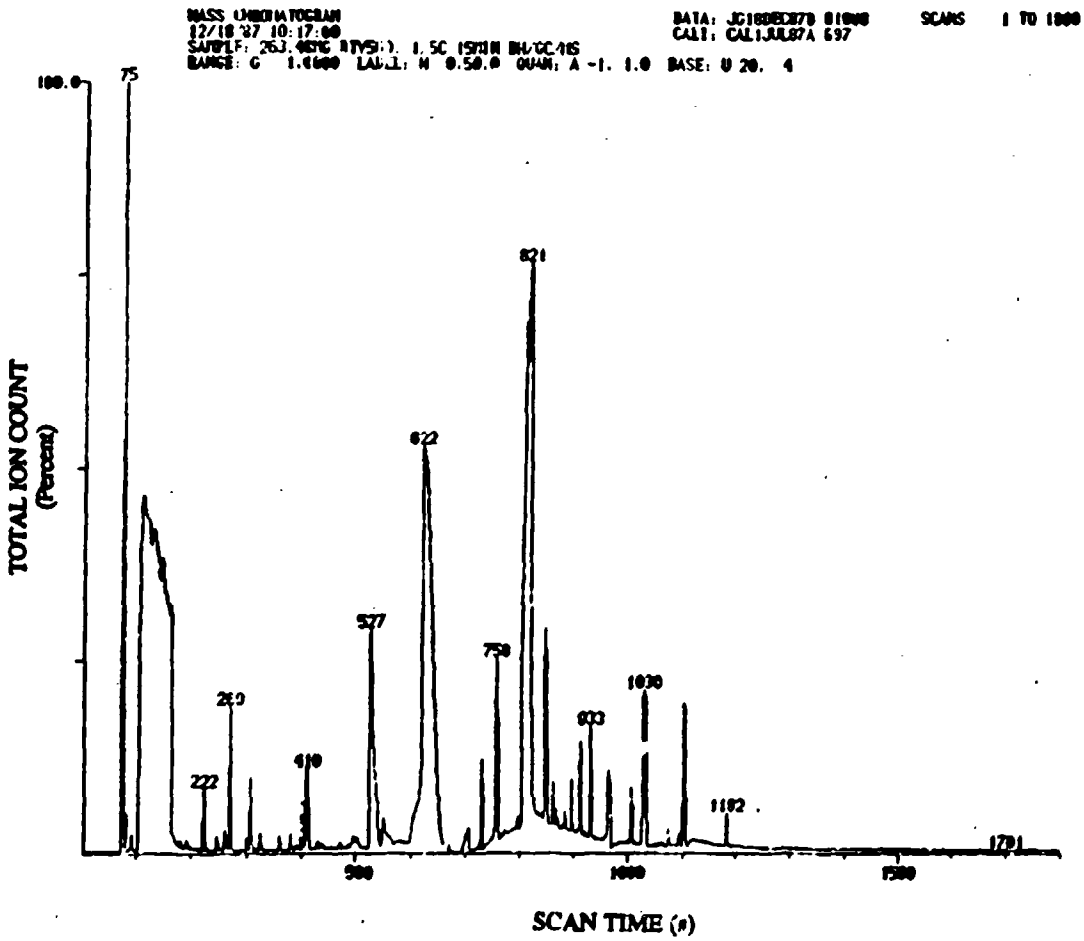


Fig. 5-33 GC/MS Chromatogram for R-2560 at 125°C. Normalized Total Ion Count Versus the Scan Time at which a Species was Detected.

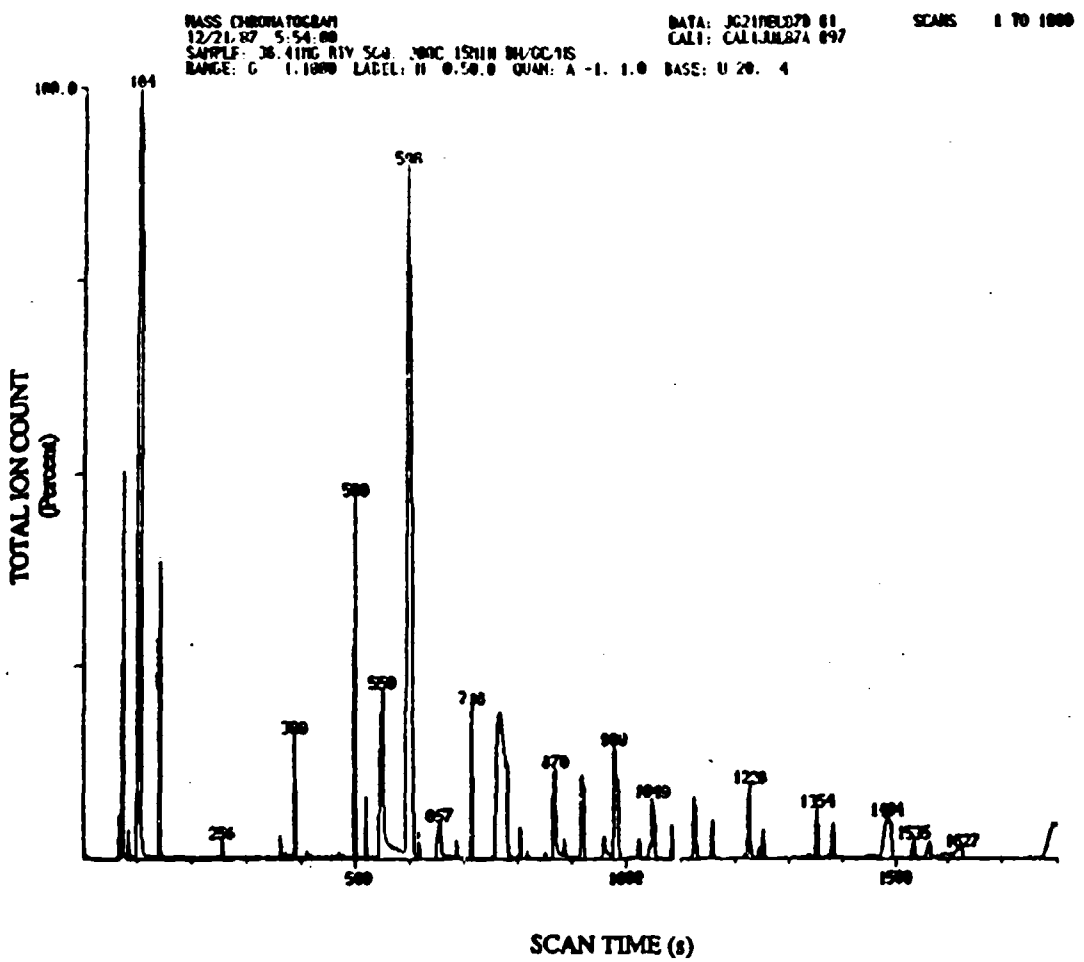


Fig. 5-34 GC/MS Chromatogram for R-2560 at 200°C. Normalized Total Ion Count Versus the Scan Time at which a Species was Detected.

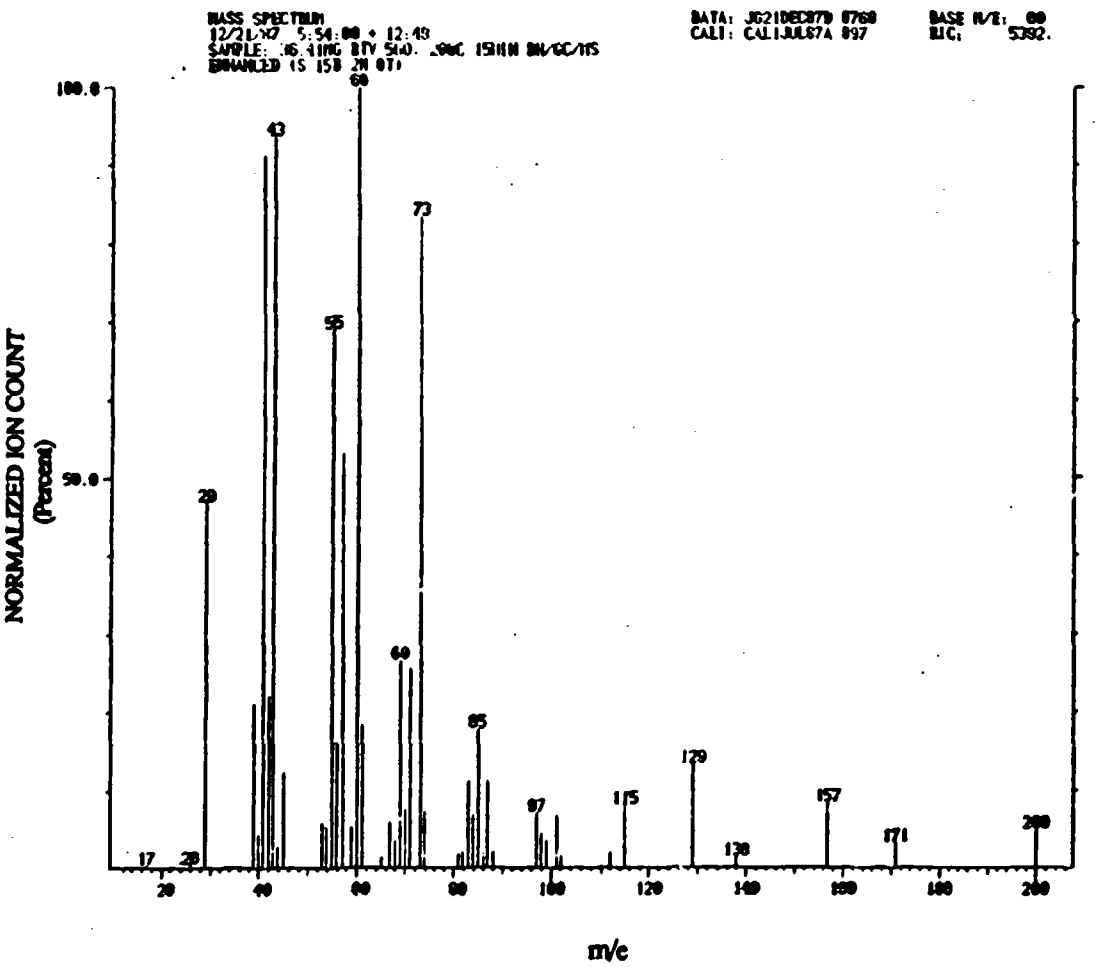


Fig. 5-35 Mass Fragmentation Pattern Obtained During the GC/MS Test of R-2560 at 200°C. Normalized Ion Counts Versus m/e Value for the Species Detected at Scan Time = 768 s.

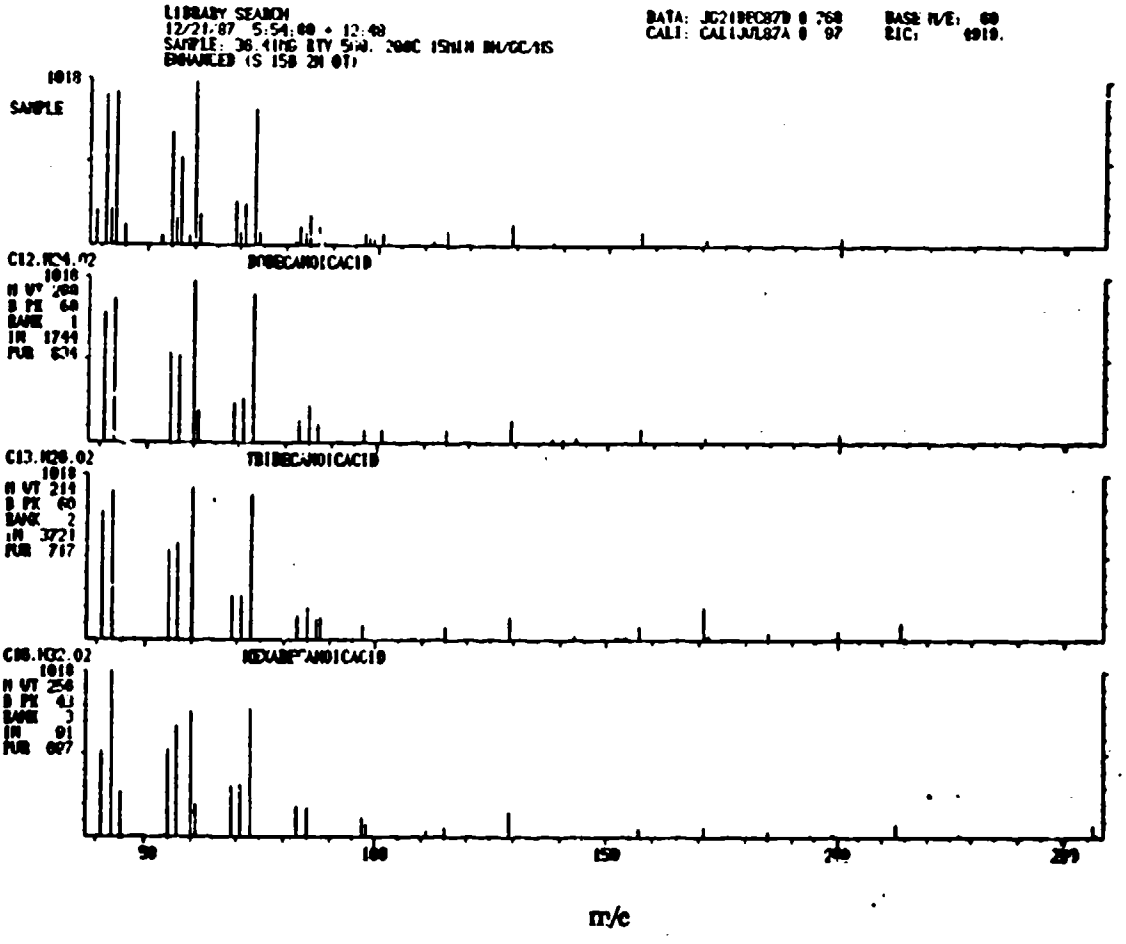


Fig. 5-36 Comparison of Mass Fragmentation Pattern at Scan = 768 s (Fig. 5-35) with the NBS Library Search. Ion Counts Versus m/e Value.

volatiles. The percentages of each species and the time in the scan at which the species was detected are listed in Tables 5-3 and 5-4. Although the GC/MS data reduction system provides these data to two decimal place precision, the experimental measurements are not made to this level of accuracy, so the numbers should be interpreted quantitatively with very great caution.

The 125°C and 200°C tests identified 24 and 30 species, respectively. In the 125°C test, 12 species had mass fractions greater than 1 percent, and 6 species were present in amounts greater than 2 percent. For the 200°C tests, the equivalent figures were 15 species greater than 1 percent and 11 greater than 2 percent. The number of significant species identified by GC/MS was, therefore, about the same number as could be separated using QTA/MS.

5.2.2.2.1.2 GC/MS Mass Fragmentation Pattern Inventory

One way to evaluate the ability of QTA/MS to identify the individual outgassed species chemically is to compare the QTA/MS fragmentation pattern data with reference data. There are two possible fragmentation pattern references - the actual fragmentation patterns measured during the GC/MS tests and the NBS library patterns which were determined to be the best match to the measured GC/MS pattern. If the identities of the outgassed species were known with confidence, the NBS library would be the preferred reference because it is an accepted standard. However, the outgassed species are in the first instance unknown chemically, and the identifications given in Tables 5-3 and 5-4 could be wrong. Although the GC/MS-measured fragmentation patterns were obtained using a different ionizer than that used in the outgassing test, they are by definition those of the volatile species in R-2560 and thus have been selected as the more reliable basis for comparison.

In the interest of compactness, the fragmentation pattern data for the 125°C and 200°C tests provided by the GC/MS test for each species in the form of plots such as Fig. 5-35 have been consolidated in Table 5-5. The list of species includes all those identified in Tables 5-3 and 5-4. Species which were detected in both the 125°C and 200°C tests have been listed twice to show the degree of correlation between the patterns. Because of the large amount of data involved, it is not practical to enter it all into the table, so the fragmentation pattern data have been summarized as follows:

(i) The major peak is listed in bold type.

(ii) Peaks greater than 0.2 of the major peak are listed in bold italics.

(iii) Peaks between 0.02 and 0.2 of the major peak are listed in regular type.

(iv) Peaks less than 0.02 of the major peak are listed in regular italics. However, not all peaks in this category have been listed because many species show several

Table 5-3

GC/MS Data for R-2560 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
73	1.14	CO_2 artifact
75	2.20	CF_2Cl_2
79	0.24	n-butane
111	44.40	1-propanol & benzene
222	0.21	toluene
269	0.74	hexamethyl cyclotrisiloxane
306	0.31	xylene isomer
410	1.07	octamethyl cyclotetrasiloxane
527	4.75	decamethyl cyclopentasiloxane
622	14.38	octanoic acid & dodecamethyl cyclohexasiloxane
730	0.43	dibutyl dipropyl silicate
758	1.61	tetradecamethyl cycloheptasiloxane
821	18.82	dodecanoic acid
848	1.77	hexadecamethyl cyclooctasiloxane
862	0.28	similar to dodecanoic acid
897	0.39	siloxane
913	0.54	unspecified silicone (alkyl silicate?)
933	0.60	octadecamethyl cyclononasiloxane
964	1.56	unspecified silicone (alkyl or aryl silicate?)
1008	0.30	siloxane
1030	2.61	cosamethyl cyclodocasiloxane
1076	0.17	
1102	1.27	docosamethyl cycloundecasiloxane
1182	0.21	tetracosamethyl cyclododecasiloxane

Table 5-4

GC/MS Data for R-2560 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
69	0.28	CO_2 artifact
75	2.13	n-butane
104	24.77	1-propanol
143	2.04	benzene
389	0.71	octamethyl cyclotetrasiloxane
500	2.39	decamethyl cyclopentasiloxane
521	0.35	siloxane
550	5.01	octanoic acid
596	30.25	alkyl silicate ?
657	1.05	decanoic acid
716	0.93	tetradecamethyl cycloheptasiloxane
768	10.86	dodecanoic acid
806	0.37	hexadecamethyl cyclooctasiloxane
870	2.33	tetradecanoic acid
919	2.54	phenyl methyl siloxane
962	0.72	eosamethyl cyclodecasiloxane
980	3.29	phenyl methyl siloxane
1025	0.27	docosamethyl cycloundecasiloxane
1045	0.27	phenyl methyl siloxane
1049	1.36	phenyl methyl siloxane
1086	0.30	tetracosamethyl cyclododecasiloxane
1127	1.01	phenyl methyl siloxane
1159	0.37	hexacosamethyl cyclotridecasiloxane
1226	1.10	phenyl methyl siloxane
1253	0.40	octacosamethyl cyclotetradecasiloxane
1354	0.79	phenyl methyl siloxane
1382	0.64	triacosamethyl cyclopentadecasiloxane
1484	2.65	MW 456 aromatic acid
1535	0.38	unknown
1565	0.44	unknown

Table 5-5

Summary of GC/MS Species Identification, Abundance, and Mass Fragmentation Pattern Data

Chemical Identification	–200°C– scan time	per cent	–125°C– scan time	per cent	Mass Fragmentation Pattern Data
CO_2			73	1.1	*12* ; 18 ; 22 ; 28 ; 44 ; *45*
CO_2	69	0.3			*12* ; 18 ; 22 ; 28 ; 44 ; *45*
CF_2Cl_2			75	2.2	31; 35; 50; 66; 85; *87* ; 101;*120*
n-butane			79	0.2	14;15;*20*; *26*; *27*; *28*; 29; *30*; *31*;32; 39;*41* ; 42; 43; 58; *77*
n-butane	75	2.1			14;15;26;*27* ;*28* ;*29* ;*31* ; 39;*41* ; 42; 43; 58; *77*
n-propanol			111	44.4†	27; 28; 29; 31; 39; 41; 42; 43;45; 59; 60
n-propanol	104	24.8			27; 28; 29; 31; 39; 41; 42; 45; 59; 60
benzene	143	2.0			*15* ;*25* ;26;37;38; 39; 49;*50* ;*51* ;*52* ; 63; 74; 76;*77* ; 78; 79
benzene			148	†	*37* ;*38* ;*49* ;50;51;52; 62 ;63; 74; 76;*77* ; 78; 79
toluene			222	0.2	*15*;*27* ;38;39; 40;41;43;45;46;50; 51; 61;62;63;64;65; 66;*74* ;*77* ; *83*; *89* ; 91; *92* ; *93*
hexamethyl cyclotrisiloxane			269	0.7	15;26;45;59;61;66;73;74;75;81;83;87;88;89. 96; 97; 103;104;105;115;119; *133* ;134; 147;161;163;165;176;177 ; 178;179;191;192;193;*207* ;208;209
xylene isomer			306	0.3	*27*;*29* ;39;50; 51; 52;53;62;63;65;77;78;79;86;89; 91;92;98;103; *105* ;*106* ;107
octamethyl cyclotetrasiloxane			410	1.1	15;30;45; 46;47;59;61;73 ;*74* ;*75*; 81; 87; 89;96;103;104; 105;110;111;112; 117;118;119;*125* ;126;*133* 134;135;147;163;165;177;179;191;*193* ; 205;207;235;240; 249; 265; 281; 282; 283
octamethyl cyclotetrasiloxane	389	0.7			45;59; *73* ;*81* ;*89* ;96;103;111;119;125 ;*133*;134;147;163;177;191;193; 207;*235*;249; 265; 281; *282*; 283
decamethyl cyclopentasiloxane			527	4.8	*15* ;45; 59; 73; *74* ;*87* ;96 ;*104* ;*118* ;*133* ;*149* ;*162* ;*170* ;*179* ;*191*;*207* ;*223* ; *237* ;*251* ; 267339;*355*
decamethyl cyclopentasiloxane	500	2.4			45; 59; 73; *74* ;*87* ;96 ;*109* ;*119* ;*133* ;*147* ;*162* ;*170* ;*179* ;*191* ;*207* ;*223* ;*237* ;*251* ; 267;*323* ;*339*;*355*
'siloxane' 521	521	0.4			45; 59; 73;*117* ;*133* ;*147* ;*191*; 207; *249* ; *265* ; 281; *369*
octanoic acid	550	5.0			*27* ; *29* ; 31;39;*41* ;*42*;*43* ;*45*;*55* ;56;57; 60;61;67;*69*;*73* ;74;84; 85;87; 97; 101; 115
alkyl silicate ?	596	30.3			41;43;55;63;79 ;83;89;*93* ;97;103;105;109;*121*; 135;137; *151*;163;177;193; 205; 221; 235 ; 264
octanoic acid and dodecamethyl cyclohexasiloxane			622	14.4	*19* ;29; *31* ;39;40; *41* ;*42*; *43* ; 44;*45* ; *55* ; 56;57;59;60;61;*69* ;*73* ;74;82; *83* ; 84;85;86;87;88;97101;111;115;117;120;134;148;164;*175* ;194;*206* ;*222* ;*237*; 264

(continued)

Table 5-5 (continued)

Chemical Identification	--200°C-- scan time	per cent	--125°C-- scan time	per cent	Mass Fragmentation Pattern Data
decanoic acid	657	1.1			27 ;28;29 ; 31;39 ;41;42;43 ;45 ;53;55 ;56;57 ; 59;60 ;61;69 ; 71;73 ; 74; 79; 83; 84;87;112;115;129
dibutyl dipropyl silicate			730	0.4	27;28;29;42 ;43 ; 55; 57;62;63 ;79 ; 83 ;93 ;105 ;121 ;133;1?5;... ; 151; 163; 179; 193; 205;221;235;263 ; 277
tetradecamethyl cycloheptasiloxane			758	1.6	18 ;28 ;40 ;45; 59; 73; 87 ; 103 ; 117 ;133 ; 147; 163 ; 179 ; 191 ; 207 ; 221;249 ; 265 ; 281; 327;341 ;399 ;415 ;503
tetradecamethyl cycloheptasiloxane	716	0.9			18 ;28 ;45; 59; 73; 85 ;117 ;133 ;147; 191;207 ;221 ;281;327 ;341 ;399 ;415
dodecanoic acid			821	18.8	18;27;29 ;39;41;43 ;45;55 ;56 ;57 ;60 ;69;71;73;83;85 ;87;97;101;111; 115;129 ; 133; 143;157;164 ;171;183 ;200;236
dodecanoic acid	768	10.9			17 ;26 ;29 ;39; 40;41;42 ;43 ;44 ;53;54;55 ;56;57 ; 60; 61;67;68;69 ;70;71;73 ; 74; 83;84;85 ;86;87;97;98;99101;112;115;129 ;138;157; 171; 200
hexadecamethyl cyclooctasiloxane	806	0.4			45 ;73;74;147; 207; 221;281;357
hexadecamethyl cyclooctasiloxane			848	1.8	15 ;28 ;45; 59;73;87 ;99 ;117 ;131 ;147 ;161;179 ;191 ;207 ;221;265 ;281;295 ;327 ; 341;415 ;591
'similar to dodecanoic acid'			862	0.3	29 ;41 ;42;43 ;55 ;57 ;60 ;61;69;71;73 ; 83;85;87;97;182 ; 115; 129; 139; 143;152;157;165;171;183; 201; 236
tetradecanoic acid	870	2.3			27 ;28;29 ;39;40; 41;42 ;43 ;52;53;55 ;56; 57 ; 58;59;60 ;61;67;68;69 ;70;71;73 74;82;83;84;85;87;97;111; 115; 129; 143; 185; 228
'siloxane' 897			897	0.4	18 ;45; 59; 73;79 ;87 ;96 ;111;131; 147 ;165 ; 207 ; 221; 236 ;281;651
'unspecified silicone (alkyl silicate?)'			913	0.5	15;26 ;45;51;56;60;65;77;89;91 ;103;105;112;119 ;121;127;133;135;143;147;149 ; 151; 154 ;158 ;165 ;166; 173;177;181;191;195 ; 209;223;239;253;254;255;269; 315; 331;346
phenyl methyl siloxane 919	919	2.5			18 ;28;43;45;51;57;65 ;73 ;75;77;83 ; 91 ;105;115;119;125; 133; 135; 141; 149; 156; 157;165;179;187; 195; 203; 221;239 ;249;253;267; 311; 327; 343
octadecamethyl cyclononasiloxane			933	0.6	15 ;32 ;45;59 ; 68 ;73;87 ;97 ;112 ;133 ;147;157 ;191; 207 ; 221;267 ;281;295 ;341;355 429
eicosamethyl cyclodecasiloxane	962	0.7			27;29;39;41 ; 42;43; 45;55; 56;57; 59;60;61;69 ; 71;73;74;83;85;87; 97;129;147
'unspecified silicone (alkyl or aryl silicate)'			964	1.6	14 ;43;51;60 ;73 ; 91; 103;105;107;119;133;135;141;156;157;165;179;187; 195;203;221;239 ;249; 253;267 ; 311; 327; 343 ;389 ; 405
phenyl methyl siloxane 980	980	3.3			14 ;18 ;28;43;57;69 ;73 ;83 ;91; 107; 121;135;149 ;165 ;177 ;185;193;197 ; 313 ;330 ;417 ; 479

(continued)

Table 5-5 (continued)

Chemical Identification	–200°C– scan time	per cent	–125°C– scan time	per cent	Mass Fragmentation Pattern Data
siloxane 1008			1008	0.3	*15* ;45; *54* ;59;73;*87* ;*96* ;*109* ;*117* ;*133* ;*147* ;*156* ;*177* ;191;207; 221; 281;*341* ;*355*
docosamethyl cycloundecasiloxane	1025	0.3			*45*; *59*; 73; 147; *207* ; 221; 281; 355
cosamethyl cyclodecasiloxane			1030	2.6	*15* ;43;45;*51*;59;*69* ;*73* ;*83* ;91;107;121;135;*149* ;*165* ;*179* ;*197* ;*207* ;*22*;237 ;*251*;*267* *313* ;*329* ;*417* ;*479*
phenyl methyl siloxane 1045	1045	0.3			73; 74; 75; 147; 221
phenyl methyl siloxane 1049	1049	1.4			*18* ;*28* ;43;45; 59;*73* ;91;107;121;135;147; *197* ; 209; 341; 403
unknown 1076			1076	0.2	28;*45* ;*59* ; 73; *82* ;*101*;*117* ;*133* ;*347* ; 207;*221*; 221;235; 281; 355
tetracosamethyl cyclododecasiloxane	1086	0.3			*45* ;*59* ; 73; 147; *207*; 221; 281; 355; 429
docosamethyl cycloundecasiloxane			1102	1.3	*15* ;43;45;59;*73* ; 91;107; 121;135;147;*165* ;*179* ; 197;209;*223* ;*237* ;*253* ;*271* ;*325* ;*341*;*387* ;*403* ;*465* ;*491*; 553
phenyl methyl siloxane 1127	1127	1.0			*28* ;43;45; 59;73;91;107;121;*135* ;136;147;193;197; 209; 281; 327; 343; *415* ;*477*
hexacosamethyl cyclotridecasiloxane	1159	0.4			*45* ;*59* ;73;*87* ;147;*207* ; 221; 355; *429* ;*503*
tetracosamethyl cyclododecasiloxane			1182	0.2	41;45;59;*73* ;74;75;*82* ;87;91;107;121;135;136;137;147;*179* ;193;197;209;*253* ; *271*; 327
phenyl methyl siloxane 1226	1226	1.1			*18* ;*28* ;45;59;73;*91*;*107* ;*121*;*135* ;136;147;193;197; 209; 221;283;*343* ;355;*401*;*479*
octacosamethyl cyclotetradecasiloxane	1253	0.4			73;74;*147* ; 207; 221; 281; 355; *429*
phenyl methyl siloxane 1354	1354	0.6			43;45; *59* ;73;*107* ;*121*;*131*;*135* ;*136* ;147;193; 197; 209; 221;283; *355*
tricosamethyl cyclopentadecasiloxane	1382	0.6			73;*131* ;*147* ; 207; 221; 281;*295* ; 355;*429*
aromatic acid mol wt 456	1484	2.7			78;107;119;141;149;151;*156* ;157;165;172;186;188;193;209; 210;218; 313; 389;452; 466
unknown 1535	1535	0.4			43; 44;55; 73;74;75;*135* ;136;147; 197; 209; 221; 283
unknown 1565	1565	0.4			73; 74;75;135;*147* ; 207; 221; 281; 355

† In the 125°C GC/MS test 1-propanol and benzene appeared as a single peak in the chromatogram so their individual abundances cannot be separated.

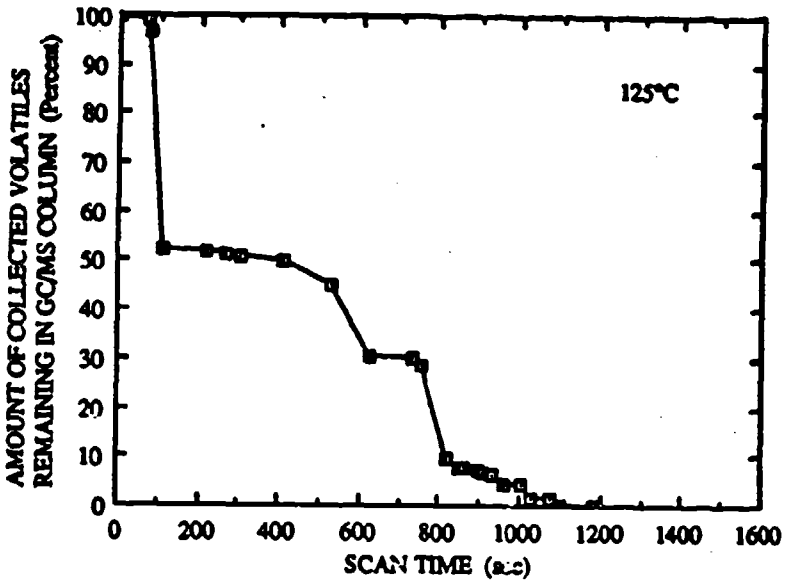
groups of peaks separated by one m/e value, especially at m/e values less than 100. Since m/e values less than 100 are common to many species, minor peaks in this range are of little value in identifying a species. All peaks greater than 100 have been noted, regardless of how small they are.

(v) The highest m/e value given on each GC/MS plot is listed. However, the range of m/e values plotted is selected by the GC/MS test operator, and in some cases the m/e range has been truncated because the peaks at higher m/e were of negligible height in the context of the GC/MS test. Hence the highest m/e value listed is not necessarily the highest m/e fragment detected during GC/MS.

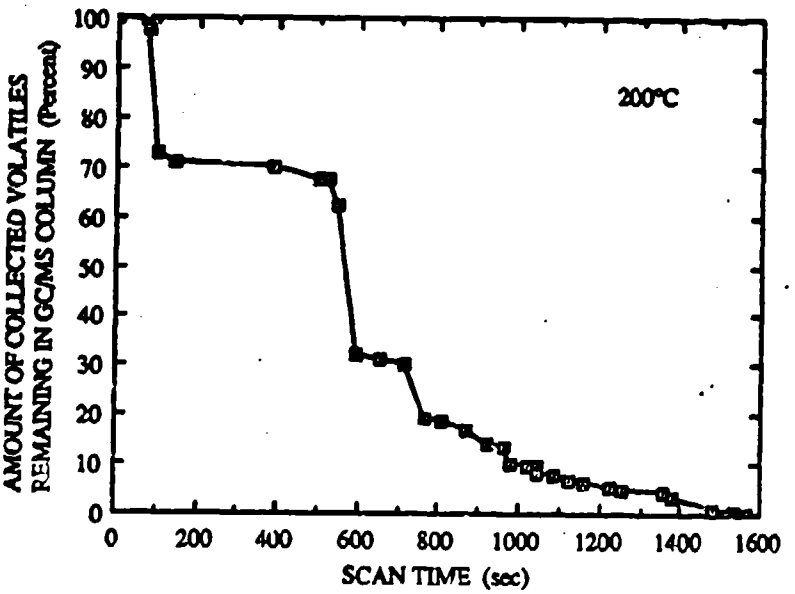
The species have been listed in order of the scan time at which they were detected. While this time has no quantitative physical meaning, the species detected at earlier scan times are generally more volatile than those detected at later scan times. The scan time is used in this section as a convenient way to reference the species in later discussions. For example, the several species identified as phenyl methyl siloxanes can be distinguished by their scan time of detection, e.g. "phenyl methyl siloxane 1045 s". Note that there is a small time difference between the scan time at which a given species was detected in the 125°C and 200°C tests.

5.2.2.2.1.3 Comparison with QTGA Data

The scan time at which a species is detected during GC/MS is the time that the species takes to pass through the chromatograph capillary column. This transit or retention time is a function of molecular weight, so the low molecular weight species are detected first and the higher molecular species are detected later in the scan. There is a rough correlation between molecular weight and vapor pressure, so the temperature at which a species evaporates from the QCM during QTGA is also a function of its molecular weight. Hence the order in which species are detected in the GC/MS test should be approximately the same as the order in which they evaporate during the QTGA test. Finally, although the test conditions are different, there should also be a rough correlation between the relative amounts of each species evolved during GC/MS and during an outgassing test. Because of this correlation a plot of mass fraction retained in the capillary column versus GC/MS scan time should be qualitatively similar to a QTGA plot of FCM versus QCM temperature. Figures 5-37(a) and 5-37(b) are plots of the retention fraction versus scan time for the 125°C and 200°C GC/MS data of Tables 5-3 and 5-4, respectively. The retention fraction at a given scan time was calculated by summing the percentages in the table from that scan time to the end of the test. Comparison of Figs. 5-37(a) and 5-37(b)with the QTGA plot of Fig. 5-6(a) shows that the shapes of the plots are qualitatively very similar. The 200°C plot has the strongest resemblance, suggesting that the proportions and perhaps types of species



(a)



(b)

Fig. 5-37 Fraction of Collected Volatile Species Remaining in GC/MS Column as a Function of Scan Time for R-2560 at (a) 125°C and (b) 200°C.

evolved in the 200°C GC/MS test resemble those outgassed in vacuum more strongly than those evolved in the 125°C GC/MS test.

Figs. 5-37(a) and 5-37(b) also resemble Fig. 5-32. The similarity between these three types of plots provides another useful check on the internal consistency of the data.

If the analogy between GC/MS retention time and FCM is valid, then the chemical identity of some of the major species can be estimated by comparison of the two figures. For example, by inspecting the 200°C GC/MS data, the species evaporating from the QCM at 158 K could be assumed to be 1-propanol, which appears at a scan time of 104 s in the GC/MS. Similarly the major species evaporating from the QCM at 198 K could be assumed to be the alkyl silicate appearing at a scan time of 596 s in the GC/MS. These identifications were confirmed by mass spectrometer data presented later. The species evaporating at 238 K and 290 K are less well defined and are more difficult to identify by analogy. According to the QTGA-GC/MS analogy the major species in the 238 K group should be dodecanoic acid, appearing at a scan time of 768 s. However, identification based on mass spectrometer data suggests that the 238 K species is cosamethyl cyclodecasiloxane. The 290 K group of species is probably a mixture of several higher molecular weight species listed in the GC/MS Tables 5-3 and 5-4.

The QTGA-GC/MS analogy is not perfect for the 125°C test either. The identification of 1-propanol could still be made, but the alkyl silicate was not detected in the 125°C test. Based on the analogy, the 238 K species would again be identified as dodecanoic acid instead of cosamethyl cyclodecasiloxane.

5.2.2.2.2 Identification of Outgassed Species Using QTA/MS Data

Table 5-2 lists the mass fragmentation pattern data for each of the species separated by QTA/MS. If the separation capability of QTA/MS were fully developed, then these species could be identified automatically by comparing them directly with the standard NBS fragmentation pattern library. Because the separation capability is not fully developed, the identification must be made manually. This has been performed by comparing the QTA/MS fragmentation data, Table 5-2, with the GC/MS fragmentation pattern data, Table 5-3. This approach was taken because there should be a high degree of commonality between the species evolved in GC/MS and those evolved in the isothermal outgassing test, particularly with respect to the most abundant species. Also, using the GC/MS data rather than the NBS library as a reference required making a smaller number of comparisons, which was an important consideration since the comparisons were made manually.

There are several reasons why the QTA/MS fragmentation patterns may not match with one or other of the GC/MS patterns:

(i) In general, different mass spectrometer ionizers will produce quantitatively and

qualitatively different mass fragmentation patterns for the same species. Hence, differences should be expected between the QTA/MS and GC/MS mass fragmentation patterns, even if the species are identical.

(ii) Because of the different test conditions, the outgassing test may evolve species not detected by GC/MS and vice versa. Indeed, there are even significant differences between the species evolved in the 125°C and 200°C GC/MS tests.

(iii) The QTA/MS fragmentation pattern data given in Table 5-2 for a particular species may not in fact be the pattern of a single species, for one of the following reasons:

- Because QTA/MS uses a single evaporation process to separate species, its temperature separation capability has limits. Hence, the fragmentation pattern nominally assigned to a single species evaporating at a particular QCM temperature may contain fragments from a slightly more volatile species which has not completely evaporated at that temperature or fragments from a slightly less volatile species which is just beginning to evaporate at that temperature.
- Many species form azeotropes, and, as a result, two or more species may evaporate at the same temperature. Also, small amounts of less volatile species can be carried away from the QCM at a lower temperature by the evaporation of a more abundant, more volatile species in which they are soluble.
- In the present test, the presence of the spurious peaks made it possible to confuse the mass spectrometer peaks produced by evaporation from the QCM crystal with peaks produced by evaporation from the QCM case.

The following section identifies each of the species listed by evaporation temperature in Table 5-2. Each of the above issues is considered in making these identifications. The identifications are summarized in Table 5-6. In Section 5.2.2.2.2.1 the fragmentation patterns produced by QTA/MS and GC/MS are compared for the two most abundant, best separated, and easily identified species. In Section 5.2.2.2.2.2 the identities of the less abundant and less well separated species are estimated.

5.2.2.2.2.1 The 198 K and 158 K Species

The most abundant species detected by QTA/MS were the 198 K and 158 K species. The differential QTGA data, Figs. 5-8, 5-10, and 5-11, indicate that these two species are relatively well separated from other species by QTA. The ability of QTA/MS to identify species is first examined for these two cases.

Table 5-6
Identification of Species Detected by QTA/MS

Evaporation Temperature	Abundance (percent)	Chemical Identity (By Comparison with GC/MC Data Tables)
98 K	8.9	Mostly CO_2
145 K	3.3	Toluene and benzene; possibly some methyl cyclosiloxane carried over
150 K	2.7	H_2O
158 K	24.7	1-propanol
170 K	1.8	Hexamethyl cyclotrisiloxane
175 K	0.2	Octamethyl cyclotetrasiloxane
185 K	0.5	Decamethyl cyclopentasiloxane
198 K	29.3	"Unspecified alkyl silicate"
210 K	2.0	No positive identification possible
220 K	3.6	Matches with "similar to dodecanoic acid" from 125°C GC/MS, but has additional uncorrelatable peaks
230 K	2.6	"Unspecified alkyl or aryl silicone"
238 K	9.8	Mostly cosamethyl cyclosiloxane, with some phenyl methyl siloxanes
250 K	2.1	Docosamethyl cycloundecasiloxane
285 K	2.5	No positive identification possible - main peaks common to many siloxane species
290 K	6.0	Aromatic acid

The 198 K Species: Figures 5-38(a) and 5-38(b) show the raw experimental mass spectra for the QTA/MS test at 198 K and the 200°C GC/MS test at 596 s, respectively. The 200°C/596 s GC/MS species is an alkyl silicate. The match is good qualitatively in that the major peaks occur at the same m/e locations. However, the quantitative match is poorer. The spectrum from the GC/MS shows fewer major peaks, while the heights of the minor peaks are less than 20 percent of the major peak. The degree of correlation is sufficient to identify the 198 K species as an alkyl silicate. However, it is appropriate to investigate the quantitative differences further.

Because of the different plot formats, the QTA/MS and GC/MS data are difficult to compare directly and so the data have been extracted from Fig. 5-38 and Tables 5-2 and 5-5 and have been entered into Table 5-7. Table 5-7 gives the magnitude of the 12 largest QTA/MS peaks for the 198 K species and the magnitude of the GC/MS peaks greater than 10 percent of the principle peak for the 596 s alkyl silicate species. The table also gives the magnitude of the GC/MS peaks corresponding to the most abundant QTA/MS peaks. Table 5-7 shows that the two spectra are qualitatively very similar, but that the QTA/MS mass spectrometer system does not resolve the m/e peaks as precisely as does the GC/MS mass spectrometer. For example, in the QTA/MS data the abundance of the m/e=152 peak is almost the same as the 151 peak, while in the GC/MS data, the m/e=152 peak is only 10 percent of the 151 peak.

To permit a better comparison of the two spectra, the QTA/MS spectrum has been modified by adding the ion counts from the poorly-resolved adjacent mass peaks at m/e equal to 62/63, 79/80, 151/152, and 235/236 and renormalizing the peak heights. The GC/MS and modified QTA/MS spectra are compared in Fig. 5-39. The three major fragment ion peaks occur at the same m/e for both spectra. With the exception of the m/e=27 and 30 peaks, which were not recorded in the GC/MS test, the 13 major peaks of each spectrum appear at the same m/e. With this modification to the QTA/MS spectrum the two spectra now agree fairly well qualitatively.

The 158 K Species: The second most abundant species is the 158 K species. Comparison of Tables 5-2 and 5-5 shows that the 158 K peak locations coincide exactly with those of 1-propanol in the GC/MS test. However, as was noted for the alkyl silicate above, the magnitude of the peaks in the two spectra is very different. For example, the 14, 15, and 19 peaks are very small in the GC/MS spectrum but are major peaks in the QTA/MS spectrum. However, the peak heights cannot be compared quantitatively because many of the QTA/MS peaks are saturated at 20120.

The 198 K and 158 K data clearly demonstrate the ability of QTA/MS to chemically identify evolved species, at least for the most abundant, best separated species. The

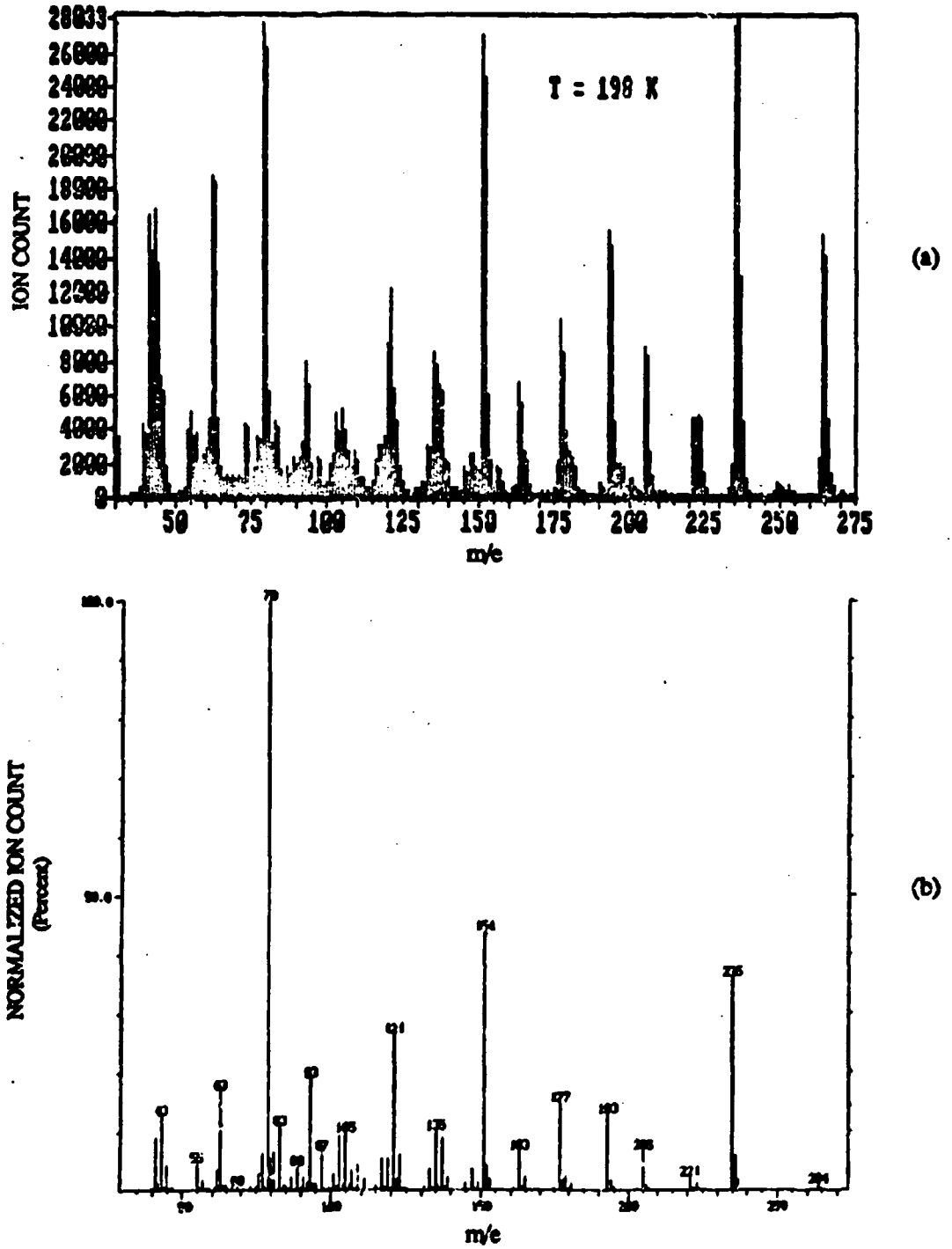


Fig. 5-38 Comparison of Mass Spectra Obtained During QTA/MS of the Outgassing Products from R-2560 at 125°C and GC/MS of the R-2560 at 200°C. (a) QTA/MS Mass Spectrum of Evaporating Flux at a QCM Temperature of 198 K and (b) GC/MS Mass Spectrum for Alkyl Silicate at Scan = 596 s.

Table 5-7

Comparison of QTA/MS Mass Spectrum at 198 K and GC/MS Spectrum for Alkyl Silicate

Mass/Charge m/e	Alkyl Silicate Spectrum by GC/MS - Peaks > 10 percent	QTA/MS Spectrum - 12 Largest Peaks	Modified QTA/MS Spectrum†
27	-	67.2	
30	-	63.1	
41	9	57.9	29
43	14	59.2	30
62	1	66.4	0
63	17	64.9	66.4
79	100	98.1	96.9
80	6	93.6	0
83	12	15.2	7.7
93	19	27.8	13.7
105	10	17.7	9.0
121	27	42.8	22.0
135	11	30.0	15.0
151	44	95.7	92.0
152	4	87.1	0
177	14	36.8	18.6
193	14	55.3	28.0
235	37	97.7	100
236	6	100	0

† Percentages from adjacent peaks 62/63, 79/80,151/152, 235/236 have been added, totals have been assigned to predominant mass number in GC/MS spectrum, and spectrum has been renormalized.

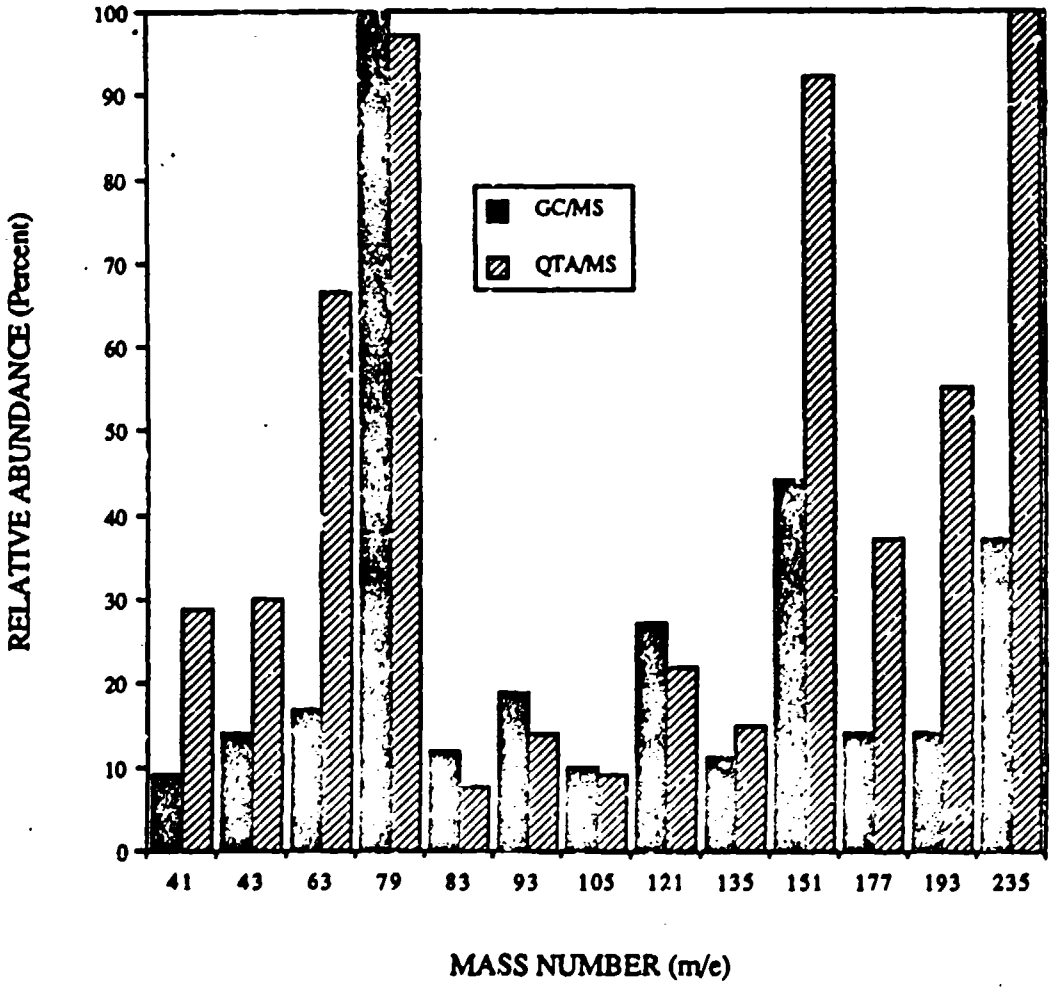


Fig. 5-39 Comparison of Mass Spectra Obtained During QTA/MS of the Outgassing Products from R-2560 at 125°C and GC/MS of the R-2560 at 200°C. QTA/MS Mass Spectrum of Evaporating Flux at a QCM Temperature of 198 K and GC/MS Mass Spectrum for Alkyl Silicate at Scan = 596 s.

1-propanol matchup is very good qualitatively, and if the mass spectrometer gain had been reduced so that the system had not saturated, the spectrum would probably have been good enough to have obtained this identification from a standard library. The alkyl silicate matchup is a better example of the capability of QTA/MS because the spectrum is more complex. It is concluded from these two examples that the capability of the QTA/MS test to separate and identify species has been demonstrated in principle.

5.2.2.2.2.2 The Less Abundant Species

This section proposes chemical identities for the less abundant QTA/MS species by comparing the QTA/MS mass fragmentation patterns from Table 5-2 with the chemically identified GC/MS mass fragmentation patterns in Table 5-5.

95 K: Ion count peaks at m/e=12-18, 27-33, and 43-48 suggest that this species peak is due primarily to atmospheric gases. These may be absorbed in the sample or an artifact of the initial effusion cell insertion into the main chamber. Since the auxiliary chamber is at a higher pressure when the isolation valve is opened at the beginning of the isothermal outgassing test, some residual atmospheric gases will pass into the main chamber.

145 K: Ion count peaks at m/e=89, 91, and 92 and the mid-40s suggest toluene. Peaks in the high 70s and low 50s suggest benzene. The evaporation temperature is consistent with the vapor pressure of these species. There are additional ion peaks for this temperature at m/e=103 and 133 which do not correlate with any species with a volatility high enough to evaporate at this temperature. These three peaks appear individually in the spectra of all the methyl cyclosiloxanes, but appear together only in hexamethyl cyclotrisiloxane and octamethyl cyclotetrasiloxane. Since many siloxanes are soluble in toluene, it is suggested that the 145 K species is a mixture of toluene and benzene, with fragments of a higher molecular weight species such as one of the smaller methyl cyclosiloxanes appearing because of a carry-over effect.

150 K: Because of the value of the evaporation temperature, the major ion peaks at m/e=18 and 19, and absence of any other peaks, this species appears to be water.

158 K: This species was identified as 1-propanol in the previous section.

170 K: This species is identified as hexamethyl cyclotrisiloxane mainly on the basis of the ion peak at m/e=207, which is the (M-15) peak. Other confirming matches occur at m/e=208-209, 176, 161-163, 147, 133, 117-119, 89, 75-78, and 73.

175 K: There are few ion peaks suitable for identifying this species. It is believed to be octamethyl cyclotetrasiloxane on the basis of the peak at m/e=281, which is the (M-15) peak.

185 K: There are few ion peaks suitable for identifying this species. It is believed to be decamethyl cyclopentasiloxane on the basis of the peak at m/e=355, which is the (M-15)

peak. There is also a match at m/e=170.

198 K: This species was identified as an alkyl silicate in the previous section.

210 K: This species cannot be identified with any confidence. Its most distinct peaks occur at m/e=279-280 and no GC/MS-identified species has a peak at these values.

220 K: This species matches with the "similar to dodecanoic acid" 862 s GC/MS species on the basis of peaks at m/e=102, 115, 171, 183, and 201. It has a prominent peak at m/e=242 which was used to locate the species. However, no m/e=242 peak was found for any of the species detected in GC/MS.

230 K: This species matches with the "unspecified silicone (alkyl or aryl)" 964 s GC/MS species. The match is based on peaks at m/e=327, 343, and 405.

238 K: This species appears to be a mixture of several species. Table 5-5 gives the mass fragmentation patterns for cosamethyl cyclodecasiloxane as determined in both the 125°C and 200°C GC/MS tests. The patterns for the two test temperatures are slightly different, and the 200°C pattern has been truncated. If these patterns have been correctly identified and are taken together, then most of the 238 K species can be identified as cosamethyl cyclodecasiloxane. However, some important peaks such as m/e=494, 403, 392, 387, and 156 cannot be associated with cosamethyl cyclodecasiloxane based on the the GC/MS data of Table 5-5. Of these, the m/e=392 and 494 peaks do not appear in any GC/MS patterns, while the m/e=403 peak appears in GC/MS at 1049 s and 1102 s, and the m/e=156 peak appears in GC/MS at 919 s, 964 s, and 1008 s. It is suggested that the 238 K species is predominantly cosamethyl cyclodecasiloxane, but may also include some 919 s and 1049 s phenyl methyl siloxanes. These latter two species are suggested because of their higher abundance in the GC/MS test and their higher volatility than the 1049 s, 1102 s, and 1008 s GC/MS species.

250 K: On the basis of matches at m/e=341, 403, and 491 this species matches with the GC/MS 1102 s species, which was identified as docosamethyl cycloundecasiloxane. However, the fragmentation pattern does not match that of the GC/MS 1025 s species which was also identified as docosamethyl cycloundecasiloxane.

285 K: Most of the fragments from this species are common to a number of other species and so cannot be used for identification. The unique fragments are in the m/e range of 372-378 (maximum at m/e=373) and 451-455 (maximum at m/e=452). Since no peaks were found in this range for any of the species evolved in the GC/MS tests this species cannot be identified.

290 K: The fragmentation pattern for this species matches very well with the pattern for the aromatic acid detected by GC/MS at 1484 s.

5.3 OUTGASSING RATES OF INDIVIDUAL SPECIES

In this section the mass spectrometer data obtained for the mixed outgassing flux during the isothermal outgassing test are analyzed and processed to determine the outgassing rates of the individual outgassed species. The data analysis procedure originally proposed in this program (see Fig. 2-2) called for determining the individual species outgassing rates from the mass spectra of the mixed outgassing flux using individual species mass fragmentation pattern data measured by QTA/MS and a deconvolution algorithm. As noted in Section 5.2.2, the QTA/MS technique was not able to provide the individual species mass spectra in a sufficiently refined form to enable the analysis to be completed in the proposed manner. Also, the mass spectrometer data did not have enough dynamic range to be qualitatively accurate. However, it was possible to work around these difficulties and determine the individual species outgassing rates by an alternative method. This section begins by discussing some fundamental aspects of the measured mass spectrometer data in Section 5.3.1. The procedure for determining the outgassing rates of the individual species from the mass spectrometer data is then presented in Section 5.3.2.

5.3.1 Mass Spectrometer Data - Basic Considerations

5.3.1.1 Data Acquisition and Output

During the isothermal test, the mass spectrometer monitored the outgassing flux by scanning the m/e range of 10 to 500 at 5-minute intervals and recording the ion count at each m/e value. Although the mass spectrometer has an available m/e range of 2 to 1023, the measurement range was truncated at 500 to reduce the amount of data to be handled. This range is generally adequate for chemically identifying most of the outgassed species, since the most abundant fragments usually occur within this m/e range. However, the major fragments of homologous series of species such as the methyl cyclosiloxanes often occur at the same m/e location as many other members of the series, in which case the major fragments are useless for tracking the behavior of a particular member of the series. Fortunately we found that many of the members of homologous series had minor but clearly unique fragments at m/e values higher than m/e = 200 and all the way up to m/e = 500, and these fragments were heavily depended on for tracking and identifying the species. It is highly likely that additional unique fragments for the higher molecular weight species could have been found at m/e values above 500. We, therefore, later regretted that the data truncation had been made at m/e = 500 and it is planned to use an m/e range up to at least 700 in future testing.

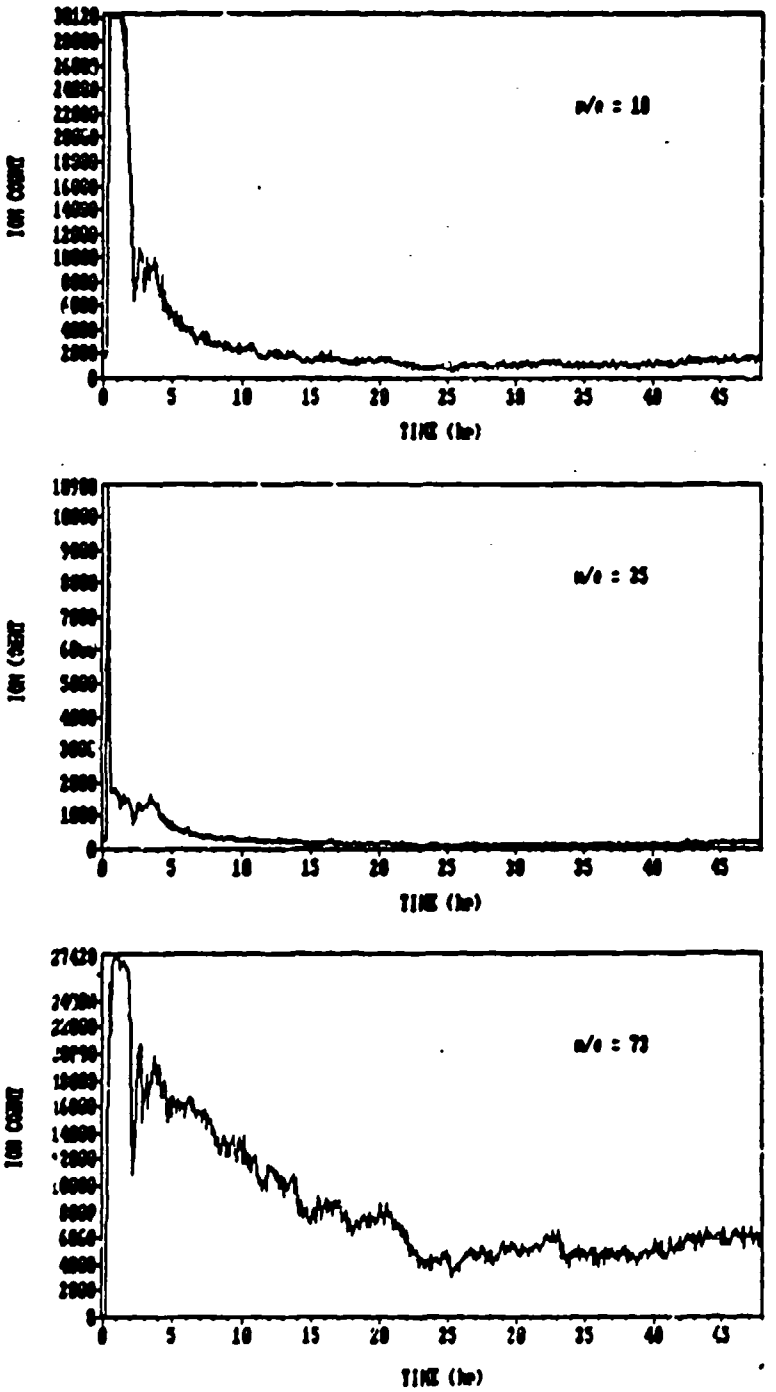
A basic limitation of the present data is saturation of the mass spectrometer electrometer at early test times. The electrometer has an upper limit to its capacity to measure ion count. When the ion count exceeds this capacity, the electrometer output does

not respond further, and instead indicates a constant maximum reading. The mass spectrometer electrometer range can be adjusted down or up, either to accommodate the high outgassing rates of the major species at the beginning of the test without saturating, or to detect the low outgassing rates of minor species at longer test times, respectively. However, with the present mass spectrometer system the electrometer range cannot be automatically changed during a test. Changing the electrometer setting would require stopping data collection, manually changing the electrometer range, and then resuming data acquisition with a new data file. While this requires only a few seconds to accomplish, the post-test correlation of the data from multiple files with different electrometer ranges is too tedious to be included in an already too complex data reduction procedure. A single electrometer setting must therefore be used for the entire test and in selecting this setting, a trade-off must be made between loss of early time data because of saturation and loss of later time data because of low signal to noise ratio. We decided in the present tests to risk sacrificing some of the early-time high ion count data for some m/e values in order to be sure of detecting the lower ion counts at longer test times. The same electrometer range setting was used for both the isothermal outgassing test and QTA/MS phases of the material sample test, for all materials. At this setting, saturation occurred at an ion count of 30120.

The primary experimental mass spectrometer data acquired were the mass spectra for m/e from 10 to 500 at 5-minute intervals throughout the test. The mass spectrometer software provides the total mass spectrum at each point in time and the variation of the ion count for each m/e value with time. All data can be provided in terms of actual ion count or as a percentage of the highest peak in graphical or tabular form. The vacuum chamber background spectrum, measured immediately before insertion of the test sample, can be subtracted from the spectra measured during the outgassing test to give the true contribution of the outgassing species.

5.3.1.2 Typical Raw Output Data

Figures 5-40 and 5-41 show examples of ion count data versus time for various typical low and high m/e values, respectively, before subtraction of the empty chamber background. All of the plots show an initially high outgassing rate followed by a decline to a lower rate, which is characteristic of all types of outgassing mechanisms. Also, all of the plots show considerable fine structure, including several maxima and minima in the first 5 hours which are discussed in more detail in Section 5.3.1.3. Some of the plots for the higher molecular weight species also show a slight increase in rate at longer evacuation times. This clearly cannot be explained by a simple depletion mechanism and may be due to the production of additional volatile components during the test as a result of continued curing of the sample.



(a)

(b)

(c)

Fig. 5-40 Mass Spectrometer Monitoring During the Isothermal Outgassing Test on R-2560 at 125°C. Plots of Ion Counts Versus Time for Low m/e Values: (a) m/e = 18, (b) m/e = 35, and (c) m/e = 73.

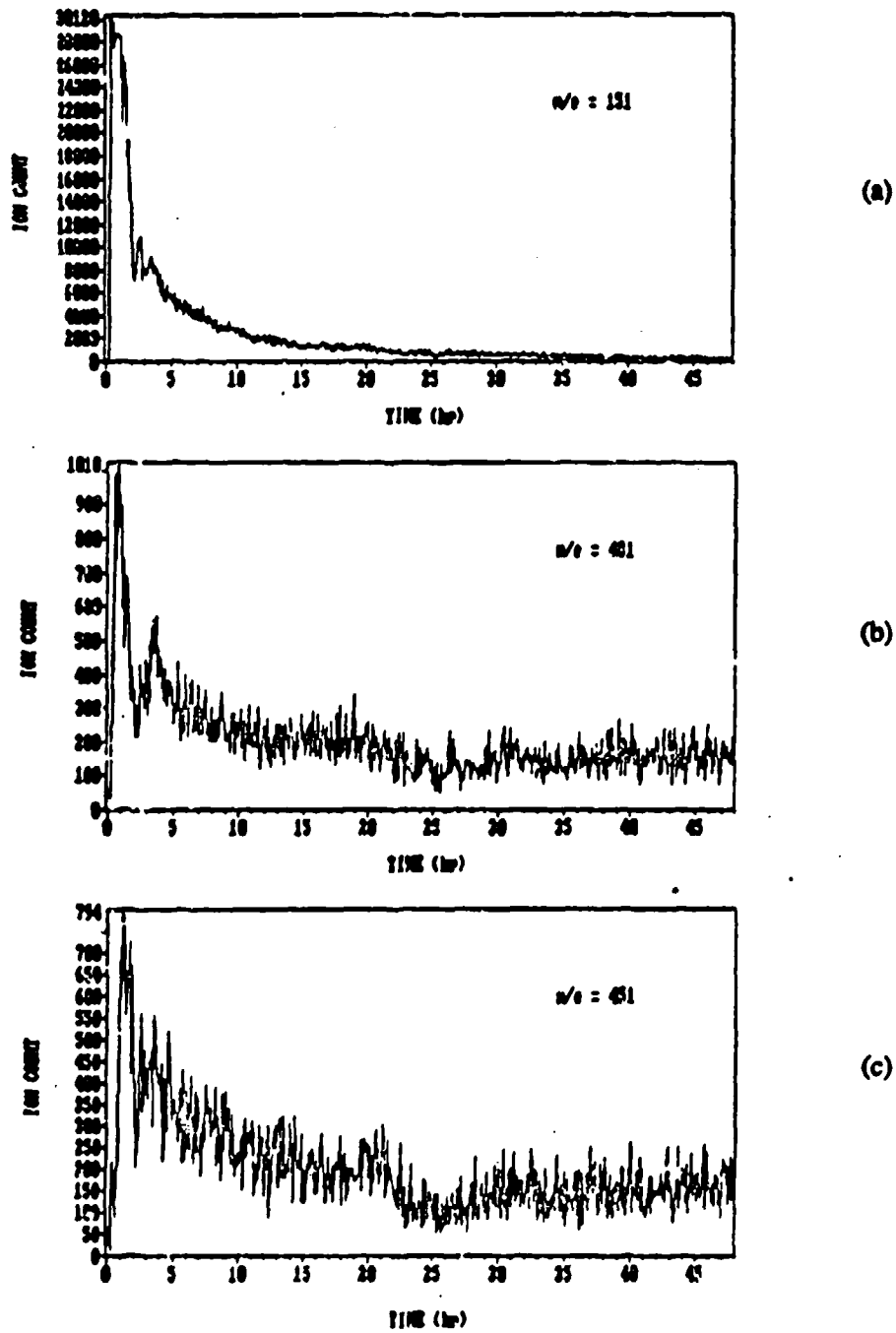


Fig. 5-41 Mass Spectrometer Monitoring During the Isothermal Outgassing Test on R-2560 at 125°C. Plots of Ion Counts Versus Time for High m/e Values: (a) m/e = 151, (b) m/e = 481, and (c) m/e = 451.

Figure 5-40(a) shows the data for the m/e 18 fragment, which was unique to water. The mass spectrometer is saturated at early times but the count falls very rapidly to a fairly constant value. Later, this section shows that when the pre-test main chamber water background is subtracted, the net water ion count is zero after a few hours of outgassing.

Figure 5-40(b) shows the data for m/e of 35 which was unique to 1-propanol. It shows that this species was almost completely outgassed within the first 5 hours.

Figure 5-40(c) shows the plot for m/e equal to 73. This fragment is common to all siloxanes and was significant throughout the test. The siloxanes have relatively high molecular weights and hence lower diffusion coefficients, and so they outgas more slowly and over longer durations than water and 1-propanol. As a result, the initial peak is less pronounced and the ion count falls more slowly with test time. The increasing peak height in the latter half of the test was observed in a large number of the higher molecular weight fragments and, as was previously mentioned, is believed to be the result of continuing curing of the test sample at the elevated test temperature of 125°C.

Figures 5-41(a), (b), and (c) show the time variation of the m/e=151, 481, and 451 fragments, which were unique to the 198 K alkyl silicate species, the 238 K, and the 285 K species, respectively. These plots show the gradual modification of the basic outgassing characteristic towards smaller initial peaks and slower rate of decline with time as the molecular weight of the parent species becomes larger.

5.3.1.3 Correlation of Mass Spectrometer and Mass Loss Data

Figure 5-42 shows the normalized average ion count (AIC) data as a function of test time. The data show a major peak shortly after the effusion cell is inserted into the main chamber, followed by several other peaks and valleys in the zero to 5-hour time period. At later times, the curve is fairly regular, with the exception that the AIC increases towards the end of the test. AIC is a function of the total outgassing flux, and the ratio of AIC to the total outgassing rate (TOGR) should depend only on the mass spectrometer electron multiplier gain and the average ionization constant of the outgassed species. Since experience has shown that the multiplier gain remains constant over periods of several days, the ratio of AIC to TOGR should vary only with the average ionization constant.

Figures 5-43(a) and 5-43(b) present a comparison of the time dependence of TOGR and AIC data. The TOGR and AIC data were extracted directly from Figs. 5-1(b) and 5-42, respectively. The very short duration AIC peak which occurs right at the beginning of the test was excluded from the plots and is discussed later in this section. The ordinate units in Figs. 5-43(a) and 5-43(b) are arbitrary and have been adjusted to permit making a simple visual comparison of the AIC and TOGR on the same graph.

Figure 5-43(a) shows AIC and TOGR for the first 10 hours of the test. The plots are

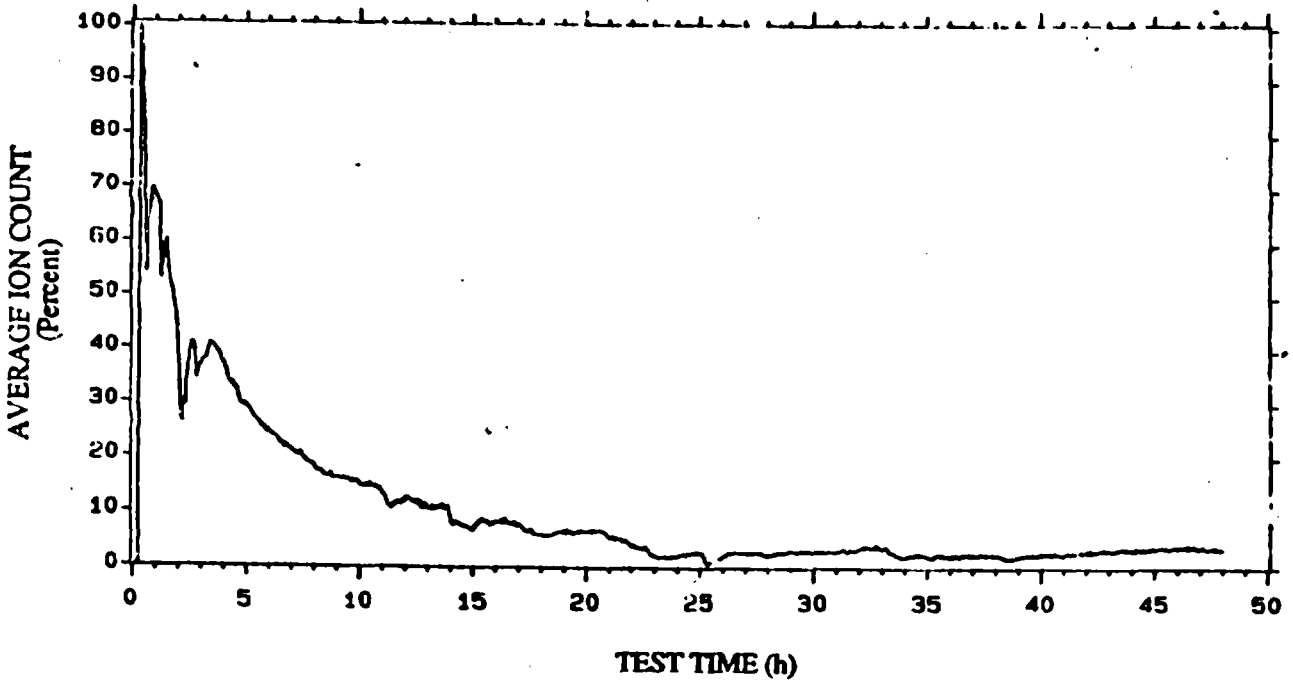
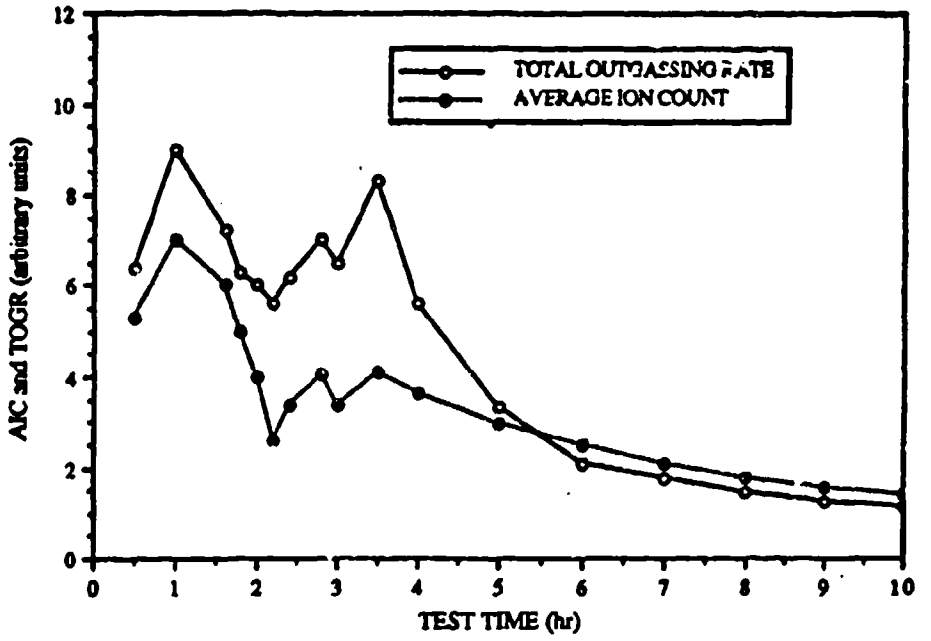
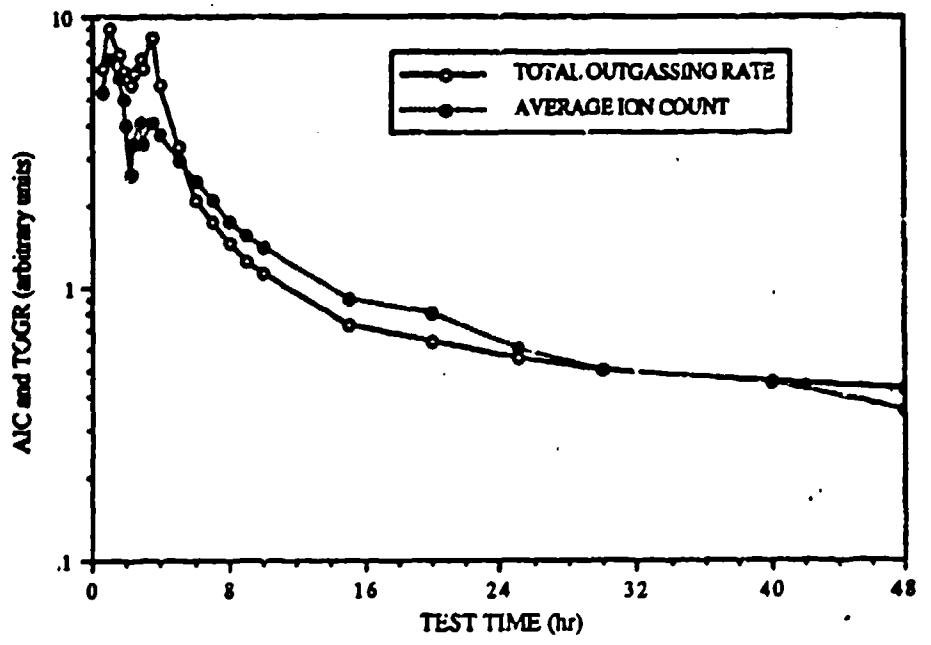


Fig. 5-42 Mass Spectrometer Monitoring During the Isothermal Outgassing Test on R-2560 at 125°C. Normalized Average Ion Count as a Function of Time.



(a)



(b)

Fig. 5-43 Comparison of Average Ion Count (AIC) and Total Outgassing Rate (TOGR) as a Function of Time During Isothermal Outgassing of R-2560 at 125°C: (a) First Ten Hours of the Test and (b) Full Test Duration.

qualitatively very similar in form. Both the TOGR and AIC data show peaks and valleys in the first 5 hours occurring at the same points in time. The coincidence of these peaks and valleys confirms that the twin peak effect observed in Fig. 5-1(b) is real and not an artifact of the QCM mass measurement system. The first peak is probably due to release of volatile species present in the sample prior to the test, while the second peak may be due to additional curing of the sample as it was heated to the 125°C test temperature.

A quantitative comparison of the TOGR and AIC curves indicates that the AIC is relatively lower than the TOGR during the first 5 hours of the test, after which the two curves appear to track each other very closely. The relatively lower values of AIC in the first 5 hours is a consequence of the saturation of the mass spectrometer for many m/e values during this time period. When saturation occurs the ion count number used by the mass spectrometer data reduction system to calculate the AIC will be systematically lower than the true value. The ion count data presented later in Table 5-8 show that the ion counts for most m/e values fall below the saturation level after about 5 hours. After this time the AIC does begin to track the TOGR accurately as shown.

Figure 5-43(b) shows the AIC and TOGR data for the entire test duration. The AIC tracks the TOGR fairly closely after the first 5 hours, indicating that the AIC is a good quantitative indicator of mass loss rates. The AIC curve does fall slightly relative to the TOGR curve as the test proceeds, possibly due to a slight decrease in the average ionization constant of the mixed outgassing flux with time.

The initial high but brief peak observed in the outgassing rate data, Fig. 5-1(b), and the AIC data, Fig. 5-42, occurs immediately following the opening of the isolation valve for insertion of the test sample. This peak is most probably due to the detection of residual atmospheric gases from the auxiliary chamber, whose pressure had not been reduced to the the level of the main test chamber at the time of insertion. It is less likely to be due to species desorbed from the surface of the sample, effusion cell, or auxiliary chamber since the auxiliary chamber had been pumped on for 5 minutes before sample insertion, and most of the adsorbed atmospheric species would have been removed by this time.

5.3.2 Outgassing Rates of Individual Species

The outgassing rates of the individual species were determined using the following four manual data reduction steps:

(i) The entire body of mass spectrometer ion peak height data was entered manually into a computerized database.

(ii) Ions for tracking the behavior of each of the outgassed species were selected using the QTA/MS data of Section 5.2.

(iii) The time dependence of the outgassing rates of each species was determined

from the time dependence of its selected tracking ions.

(iv) The absolute outgassing rate of each species was calculated by multiplying its time-dependence characteristic by an appropriate proportionality constant.

These steps are described in the following sections.

5.3.2.1 Data Inventory

The ion count data for the full 10 to 500 m/e range were printed out in tabular form by the mass spectrometer data system for test times of zero, 0.333, 1, 5, 10, 20, 30, 40, and 48 hours. These data were then entered into a Microsoft Excel database worksheet on the Macintosh computer to create Table 5-8. The spacing of these test times was considered to be adequate for characterizing the time-dependence of the data for modeling purposes. The zero time data characterized the main chamber background 15 minutes prior to insertion of the effusion cell and test sample. Sample insertion into the main chamber and initiating of heating to 125°C occurred at 0.25 hour. The 0.333-hour data were recorded 5 minutes after the time of insertion of the effusion cell into the main test chamber. By 1 hour, the sample had reached the test temperature of 125°C. (The test start-up procedures and timing are given in more detail in Table 4 -1.)

The data for 0.333 hour have been entered into the table in both absolute and background-subtracted form to show more clearly those m/e values that were saturated at the beginning of the test. Many of the lower m/e values were saturated at 30120 at the beginning of the test, as well as the m/e=121, 151, 177, and 235 ion peaks associated with the 198 K alkyl silicate species. By 5 hours, saturation occurs only at m/e values of 27, 42, and 43.

The data for times of 1 hour through 48 hour were entered into the table in background subtracted form only.

5.3.2.2 Selection of Characteristic Fragments

There are two possible methods for tracking individual species in the mixed outgassing flux. The first method is to determine the unique fragmentation pattern of each outgassed species using QTA/MS and then to enter these individual patterns and the mass spectra for the mixture of species measured at each point in the outgassing test into a deconvolution algorithm to resolve the contributions of each species. This option is not feasible at this time because the QTA/MS test was unable to separate the species sufficiently to produce reliable single species fragmentation patterns. Also, although deconvolution algorithms are commercially available, there would have been insufficient time and funding available to adapt them to the present test. Finally, because of the saturation issue the ion count data are not quantitatively accurate at early test times and so could not be used with confidence in a deconvolution procedure.

Table 5-8

Inventory of Mass Spectrometer Ion Count Data from the Isothermal Outgassing Test

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>		<chamber background subtracted>							
10	68	302	234	76				20		
11	51	444	393	99	8	17	5	45		27
12	440	16980	16540	5900	2578	1052	558	324	104	312
13	350	26520	26170	8530	3630	1492	736	272	334	280
14	2134	30120	27986	26806	17166	4386	2646	700	764	1106
15	1992	30120	28128	28128	28108	8908	3408	1408	1548	2238
16	3040	30120	27080	27080	26040	7300	2500	1081	780	1420
17	2668	30120	27452	27452	10092	3692	1552	342	554	1112
18	2132	30120	27988	27988	3188	390				
19	1992	30120	28128	27208	3968					
20	177	22900	22723	10923	4183	851	511	113	243	409
21	174	19520	19346	2666	924	132	63			15
22	103	3042	2939	481	247			3		
23	94	692	598	64	109					
24	51	23674	23623	1221	667	151	51	28	82	20
25	46	14060	14014	6234	3614	912	366	151	236	234
26	105	29800	29695	27975	24815	6035	1865	1227	1185	1193
27	652	30120	29468	29468	29468	17768	7228	3548	3208	3368
28	21820	30120	8300	8300	8300	7300				
29	19360	30120	10760	10760	10760	9160				
30	3780	30120	26340	26220	25980	17480	4960	1600	1720	1720
31	350	29820	29470	29470	29310	27270	11510	6210	5750	5870
32	12680	30120	17440	17440	16620	14200				
33	11440	30120	18720	17640	800					
34	1754	17440	15686	6446	2626					
35	326	10900	10574	1334	544					
36	71	3200	3129	1309	705	159		59	41	20
37	86	13320	13234	7174	3974	834	249	100	219	211
38	83	26700	26617	13497	7277	1919	617	413	329	529
39	407	30120	29713	29253	20793	4993	2029	1127	823	1037
40	906	30120	29214	28874	14154	4094	1362	648	312	538
41	694	30120	29426	29426	28266	10866	4426	2300	1662	2026
42	291	30120	29829	29829	29829	10669	4709	2657	1965	2107
43	892	30120	29228	29228	29228	10448	5248	288	2[illegible]	2768
44	1850	30120	28270	27610	22390	8330	3810	1650	[illegible]	1970
45	1562	30120	28558	28138	10158	3838	1474	882	39[illegible]	1026
46	268	28560	28292	23392	6952	2582	1500	804	91[illegible]	804
47	101	9340	9239	5979	1651	679	449	257	395	281
48	72	3304	3232	1926	508	286	229	84	100	46
49	50	850	800	656	317	240	86	43	30	54
50	61	1252	1191	1959	793	711	253	127	47	174
51	39	1658	1619	2479	977	655	415	270	267	237
52	18	3360	3342	2814	1152	618	306	191	258	282
53	26	4380	4354	3554	1184	676	283	128	242	236
54	70	21240	21170	15190	3650	2392	1026	440	294	616
55	124	27260	27136	19016	4336	3216	1628	714	508	490
56	109	20780	20671	14791	4711	2473	1501	787	685	917
57	67	22320	22253	15333	6033	2727	1893	1179	895	1185
58	40	29240	29200	22480	13060	3120	1476	930	824	846
59	94	30120	30026	30026	18946	3926	1986	1000	796	890
60	38	30120	30087	30082	17182	3822	1816	948	862	732
61	71	28040	27969	13609	6409	2849	1497	701	747	549
62	43	30120	30077	29177	6537	3117	1333	625	301	305
63	36	30120	30084	29884	6084	2828	1094	618	294	270
64	45	13640	13595	8515	1619	613	281	143	74	78
65	60	8300	8240	3580	738	374	175	127	43	106
66	51	5180	5129	2525	693	331	152	95	37	117
67	47	4780	4733	2853	829	497	239	180	100	198
68	70	4360	4290	2532	678	548	175	216	121	106
69	31	4380	4349	5169	1253	1097	601	465	248	136
70	63	4080	4017	4617	1155	841	595	216	135	120
71	112	3720	3608	4268	1094	948	612	268	191	430

Table 5-8 (continued)

	<-------- TEST TIME - HOURS -------->									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>		<-------- chamber background subtracted -------->							
72	72	3660	3588	4008	1056	792	518	276	194	376
73	69	14620	14551	27311	15171	13311	8671	5351	4811	6111
74	34	12860	12846	26346	13326	11506	7666	4886	4606	5506
75	16	5120	5104	8324	3284	3002	2254	1364	1544	1414
76	61	12240	12179	5559	1709	1569	1363	1001	1171	1069
77	55	20240	20185	10385	2031	1485	839	717	865	1063
78	37	20380	20343	10543	2413	1541	651	833	771	927
79	106	30120	30014	29654	14514	6854	2766	1354	826	466
80	56	30037	29981	28364	12604	5764	2490	1198	750	452
81	54	20240	20226	10586	2850	1214	550	298	262	85
82	67	15120	15053	6813	1693	705	238	105	186	6
83	69	26280	26211	10011	1891	781	443	289	177	214
84	76	24420	24344	8924	1804	736	340	292	138	206
85	27	7680	7653	4153	945	873	361	227	211	249
86	35	4260	4225	3585	833	725	327	263	118	217
87	33	7760	7727	4107	799	525	242	97	114	132
88	25	7360	7335	4275	761	371	209	101	154	100
89	52	14540	14488	4968	992	536	245	193	242	294
90	42	12980	12938	4118	856	680	307	147	282	217
91	52	13900	13848	8728	2834	2206	1168	734	730	692
92	48	21000	20952	95323	2380	1984	920	610	632	646
93	32	30120	30088	18048	2888	1550	856	292	255	310
94	31	28380	28349	14609	2573	1202	569	216	127	100
95	71	8400	8329	3789	643	323	145	96	54	40
96	38	4560	4522	2060	434	444	99	116	78	85
97	31	11780	11749	6889	933	839	240	223	192	113
98	41	9840	9799	4419	919	671	243	176	148	65
99	95	3116	3021	1785	329	201	103	67	105	20
100	50	5160	5110	2032	474	206	174	113	135	15
101	52	10240	10188	4528	790	512	266	223	225	93
102	28	14500	14472	5372	14989	732	548	334	247	207
103	70	26460	26390	9250	1808	996	642	400	322	254
104	37	22060	22023	7983	1491	939	575	337	260	238
105	55	28660	28605	11565	2321	1289	627	439	393	275
106	27	22340	22313	9113	1947	881	543	343	281	222
107	49	13100	13051	6051	1437	1001	507	264	233	225
108	29	10560	10531	4271	993	769	359	222	215	159
109	50	12480	12430	4870	1008	504	257	282	102	134
110	41	7520	7476	3058	686	534	212	192	98	69
111	43	6180	6137	2651	843	355	207	60	68	145
112	28	3480	3452	1716	454	292	155	62	93	106
113	64	1798	1734	914	240	221	60	104	34	27
114	46	3640	3594	1812	576	209	98	99	69	73
115	80	4880	4800	2858	626	500	175	77	116	81
116	77	13380	13303	4543	903	725	435	329	167	233
117	38	17300	17262	6142	1254	960	7854	586	548	578
118	47	19380	19333	6973	1675	887	741	407	397	319
119	44	21740	21696	7956	2054	912	608	328	580	392
120	37	29060	29023	20343	2967	1625	919	347	349	381
121	71	30120	30049	24309	3789	2013	1139	347	289	335
122	42	21640	21598	12338	2026	948	562	284	209	158
123	50	19880	19830	6990	1178	610	358	187	115	110
124	34	7260	7226	2730	442	362	131	90	74	53
125	31	2194	2163	947	271	319	51	104	120	96
126	43	960	917	797	255	251	39	129	78	62
127	65	988	923	747	211	152	97	41	50	8
128	39	436	397	489	196	219	32	36	41	49
129	24	1678	1654	2154	686	422	180	114	13	74
130	31	1518	1487	1807	627	311	152	65	23	71
131	62	3520	3458	2072	412	290	159	157	120	42
132	57	3700	3643	1827	351	249	259	81	106	109
133	28	17240	17212	6372	1538	812	374	266	219	199
134	49	16060	16011	5551	1263	797	473	255	186	252
135	58	28000	27942	27522	13582	12202	6882	4682	5062	5462
136	64	26860	26796	27096	12316	11316	6376	4276	4556	5076
137	19	27100	27081	12161	3641	3261	1791	1431	1385	1503
138	73	23580	23507	10427	1845	1319	823	445	297	363
139	44	8200	8156	2858	634	370	195	159	102	112

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	(includes chamber background)		(chamber background subtracted)							
140	36	7160	7124	4210	470	226	237	124	85	59
141	18	1770	1752	986	263	207	143	62	43	129
142	17	1146	1129	865	222	155	159	90	111	108
143	22	1042	1020	1036	324	205	147	71	57	71
144	51	1024	993	1103	301	82	110	59	35	33
145	34	6100	6066	2602	524	408	171	192	106	78
146	37	5460	5423	2367	455	345	135	152	83	91
147	34	15140	15106	8826	2769	1922	1836	1196	1012	1324
148	34	13440	13406	7966	2832	1946	1720	1024	1110	1138
149	90	10120	10030	6410	1454	1018	428	302	378	460
150	64	13740	13676	5836	1194	1070	359	257	249	231
151	60	30120	30060	28480	5560	2820	1328	559	302	278
152	131	29620	29489	26829	4709	2679	1079	505	207	58
153	66	15860	15794	7994	1580	770	292	176	104	138
154	64	6900	6836	2914	634	414	213	164	223	211
155	68	1546	1468	1556	586	372	234	122	197	135
156	57	1630	1573	3163	1279	[illegible]057	827	529	471	645
157	23	1588	1565	3137	1249	[illegible]7	743	549	461	605
158	42	910	868	1676	430	[illegible]4	230	185	156	245
159	26	750	724	486	166	160	95	97	38	57
160	40	756	716	502	189	62	40	40	125	26
161	30	2696	2666	720	238	267	314	239	654	426
162	18	5540	5522	1682	416	248	346	215	616	338
163	49	28100	28051	9251	1505	659	427	163	234	291
164	47	24960	24913	7753	1241	593	425	85	150	238
165	47	10580	10533	4113	695	649	361	174	196	238
166	98	7440	7342	2948	710	528	276	98	99	126
167	63	2546	2483	1229	289	181	66	91	67	130
168	64	1328	1264	568	206	121	26	60		17
169	39	514	475	299	157	164	40	50	4	28
170	25	372	347	270	169	155	45	76	41	26
171	31	384	353	441	199	272	142	64	90	38
172	44	562	518	518	173	233	145	14	84	9
173	40	498	458	324	168	178	90	10	108	60
174	70	1120	1050	418	81	37	12		7	23
175	43	2138	2095	787	156	122	32	44	25	57
176	55	16500	16445	6025	875	645	228	46	17	63
177	126	30120	29994	13854	2712	1110	536	302	45	75
178	85	28340	28255	13055	2229	811	433	253	90	47
179	54	15100	15046	5646	1387	812	480	257	125	237
180	28	9460	9432	3412	878	444	386	162	161	180
181	21	6760	6739	2835	755	421	249	258	209	151
182	27	4540	4513	1277	491	303	181	171	148	86
183	39	1250	1211	519	268	329	128	192	116	109
184	28	444	416	386	218	215	105	130	117	67
185	55	358	303	527	243	192	150	65	124	58
186	80	227	147	770	320	169	124	117	36	56
187	26	249	213	960	502	270	217	92	109	109
188	41	308	267	487	327	147	82	44	61	106
189	38	362	324	316	129	104	87	15	44	46
190	34	2340	2306	1318	370	219	214	113	126	156
191	66	2812	2746	1800	360	332	162	208	133	119
192	38	1668	1630	926	215	186	125	64	148	129
193	32	27040	27008	17944	3368	1984	1070	620	564	482
194	39	26940	26901	17221	3421	1729	989	643	591	479
195	50	11200	11150	5990	1458	938	646	438	410	678
196	57	4180	4123	4003	1195	897	693	435	337	419
197	69	1192	1123	11671	4331	4151	3131	2317	1863	2705
198	33	914	881	10707	4127	3887	3025	2135	1705	2515
199	27	522	495	3553	1653	1223	959	777	739	917
200	16	424	408	1314	528	422	326	237	245	346
201	22	344	322	1100	326	240	137	169	52	130
202	47	302	255	325	269	238	117	102	70	63
203	54	566	512	338	191	150	61	63	33	33
204	50	562	512	320	148	125	56	48	104	11
205	23	26380	26357	8977	1352	847	501	325	81	277
206	21	25180	25159	8199	1289	773	335	311	99	207
207	48	8570	8477	3032	876	726	460	260	23.	276

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>		<chamber background subtracted>							
208	52	4400	4348	2346	678	536	392	176	219	428
209	32	1552	1520	1526	612	434	344	309	254	274
210	37	698	664	1234	556	374	281	268	264	186
211	21	334	313	677	361	219	237	153	172	151
212	30	231	201	450	554	203	169	145	138	88
213	28	234	206	248	228	52	37	73	25	77
214	30	214	184	179	206	89	43	28	99	33
215	21	176	155	166	167	79	92	86	49	44
216	24	221	197	424	400	259	135	85	86	145
217	41	232	191	345	329	141	109	107	63	88
218	81	203	122	863	315	195	102	127	140	148
219	50	454	394	938	428	314	151	173	150	184
220	47	666	619	431	289	109	94	19	27	53
221	62	13240	13178	4878	1210	1008	758	366	340	522
222	88	12200	12112	4372	1208	860	700	309	251	396
223	54	10320	10246	3326	1038	674	418	248	150	265
224	25	9020	8995	2981	931	449	278	193	197	199
225	20	2726	2696	980	322	217	179	47	128	74
226	83	870	787	457	173	41	4			43
227	41	299	258	222	76	115	10	4	18	39
228	47	296	249	233	128	51	34			18
229	69	241	172	1878	122	28	104			
230	46	165	119	81	131	22	45		52	52
231	36	218	182	89	174	39	55	3	18	15
232	39	620	581	264	161	30	43	33		24
233	52	1636	1584	496	196	17	43	33	17	16
234	74	13280	13206	3410	618	189	80	34		39
235	43	30120	30077	27997	7157	2977	1373	1003	485	323
236	38	30120	30082	27322	6062	2674	998	892	356	235
237	28	28540	28512	10452	2094	1072	318	258	144	106
238	24	11640	11616	3556	852	346	208	123	101	96
239	63	2668	2605	1035	341	287	159	79	77	73
240	42	712	670	422	304	263	130	13	61	27
241	36	228	192	275	243	165	80	125	43	77
242	40	260	220	167	149	60	40	656	17	47
243	60	259	199	70	72	57	36			6
244	60	332	272	63	54	8	3			23
245	72	248	176	39	70	11	22		4	
246	61	206	145	54	126	9				12
247	24	185	161	104	117	65	39	81	21	50
248	22	1026	1004	650	369	229	125	76	135	79
249	15	1542	1527	1027	415	331	165	117	139	273
250	53	1110	1057	1481	499	287	172	68	137	172
251	52	778	726	1518	566	474	214	83	187	123
252	69	614	545	1713	395	491	387	85	64	157
253	39	662	623	209	537	593	493	143	193	243
254	66	432	368	1236	544	384	193	147	84	13.
255	49	367	318	1361	549	405	269	193	124	135
256	64	426	362	1020	416	247	98	116	65	123
257	49	239	190	505	200	159	39	131	70	73
258	80	242	162	406	145	129	97	28		37
259	58	241	183	762	516	354	229	274	190	204
260	27	208	181	677	471	288	221	292	1656	214
261	45	196	151	225	249	149	83	61	57	137
262	44	270	226	81	1	126	5	33	50	24
263	73	4100	4027	967	21	69	19	30		
264	35	16780	16745	3145	679		122	106	55	9
265	22	14560	14538	2562	753		111	86	86	42
266	92	5338	5246	954	93		72		9	17
267	65	1950	1885	1575	613		189	254	150	154
268	54	1046	992	1276	393		153	150	140	186
269	53	544	491	531	270			78	82	112
270	45	302	257	529	157			94	89	87
271	64	213	149	340	107				9	6
272	39	181	142	237	94				51	48
273	75	181	106	105	93	4				
274	62	249	187	92	77	1				
275	50	185	135	94	111	64				25

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>					<chamber background subtracted>				
276	38	179	141	105	87	18	26	38	20	36
277	46	251	205	74	57	39	54	47	23	28
278	42	274	232	94	144	78		43	28	14
279	49	668	619	149	192	58	75	17	57	18
280	37	606	569	247	185	75	110	71	39	67
281	43	1840	1797	1299	609	571	353	251	489	333
282	39	1660	1621	1347	599	467	321	201	373	275
283	27	974	947	807	407	359	286	200	200	236
284	36	442	406	356	251	188	186	185	121	69
285	84	312	228	226	110	77	30	37		
286	109	188	79	148	38	4				
287	34	147	113	96	114	48	7		16	28
288	109	298	189	34						
289	57	275	218	63	62				1	
290	68	193	125	13	80	37				
291	74	142	68	0	83		13			
292	35	252	217	85	105	37	13	13	26	11
293	82	366	284	129	58	40	24	4	6	
294	94	358	264	169	124					
295	85	268	183	170	149	176	29		51	15
296	57	202	145	205	164	152	26	37	26	78
297	26	212	186	290	233	131	42	67	68	111
298	23	196	173	255	229	121	70	96	40	79
299	29	177	148	265	214	100	85	62	46	101
300	26	248	222	194	117	61	82	9	31	55
301	52	230	178	169	122	3	4		6	42
302	38	167	129	107	102	59	3		43	12
303	28	155	127	85	86	47	26	7	22	46
304	33	116	83	56	79	38			4	27
305	35	127	92	41	89	47	5			
306	60	1392	1323	50	88		32			
307	68	287	219	145	78		20		9	
308	62	198	136	105	154	15			44	
309	25	206	181	186	145	53	43	112	63	23
310	26	288	262	542	249	189	169	51	75	126
311	51	300	249	725	235	223	178	69	61	143
312	56	358	302	1192	514	236	212	101	99	112
313	32	360	328	1272	672	259	296	147	169	206
314	39	219	180	687	399	233	177	125	86	111
315	34	281	247	668	356	222	187	218	50	88
316	29	179	150	327	225	165	58	97	60	45
317	54	198	144	202	165	104	36	70	4	32
318	75	233	158	68	40	22				
319	89	257	168	28	4			10		
320	88	189	101	77	46	29				31
321	66	223	157	44	57	24		3		12
322	49	249	200	78	73	15		14		41
323	44	239	195	163	89	45	72	35		19
324	27	174	147	141	123	84	62	166	12	31
325	27	315	288	591	262	244	191	92	96	87
326	17	358	341	477	266	202	213	65	75	140
327	29	1096	1067	1883	619	641	441	311	333	409
328	76	1056	980	1784	576	502	368	236	754	260
329	81	714	633	1653	449	407	279	125	188	231
330	75	546	471	1511	347	371	313	108	77	261
331	37	368	331	7655	313	174	121	54	84	144
332	41	255	214	399	275	84	53	38	56	50
333	19	225	206	149	199	71	63	37	54	55
334	44	250	246	94	143	14	15	5	92	2
335	51	178	127	46	125	1		7	35	
336	60	194	175	11	63		11		30	
337	68	216	158	56	42		18		9	48
338	56	163	107	56	57	34	52			18
339	32	346	314	91	91	82		57	53	48
340	53	262	209	161	109	81	35	44	5	
341	36	674	638	956	341	286	144	102	112	232
342	61	632	571	837	309	217	230	90	80	142
343	60	505	446	674	349	236	215	214	44	106

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>		<chamber background subtracted>							
344	23	346	323	631	313	268	247	225	139	90
345	49	376	327	387	158	95	79	65	66	77
346	41	291	250	159	96	88	65	5	27	56
347	39	277	238	207	158	66	65	23	35	26
348	33	258	225	82	116	52	49	33		34
349	27	184	157	44	101	37	68	10	24	28
350	37	144	107	72	85	41	19	4	71	24
351	47	227	180	82	107	1			9	30
352	40	282	242	45	136	10	33		16	26
353	25	254	229	99	192	93	34	39	16	8
354	21	242	221	103	157	40	24	86	7	19
355	39	716	677	757	337	257	485	305	253	353
356	21	648	627	673	331	271	373	339	241	250
357	67	338	271	257	199	283	104	63	106	111
358	68	289	221	244	139	107	61	52	95	121
359	92	214	122	163	107	61				
360	94	237	143	101	56			9		
361	48	269	221	53	40	37	3	49		14
362	28	234	206	69	82	3	43	14	68	53
363	19	204	185	77	82	46	17	48	79	82
364	35	224	189	75	103	64	19	15	12	9
365	41	222	181	71	53	58	11		46	59
366	45	195	150	22	112	38		14	18	19
367	24	206	182	84	131	82	78	26	136	61
368	40	201	161	79	102	57	59	57	77	23
369	28	203	175	90	1212	85	134	84	38	64
370	44	186	142	177	144	26	111	23	18	62
371	102	182	80	173	75		28		6	
372	79	219	140	252	62	66	29			73
373	91	245	214	763	359	245	203	83	134	199
374	76	181	105	602	246	118	177	35	38	102
375	46	182	136	490	280	120	200	78	66	128
376	58	222	164	252	147	68	44	40	18	59
377	46	228	182	254	131	58	129	16	44	56
378	25	245	220	183	127	63	64	13	21	64
379	60	283	223	120	92		12	8		
380	44	259	215	98	79	29	1	15		4
381	44	251	207	82	57	25	1			22
382	27	289	262	85	42	21	49			53
383	15	342	327	137	137	44	84	36	82	65
384	19	212	193	151	149	54	60	24	14	26
385	42	263	221	171	88	11	45	35	15	
386	73	241	168	135	48				9	
387	20	227	207	350	240	191	162	50	53	86
388	34	244	210	390	257	183	190	36	100	66
389	53	266	213	755	353	291	279	99	126	111
390	38	258	220	612	332	234	215	112	139	162
391	50	290	240	450	288	235	172	73	108	158
392	56	372	335	494	229	165	120	106	116	146
393	24	268	244	234	213	102	86	102	47	92
394	26	214	188	165	139	81	30	42	21	72
395	58	248	190	132	116		9			3
396	43	192	150	53	84	17		8	16	9
397	51	219	168	14	91	54	16		26	11
398	32	211	179	67	101	70		7	11	15
399	63	276	213	58	136	50	4			17
400	42	294	253	101	154	75	26	75	43	15
401	42	231	189	288	191	67	43	114	121	44
402	43	275	232	254	139	55	66	91	74	91
403	53	267	214	653	265	285	225	64	94	149
404	43	228	185	623	241	234	243	64	107	140
405	50	912	862	1258	602	240	294	245	276	171
406	26	934	908	1192	584	210	271	173	235	142
407	17	472	455	661	437	147	109	152	105	157
408	37	364	327	347	228	92	36	53	102	63
409	42	278	236	102	1323	77		2	47	17
410	62	260	198	78	24	6				36
411	50	173	123	75	18	39	27	47	2	19

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<include chamber background>		<chamber background subtracted>							
412	41	318	277	60	61	42	10		11	
413	33	248	215	74	70	19	3			16
414	89	235	146	72	46					
415	42	378	336	338	124	69	63	70	71	67
416	55	289	234	285	119	74	75	56	33	46
417	33	412	379	523	265	156	143	219	97	171
418	30	315	285	518	235	173	134	153	108	123
419	19	326	307	317	180	94	165	107	70	92
420	46	340	294	237	104	102	99	129	101	
421	65	370	305	158	135	54	23	26	49	
422	42	268	226	127	126	6	27	51	37	
423	24	271	247	61	1212	58	20	39	32	3
424	100	262	162		30					
425	86	276	190	22	93					
426	38	232	194	59	85	40	31		12	
427	22	204	182	64	77	14	107	17	23	39
428	40	205	165	41	97	90	42	1		20
429	28	412	384	468	358	234	171	185	121	77
430	57	424	367	357	345	189	139	131	76	66
431	41	358	317	293	188	169	76	119	57	23
432	81	236	155	211	81	66	88	33		
433	55	216	161	75	75	8	62	29		
434	48	253	205	166	105	47	9	3	1	13
435	54	278	224	135	73	39	36	47	26	
436	44	237	193	63	108	26	30	92		4
437	26	272	246	119	120	36	48	62		20
438	23	252	229	89	124	42	35	35	38	44
439	25	145	123	93	82	56	31	15	39	42
440	19	225	206	98	79	20	22	20	44	43
441	56	227	171	60	82	14		19	9	11
442	40	234	194	63	100	78	10	42	20	1
443	84	223	139	37	7	20	9			
444	41	218	177	114	93	29	36			25
445	37	228	191	100	90	26	28	10	3	22
446	35	183	148	133	137	80			43	4
447	39	166	127	137	51	57	17	15	38	
448	61	225	164	121	69	13	11	7		
449	61	201	140	165	105	23	68			2
450	38	233	195	167	152	43	77	27	18	23
451	25	215	190	613	317	188	156	192	235	166
452	68	356	288	480	338	177	107	159	91	79
453	50	370	320	442	336	150	70	86	85	29
454	51	189	138	329	212	95	36	55	87	1
455	28	192	164	144	181	56	28	68	27	19
456	68	191	123	106	71	5		18	18	
457	45	208	163	137	86	90	2		34	
458	33	216	183	135	149	50	14	25	77	6
459	42	191	149	130	107	15	50		18	72
460	38	241	203	94	77	40	22	5	38	42
461	26	280	254	126	101	43	54	17	43	39
462	24	254	230	125	110	61	44	2	55	61
463	34	285	251	200	166	114	83	32	29	67
464	79	190	111	199	117	67	23			26
465	47	238	191	281	236	184	122	49	44	114
466	72	212	140	308	248	85	97	33	29	56
467	71	165	94	373	218	116	66	42	54	80
468	39	158	119	339	179	140	56	45	80	75
469	58	191	133	134	29	97	24	13	58	12
470	40	261	221	118	61	94		6	25	7
471	48	276	228	60	60	19	4	1		21
472	51	204	153	55	56		26		1	
473	33	172	139	70	129	36	22		26	
474	71	195	122	4	67	15				
475	41	247	206	91	117	31	4		42	9
476	35	257	222	98	154	33	22	24	27	45
477	41	226	185	237	81	45	49	28	43	48
478	33	204	171	272	107	62	87	29	60	43
479	29	472	443	1575	377	295	192	165	171	103

Table 5-8 (continued)

	TEST TIME - HOURS									
m/e	0	0.333	0.333	1	5	10	20	30	40	48
	<includes chamber background>		<chamber background subtracted>							
480	53	516	463	1365	347	263	174	168	172	104
481	54	466	412	844	208	168	205	84	130	130
482	66	236	170	389	92	132	65	25	35	83
483	48	180	132	226	111	9		5	34	3
484	27	262	235	178	111	67	9	51	23	13
485	35	261	226	163	103		14	19	36	20
486	43	188	145	54	113		24	7		30
487	25	205	180	54	125	20	27	34	21	28
488	37	366	329	40	76	93	27	4	30	13
489	23	346	323	85	126	55	31	89	71	22
490	71	307	236	22	76		13	3		
491	64	258	194	123	161	47	30	10		22
492	46	188	142	116	184	47	23	67	3	12
493	26	163	137	178	114	46	24	60	34	53
494	42	248	206	136	58	50	38		22	53
495	25	272	247	113	43	41	43	1	28	95
496	34	287	253	84	37	50	59	7	27	40
497	29	276	247	100	94	25	33	74	25	14
498	65	306	241	1	41			32	18	
499	47	259	212	48	59		15			45
500	37	271	234	65	78	27	30	5		26

The second option is to track a species using one or more unique m/e fragments, if such ions are available. The time-dependence of the outgassing rate of the parent species should be the same as the time-dependence of these ions. This was the procedure selected for analyzing the data of Table 5-8.

A list of candidate ions for tracking each species were identified by inspecting Table 5-2. Some species, such as the 198 K alkyl silicate, had several unique ions, while other species had few or no absolutely unique ions. For the latter species, ions were selected which were not truly unique but which were considerably more abundant for that species than for the others and so could possibly be used to track that species with an accuracy acceptable for the present purposes. For this reason it is more appropriate to refer to the ions listed in Table 5-9 as 'tracking ions' rather than 'unique ions'. The ions selected for tracking each species are listed in Table 5-9.

It was more difficult to select unique ions for the lower molecular weight species because their major peaks frequently coincided with fragments from high molecular weight species. For the higher molecular weight species, many of the major fragments were coincident, such as the 73, 135, and 147 peaks for the siloxanes. However, for the high molecular weight species, it was generally possible to identify ions at high m/e values which, although not very abundant, were clearly unique. During this search for unique ions for the high molecular weight species, we concluded that during the outgassing test, it would have been very useful to have recorded mass spectrometer data for m/e values considerably higher than the arbitrary cut-off of 500 .

The tracking ions for each species were then entered into the Table 5-8 Excel database worksheet as selection criteria. Using the Excel data extraction feature the data for ion count versus time for each of the candidate unique ions were extracted from the main database and entered into a separate worksheet dedicated to that outgassed species. The ion count data for each m/e were then plotted versus time.

As an example of this procedure, Figs. 5-44(a), 5-44(b), and 5-44(c) present plots of the time dependence of the tracking ions selected for the 198 K, 210 K, and 150 K species, respectively.

Figure 5-44(a) shows the time dependence for the 198 K tracking ions. For this species there were several unique ions, and the figure shows that the level of agreement between the time-dependent data for the various ions was good. The data for the ion at m/e=177 show some scatter, but only at ion count values of the order of 100 or less, which was in the noise range for this test.

Figure 5-44(b) shows the tracking ions for the 210 K species. There were only two unique ions for this species and these ions had low abundances, so the data had significant

Table 5-9

Tracking Ions for the Various Outgassed Species

SPECIES LOCATION	IONS SELECTED FOR TRACKING (m/e)
95 K	15;16;17;44;45
145 K	49;50;51;75;89;91;92;103;117;133
150 K	18;19
158 K	38;39;40;41;42;43;44;[illegible]8-59;60;61
170 K	161;162;163;170;207;208
175 K	281;282
185 K	358
198 K	63;80;83;121;151;177;193;235;265
210 K	279;280
220 K	183;184;202;203;243;243;244
230 K	327;328;329;365;366;367;405;406;407;408;420;421;422
238 K	344;401;417;418;419;480;481;482;494;495;496
250 K	341;342;403;404;491;492;493
285 K	373;374;375;376;389;390;451;452;453;454;455
290 K	187;197;198;209;216;217;218;219;259;260;391;392;465;466;467;468

scatter.

Figure 5-44(c) shows the ion count for the m/e=18 ion, which was associated only with water. The curve fit on Fig. 5-44(c) shows that the ion count clearly decreases exponentially with time. Characteristically, diffusion-controlled outgassing decreases with a -1/2 power dependence on time in the initial stages of outgassing and then exponentially with time at later times. Figure 5-44(c) is thus consistent with the later stages of diffusion-controlled outgassing of water.

5.3.2.3 Outgassing Rate Time Dependence for Each Species

The contributions of the tracking ions for each species were summed. The summing process served to reduce random noise and generate the best available time-dependence characteristic for each species. For example, Fig. 5-44(b) shows how summing smooths out some of the noise in the limited data available for the 210 K species. The summed ion counts for the various species were then entered into another data base for final processing.

From this procedure, we found that water, the 150 K species, is the only species outgassed from R-2560 which had a time-dependent outgassing consistent with depletion of a fixed initial concentration by diffusion-controlled outgassing, i.e., a -1/2 power dependence on time in the initial stages of outgassing, followed by an exponential

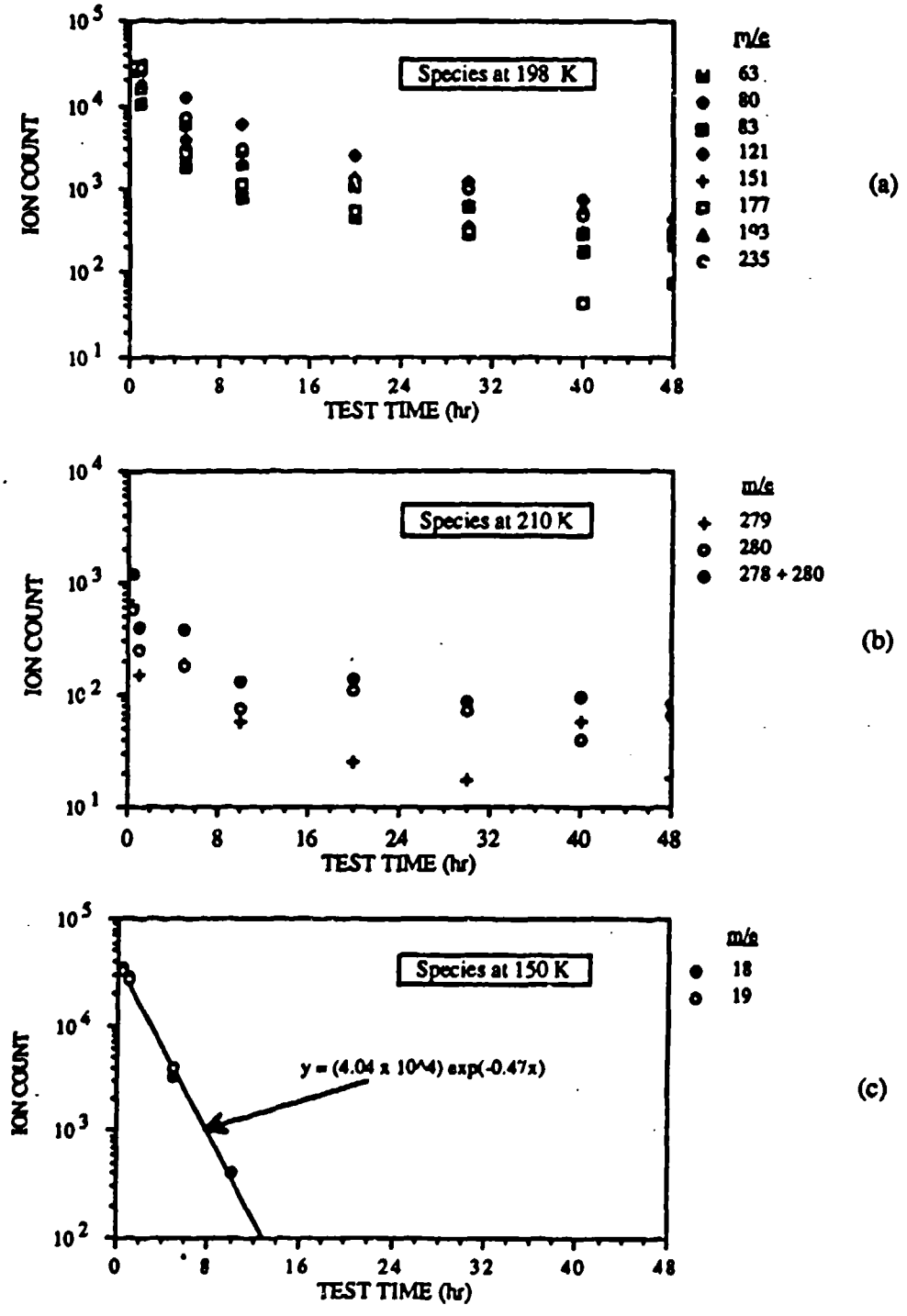


Fig. 5-44 Time Dependence of the Ion Count for the Tracking Ions for Three Species Outgassed from R-2560 at 125°C: (a) 198 K Species, (b) 210 K Species, and (c) 150 K Species.

dependence on time during the later stages. The outgassing rates of all other species tend to be more extended with time, as though additional volatile species are being actively produced during the test. The explanation may be that water occurs in the sample only as a result of its exposure to the atmosphere and outgasses by simple diffusion of this fixed initial concentration. The other outgassed species occur as a result of the chemistry of curing of the RTV and so continue to be produced as the sample cures at the elevated test temperature of 125°C. As a result, their outgassing rates at longer test times remain at higher values than would be expected from the fixed initial concentration model.

5.3.2.4 Calculation of Individual Species Outgassing Rates

If the ionization constant of the outgassing flux is constant, the outgassing rate of a particular species at a given time, t, should be directly proportional to the total ion count of its tracking ions. This relationship is expressed by Eq. (5.8).

$$OGR_j(t) = P_j \times I_j(t) \qquad (5.8)$$

$$\int^t OGR_j(t)\,dt = P_j \times \int^t I_j(t)\,dt$$

where $OGR_j(t)$ is the outgassing rate, $I_j(t)$ is the total ion count of the tracking ions, and P_j is the proportionality constant for the j^{th} species at time, t. The outgassing rate of the j^{th} species is related to the total sample mass loss by Eq. (5.9).

$$A_s \int^t OGR_j(t)\,dt = (TML \times m_{si} \times f_j) \qquad (5.9)$$

where TML is the sample total mass loss, m_{si} is the sample initial mass, A_s is the exposed surface area of the sample, and f_j is the fraction of the j^{th} species in the outgassing products. Combining Eqs. (5.8) and (5.9) gives the following expression for P_j.

$$P_j = (TML \times m_{si} \times f_j) \div (A_s \int^t I_j(t)\,dt) \qquad (5.10)$$

The ion count integral for the tracking ions is related to the area under a plot of the total tracking ion count versus time for the j^{th} species, A_j, by Eq. (5.11)

$$\int^t I_j(t)\,dt = A_j \times 3600 \qquad (5.11)$$

The factor of 3600 in Eq. (5.11) accounts for the abscissa of the time-dependent ion count plots being presented in hours rather than seconds. A_j can be calculated from the ion count plots using the following modified Trapezoidal Rule expression:

$$\begin{aligned} A_j = {} & I_j(0.333) \times (0.5 - 0.25) \\ & + I_j(1) \times (1.5 - 0.5) \\ & + (I_j(1) - ((I_j(1) - I(5)) \times 2.25/4)) \times (5 - 1.5) \\ & + ((I_j(5) + I_j(10))/2) \times (10 - 5) \\ & + ((I_j(10) + I_j(20))/2) \times (20 - 10) \\ & + ((I_j(20) + I_j(30))/2) \times (30 - 20) \\ & + ((I_j(30) + I_j(40))/2) \times (40 - 30) \\ & + ((I_j(40) + I_j(48))/2) \times (48 - 40) \end{aligned} \qquad (5.12)$$

The mass of the R-2560 sample tested at 125°C was 2.40841 g, and the TML measured in situ was 1.255 percent. The exposed sample area was 1.43 cm^2. Combining the above equations and data gives the following expression for the proportionality constant.

$$\begin{aligned} P_j &= ((0.01255 \times 2.40841 \times f_j)/1.43) \div (A_j \times 3600) \\ &= 5.8713 \times 10^{-6} \times f_j / A_j \end{aligned} \qquad (5.13)$$

The fractions f_j of each species in the total mass outgassed as calculated from mass spectrometer data are given at the bottom of Table 5-2. The proportionality constants P_j have been calculated for each species using Eqs. (5.12) and (5.13) and the Table 5-2 data for f_j. The outgassing rates of each species at each point in time have then been calculated from the ion count data using Eq. (5.8) and have been presented in Table 5-10.

The data of Table 5-10 have been plotted in Fig. 5-45. The more volatile species show a much greater decrease in outgassing rate with time than the less volatile species. Also, inspection of Table 5-10 and Fig. 5-45 shows that the outgassing rate of the more volatile species is highest right at the beginning of the test, at 0.333 hour. On the other hand, the outgassing rate of several of the less volatile species rises from 0.333 hour to 1 hour. This lends support to the proposition that the sample continues to cure as it is heated to 125°C, and perhaps all through the test period.

Figure 5-46 compares the total outgassing rate, extracted from Fig. 5-1(b), with the total outgassing rate calculated by adding all of the individual rates in Table 5-10. When it is remembered that mass spectrometry is not a quantitatively precise technique and that the mass spectrometry-derived outgassing curve is based on manual analysis of the data, the agreement between the two curves is generally good. The two peak structure in the

Table 5-10

Outgassing Rates of the Individual Species

Species Evaporation Temperature	Exposure Time (hr)							
	0.333	1	5	10	20	30	40	48
95 K	1.0×10^{-7}	7.7×10^{-8}	3.1×10^{-8}	1.0×10^{-8}	4.1×10^{-9}	1.8×10^{-9}	1.6×10^{-9}	2.5×10^{-9}
145 K	4.5×10^{-8}	2.2×10^{-8}	6.1×10^{-9}	4.6×10^{-9}	2.7×10^{-9}	1.7×10^{-9}	1.7×10^{-9}	1.7×10^{-9}
150 K	5.7×10^{-8}	4.6×10^{-8}	5.3×10^{-9}	6.6×10^{-10}	0	0	0	0
158 K	1.6×10^{-7}	1.4×10^{-7}	9.5×10^{-8}	4.9×10^{-8}	1.3×10^{-8}	5.9×10^{-9}	5.8×10^{-9}	6.4×10^{-9}
170 K	3.6×10^{-8}	1.3×10^{-8}	2.8×10^{-9}	1.9×10^{-9}	1.4×10^{-9}	8.1×10^{-10}	1.4×10^{-9}	1.3×10^{-9}
175 K	9.8×10^{-10}	7.6×10^{-10}	3.5×10^{-10}	3.0×10^{-10}	1.9×10^{-10}	1.3×10^{-10}	2.5×10^{-10}	1.6×10^{-10}
185 K	1.5×10^{-9}	1.6×10^{-9}	9.3×10^{-10}	7.2×10^{-10}	4.1×10^{-10}	3.5×10^{-10}	6.4×10^{-10}	8.1×10^{-10}
198 K	4.0×10^{-7}	3.0×10^{-7}	7.1×10^{-8}	3.3×10^{-8}	1.6×10^{-8}	8.3×10^{-9}	4.8×10^{-9}	4.0×10^{-9}
210 K	1.9×10^{-8}	1.1×10^{-8}	3.2×10^{-9}	2.1×10^{-9}	2.1×10^{-9}	1.4×10^{-9}	1.5×10^{-9}	1.3×10^{-9}
220 K	2.0×10^{-8}	1.2×10^{-8}	7.8×10^{-9}	6.8×10^{-9}	3.2×10^{-9}	3.0×10^{-9}	2.3×10^{-9}	2.2×10^{-9}
230 K	8.1×10^{-9}	1.2×10^{-8}	5.1×10^{-9}	3.2×10^{-9}	2.5×10^{-9}	1.9×10^{-9}	2.3×10^{-9}	1.9×10^{-9}
238 K	2.6×10^{-8}	4.2×10^{-8}	1.6×10^{-8}	1.2×10^{-8}	1.1×10^{-8}	9.1×10^{-9}	7.7×10^{-9}	8.3×10^{-9}
250 K	5.6×10^{-9}	9.4×10^{-9}	4.4×10^{-9}	3.1×10^{-9}	2.5×10^{-9}	1.2×10^{-9}	1.2×10^{-9}	2.0×10^{-9}
285 K	4.1×10^{-9}	1.0×10^{-8}	5.8×10^{-9}	3.3×10^{-9}	2.9×10^{-9}	1.8×10^{-9}	1.7×10^{-9}	1.9×10^{-9}
290 K	4.8×10^{-9}	2.4×10^{-9}	1.1×10^{-9}	8.8×10^{-9}	6.6×10^{-9}	4.9×10^{-9}	4.1×10^{-9}	5.6×10^{-9}
Totals	8.9×10^{-7}	7.2×10^{-7}	2.7×10^{-7}	1.4×10^{-7}	6.8×10^{-8}	4.2×10^{-8}	3.7×10^{-8}	4.0×10^{-8}

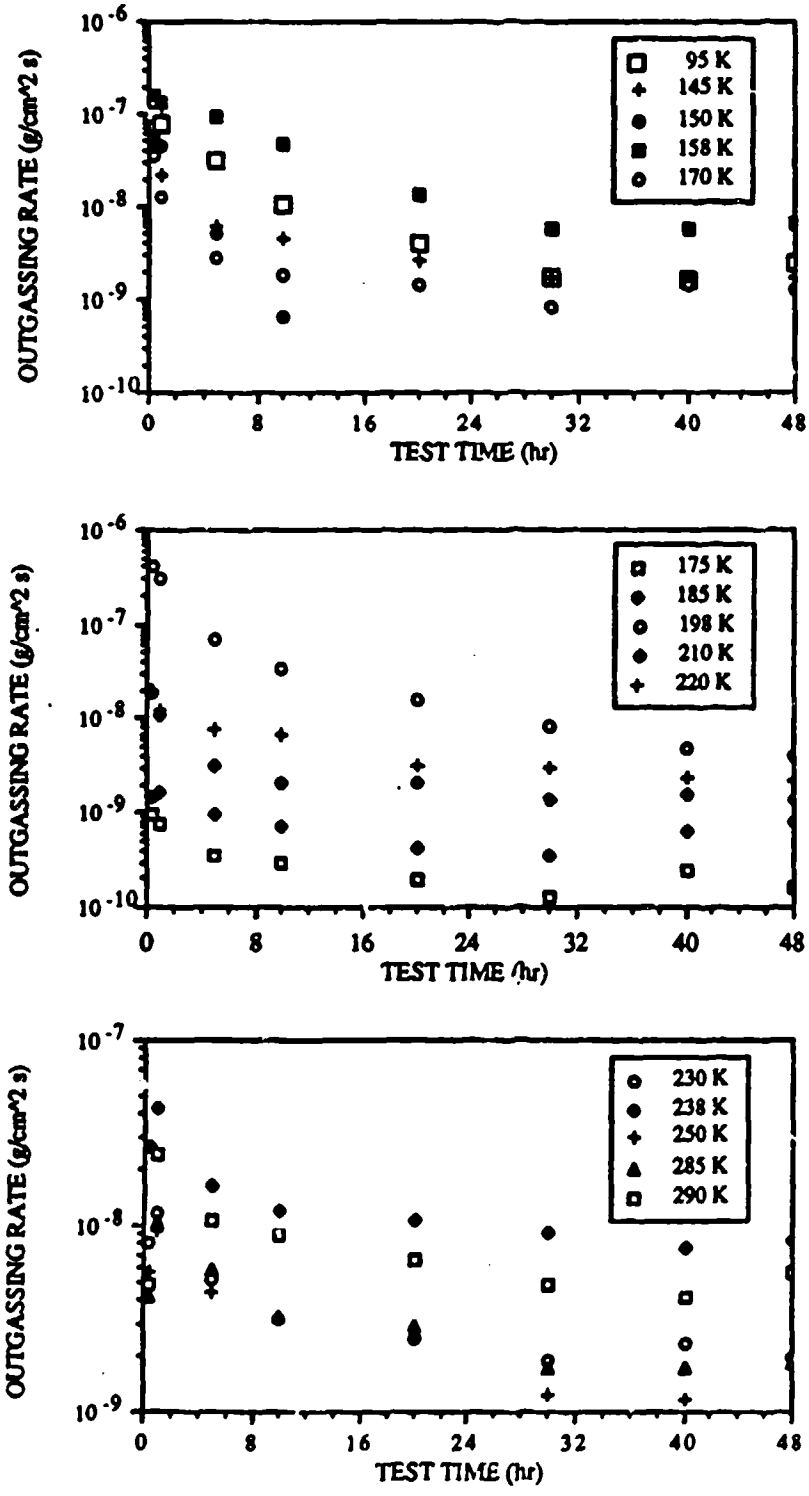


Fig. 5-45 Outgassing Rates of the Individual Species from R-2560 at 125°C.

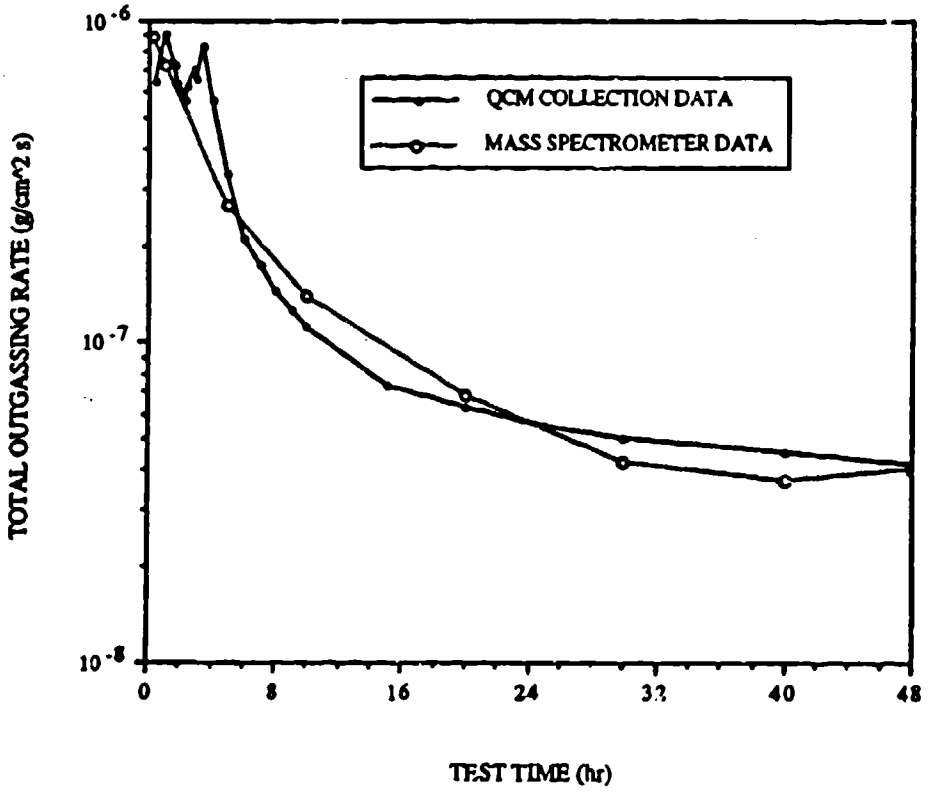


Fig. 5-46 Comparison of the Total Outgassing Rate Measured by QCM Collection and Calculated from Mass Spectrometer Ion Count Data for R-2560 at 125°C.

0.5-hour time period does not appear in the mass spectrometer-derived curve because of the specific test times selected for analyzing the isothermal test mass spectrometer data. At later times, the mass spectrometer data indicate a slightly higher outgassing rate in the 5- to 20-hour period, and a slightly lower outgassing rate in the 20- to 48-hour time period than the QCM collection data. The calculation of total outgassing rate from the ion count data was made on the assumption that the ionization constant does not change throughout the test. In fact, the changing relationship between the two outgassing curves with time could be credibly explained by a decrease in the ionization constant with time as the species-mix in the outgassing flux changes with time.

We reached a similar conclusion by comparing the AIC and total outgassing rate data in Section 5.3.1.3 and Fig. 5-43.

Section 6

MATERIAL DATABASE MEASUREMENT PROGRAM

This section presents the results of the measurement program in which the test method was exercised and demonstrated by using it to create a material database. Section 6.1 describes the material test program. Section 6.2 reviews the types of data included in the database. The main body of the database is presented in the Appendix.

6.1 MATERIAL TEST PROGRAM

6.1.1 Test Matrix

Table 6-1 lists the 20 sample materials tested. The materials were selected by the Air Force Materials Laboratory. The list includes five principal groups of materials - adhesives, films and sheet materials, oils and greases, paints and thermal control coatings, and carbon-reinforced composites.

The original nominal goal of the test program was to test 25 materials. Because of the developmental nature of the test method, some evolutionary changes were made to the apparatus, test procedure, data acquisition, and data output during the early part of the test program. Because of these changes, we decided to retest a number of materials. Also, a number of tests had to be repeated because of unexpected events such as storm-caused power failures. As a result, although 26 material tests and an additional 7 empty effusion cell checkout tests were performed during the program, the database contains only 20 materials.

6.1.2 Material Sample Sources

The adhesives and films and sheet materials were all standard aerospace materials and were obtained from controlled Lockheed stock. In the absence of an industry-wide standard specification system to establish compliance and traceability, the material sample specification includes the Lockheed EPS (Engineering Purchase Specification) number. In the Lockheed system, materials are identified by the LMSC Raw Material Convenience Number, which approves a material and identifies it by a seven-digit Engineering Purchase Specification (EPS) number which describes its peculiar characteristics (type, class, dimension, etc.). Compliance of the material is verified, before acceptance, by the Lockheed Material and Process Control Laboratory Standard test material samples were purchased according to the EPS number. Where applicable, standard material samples are prepared and applied according to a Lockheed specification.

The Brayco oil and the Braycote grease were donated by Burmah-Castrol Inc. The

Table 6-1
Sample Material Data

MATERIAL FAMILY	COMMON NAME	DESCRIPTION	MANUFACTURER OR OTHER SOURCE
Adhesives	R-2560	Elastomer, silicone, room temperature vulcanizing	McGhan-NuSil Corporation
	RTV 566	Compound, silicone, controlled volatility, low temperature	General Electric Corporation
	DC 93-500	Silicone, two component, room temperature vulcanizing, controlled volatility	Dow Corning Corporation
	DC 6-1104	Sealant, controlled volatility, silicone	Dow Corning Corporation
Films	Kapton	Polyimide plastic film, 0.001 in thick x 18 in wide	E. I. Dupont de Nemours
	Mylar	Polyethylene terephthalate film, 0.005 in thick x 48 in wide	E. I. Dupont de Nemours
	FEP Teflon	Fluorinated ethylene propylene plastic film, 0.001 in thick x 48 in wide	E. I. Dupont de Nemours
Oils and Greases	Braycо 815Z	Oil, perfluorinated, polyether, low volatility	Bray Oil Company
	Braycote 600	Grease, perfluorinated, polyether, low volatility	Bray Oil Company
	Krytox 143AD	Lubricant, oil, perfluoroalkylpolyether	E. I. Dupont de Nemours
	Vakote MLD73-91	Oil, hydrocarbon	USAF/AFWAL/MLBT
Paints and Thermal Control Coatings	S/13G/LO-V10	Paint, thermal control, low outgassing, white, SWS V-10 silicone binder, ZnO pigment	IIT Research Institute/ Univ. of Dayton Res. Inst.
	Chemglaze Z306	Coating, polyurethane, one component, flat black	Lord Corporation
	DC Q9-6313	Thermal control coating, polysiloxane resin, silver flake	Dow Corning/Lockheed, developed under USAF/AFWAL/MLBT contract
	Aremco 569	Thermal control coating, inorganic, Al_2O_3 pigment, K_2SiO_3 binder	Aremco Corporation
	LMSC 1170	Thermal control coating, transparent silicate, Al_2O_3 pigment, K_2SiO_3 binder	Lockheed Corporation
Carbon-Reinforced Composites	AS4/PEEK	AS4 carbon fiber, Victrex polyetheretherketone thermoplastic matrix	Imperial Chemical Industries Ltd
	AS4/PPS	AS4 carbon fiber, polyphenylene disulphide thermoplastic matrix	Phillips Petroleum Company
	AS4/3501-6	AS4 carbon fiber, DEGBA resin (MY 720) thermoset epoxy matrix	Source A: Hercules/Ciba Geigy Source B: USAF/AFWAL/MLBT

VacKote and the Krytox oil samples were supplied by AFWAL Materials Division and E.I. Dupont de Nemours Co., respectively. All of the oils and greases were supplied in sealed plastic or glass containers.

The S/13G/LO-V10 paint samples were prepared and shipped to Lockheed by the University of Dayton Research Institute. The LMSC 1170 thermal control coating was a developmental material prepared and supplied by the LMSC Materials and Processes Engineering organization. The remaining paints and thermal control coatings were obtained from controlled Lockheed stock, and test samples were prepared according to standard Lockheed specifications.

The AS4/PEEK, AS4/PPS and AS4/3501-6 (Source A) carbon-reinforced composite materials were prepared and supplied by Martin-Marietta of Oak Ridge, TN. The AS4/3501-6 (Source B) material was nominally the same as the composite supplied by Martin Marietta but was prepared and supplied by AFWAL/MLBT.

All standard materials were prepared and handled according to standard Lockheed procedures, which should be typical of the industry. For nonstandard, and/or developmental materials, the need to maintain sample cleanliness, the nature of the intended testing, and the necessity that the samples be representative of the bulk parent material were stressed to the suppliers.

6.1.3 Test Sample Preparation

The test sample geometry for each material was selected according to the guidelines of Section 4.1.

The four adhesives tested were poured or injected before curing into cylindrical open-ended stainless steel tubes approximately 1.00 inch long by 0.375 inch diameter. This geometry constrained diffusion within the sample to be one-dimensional flow along the the axis of the tube.

The five thermal control coatings and paints were applied to aluminum disks 1.00 inch diameter by 0.25 inch thick.

Film and sheet materials were tested in as-supplied form. Test samples of the 1 mil FEP Teflon and the 5-mil Mylar films were cut from 48-inch-wide rolls of sheet material. Test samples of the 1-mil Kapton were cut from 18-inch-wide rolls of sheet material.

The greases and oils were placed in small aluminum foil or stainless steel dish holders in the effusion cell. The holders maintained constant surface area for evaporation and permitted the samples to be weighed. The aluminum foil holders weighed approximately 1.5 g while the stainless steel holders weighed approximately 9.0 g.

Composite materials were tested in as-supplied form, without the use of special holders. The composite materials were typically supplied as 1.00-inch-square samples

about 0.050 inch thick.

6.1.4 Test Parameters

Table 6-2 lists the test parameters. The sample temperatures were selected according to the guidelines of Section 4. All materials were tested at 125°C and 75°C. Six materials were also tested at 25°C, while a seventh was tested at 100°C. The remaining materials were not tested at a third temperature in the interests of making the best use of available funds.

6.1.5 Data Acquisition

Table 6-2 lists the data measured for each combination of material and temperature.

6.1.6 Data Reduction and Presentation

Table 6-2 lists data that have been reduced to date. All of the QCM collection data have been reduced to obtain total outgassing rates and deposition data and are presented in the database. GC/MS data for the materials are also presented in the database. No mass spectrometer data are included. Because of the acknowledged level of difficulty involved in analyzing the mass spectrometer data, the statement of work for the Phase II Extension did not require it to be reduced and presented. This level of difficulty is well demonstrated for the example of R-2560 at 125°C given in Section 5. Also, because of funding limitations, the deposition data for the 150 K, 220 K, and 298 K QCMs were not reduced to the same level of detail described in Section 5 for the example of R-2560 at 125°C.

The contents of the database is described in more detail in Section 6.2.

6.2 DATABASE CONTENTS

Section 6.2.1 lists the data presented in the database. Section 6.2.2 gives comments on particular items of data.

6.2.1 Data Categories

The database contains, for each combination of material type and test temperature, the following categories of data:

- Test Information Summary Sheet
- Isothermal Outgassing Test:
  - Total mass loss (TML) as a function of time.
  - Total outgassing rate per unit exposed surface area as a function of time.
  - Volatile Condensable Material (VCM) deposited on the 150 K, 220 K, and 298 K QCMs as functions of time.
- C_A Test:
  - Fraction of total outgassing products remaining on the 90 K collector QCM as a function of QCM temperature during QTA.

Table 6-2

Test and Data Reduction Matrix

SAMPLE MATERIAL	TEST TEMP (°C)	MEASUREMENTS PERFORMED: ISOTHERMAL TEST - QCM FREQUENCY - 90 K	50 K	220 K	298 K	MASS SPEC ION COUNT	QCM THERMAL ANALYSIS - QCM FREQUENCY - 90K	150K	220K	298K	MASS SPEC ION COUNT	QCMS TEST 25°C	200°C	DATA REDUCTION COMPLETED: TML	O/G RATE	VCM AT 150K, 220K, AND 298K	Q1/GA	QTA/MS	DG RATES FOR EACH SPECIES	QCMS
R-2566	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
RTV 566	125	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x		x			x	x	x	x			
DC 93-500	125	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x				x			x	x	x	x			
DC 6-1104	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x								x	x	x				
Kapton	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x		x			x	x	x	x			
Mylar	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
FEP Teflon	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
Braycote 815Z	125	x	x	x	x		x	x	x	x				x	x	x	x			
	75	x	x	x	x		x	x	x	x				x	x	x	x			
	100	x	x	x	x		x	x	x	x				x	x	x	x			
Braycote 600	125	x	x	x	x		x	x	x	x				x	x	x	x			
	75	x	x	x	x		x	x	x	x				x	x	x	x			
	25	x	x	x	x		x	x	x					x	x	x	x			
Krytox 143AD	125	x	x	x	x		x	x	x	x				x	x	x	x			
	75	x	x	x	x		x	x	x	x		x	x	x	x	x	x			x
	25	x	x	x	x		x	x	x					x	x	x	x			
Vacuum ML-D73-91	125	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
	75	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	25	x	x	x	x	x	x	x	x		x			x	x	x	x			
S13G/LO-V10	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
Chromglass 2506	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			
DC Q9-6313	125	x	x	x	x	x	x	x	x		x			x	x	x	x			
	75	x	x	x	x	x	x	x	x		x			x	x	x	x			
	25	x	x	x	x	x	x	x	x		x			x	x	x	x			
Aremco 569	125	x	x	x	x	x	x				x			x	x	x	x			
	75	x	x	x	x	x	x				x			x	x	x	x			
	25	x	x	x	x	x	x				x			x	x	x	x			
LMSC 1170	125	x	x	x	x	x	x				x			x	x	x	x			
	75	x	x	x	x	x	x				x			x	x	x	x			
	25	x	x	x	x	x								x	x	x	x			
AS4/PEEK	125	x	x	x	x	x	x				x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x				x			x	x	x	x			
AS4/PPS	125	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x		x			x	x	x	x			
AS4/3501-6 Source A: Morton Materials	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x				x			x	x	x	x			
AS4/3501-6 Source B: USAF/AFWAL	125	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x
	75	x	x	x	x	x	x	x	x	x	x			x	x	x	x			

- Rate of evaporation from the 90 K collector QCM as a function of QCM temperature during QTA.

- GC/MS Test:
  - Identification of the species evolved in the 125°C and 200°C GC/MS tests.
  - Fraction of material remaining in the GC/MS column versus scan time for the 125°C and 200°C GC/MS tests.

6.2.2 Comments on Data Categories

6.2.2.1 Test Information Summary Sheet

The data for each material are preceded by a data sheet which summarizes the test conditions and sample specifications. The computer file numbers in which the raw data are recorded are given. The sample surface area, the initial sample weight, test duration, and the ex situ total mass loss calculated from the pre- and post-test laboratory balance weighings are included in this section.

Comments on the conduct of the test are included where appropriate. Comments include the sample description, source, geometry and any test variations from the standard procedure. If the comment is lengthy or applies to several material tests, there is a reference to a numbered note in Section A.1.4.

6.2.2.2 Isothermal Outgassing Test Data

The TML and VCM data presented include all recorded data points, with no omissions or smoothing. Some of the data show periodic frequency shifts which are functions of the apparatus data acquisition and/or temperature control system. This is particularly apparent for tests in which the amount accumulated was very small. It is appropriate for the user to smooth these data graphically, since these periodic variations do not reflect real changes in either outgassing or deposition kinetics.

Because outgassing rates are calculated by direct differencing of the QCM frequency data, the effect of random and systematic fluctuations in frequency are amplified. As discussed in Section 5.1, this source of scatter can be reduced by averaging over longer data intervals. The outgassing rate data presented in the database have all been smoothed by differentiating the frequency data over time intervals appropriate for reducing the noise and defining the character of the curve. These time intervals and the repetition of the smoothing technique varied between materials. In general, as the test method matured and apparatus modifications were made to reduce the apparatus induced noise, the quality of the outgassing rate curves also improved. Thus, less smoothing or averaging was required to firmly define the curves. This was also the case for the high outgassing materials which had large deposition rates on the QCMs and, therefore, large signal to noise ratios.

As discussed in Section 5.2, the VCM data can be further reduced to obtain

deposition and evaporation rate data. This additional data reduction has not been performed for the main body of data because of insufficient funding. However, the user should be able to perform an analysis similar to that of Section 5.1 using the VCM data provided.

No isothermal outgassing test mass spectrometer data have been included because the magnitude of the necessary data analysis and presentation task was outside the funding capacity of this contract.

6.2.2.3 QTA Test Data

Only the QTGA data for the 90 K QCM have been included, because, as shown in Section 5.2, the QTGA plots for the 150 K, 220 K, and 298 K QCMs do not contain any additional useful data.

The linear-linear plot of evaporation rate versus QCM temperature is included since it clearly defines the evaporation rate regimes of the different species. The evaporation rate data have been calculated by differentiating the frequency data over time intervals appropriate for resolving the different evaporating species. See Section 5.2 for an analysis of the effect of interval size on smoothness and definition.

No QTA/MS data have been included in the database because the magnitude of the task of analyzing and presenting them as described in Section 5.2 would be outside the funding capacity of this contract. However, the data will be retained on computer disk and tape files by Lockheed for future retrieval and dissemination.

6.2.2.4 GC/MS Test Data

The GC/MS data include a species summary of the normal data output from this type of test. The mass fragmentation patterns of the various evolved species are not supplied due to space limitations. The GC/MS mass fragmentation pattern data would be required if an analysis of the QTA/MS data in the manner described in Section 5.2 were to be made. Since the QTA/MS are not included in the the current database there is no reason to include the GC/MS data on this account. The GC/MS data would also be useful if the user wished to verify the chemical identification of the evolved species made by the Lockheed Analytical Chemistry Group. It was believed that the number of users who would wish to make this verification on a routine basis would be too small to justify the manpower and space required for inclusion of this immense amount of data. These data, however, will be retained on file by Lockheed, to be consulted upon request.

Section 7

CONCLUSIONS AND RECOMMENDATIONS

Section 7.1 presents the conclusions that were reached about the performance and utility of the test method. Section 7.2 presents recommendations for improving the test method, implementing the data, and extending its scope.

7.1 CONCLUSIONS

The test method has been demonstrated to be capable of measuring detailed data on the kinetics of outgassing and deposition with a high degree of accuracy and repeatability. The apparatus is sufficiently robust for the method to be used for routine testing with minimum down time.

The capability for measuring the outgassing and deposition rates of each individual outgassed species was established as an objective at the beginning of the program. It was recognized at the time that this was a very ambitious objective that could not be reached without developing what amounted to a new analytical chemistry tool. The new tool was an in situ chromatography technique referred to as QTA/MS, which combines QCM thermal analysis with mass spectrometry. QTA/MS has not yet been developed to the point at which it can be used to support the ambitious fully-computerized data reduction procedures for determining individual species outgassing rates originally proposed as a program objective. However, Section 5 presents a manual method for determining the individual species outgassing rates which demonstrates that this objective has been reached in principle. The manual data reduction technique is very labor intensive, and funds were insufficient to analyze all of the experimental data obtained in the database measurement program in this manner. It is believed that the ultimate objective of a fully computerized method to determine individual species behavior is reachable if we make the minor apparatus modifications discussed below.

The major overall issue to emerge from the program is that of cost effectiveness and utility. The motivation for conducting the program was to generate the detailed kinetic data needed to support system modeling. The contamination modeling community traditionally likes to obtain as much kinetic data as possible to support their models in order to maximize realism. However, kinetics data are much more costly to obtain per material than the ASTM E 595 type screening test data, and cost effectiveness considerations will place a limit to the amount of data detail that can be profitably used to support system design analyses. It is believed that the new test method can currently provide a more detailed level

of material outgassing/deposition kinetics characterization than is necessary for most program applications. Some input is now needed from the user community to help identify the most cost effective format for the test method and database.

The following sections discuss specific aspects of the test method apparatus and procedure.

7.1.1 Basic Test Approach

The QCM collection technique has proven to be a very convenient and accurate method for measuring total mass loss and total outgassing rate. The major potential systematic weakness of the collection method is its inability to detect species which do not condense at the collector temperature. However, the percentage of these species in the outgassing products of polymers is usually negligibly small, and the inclusion of a mass spectrometer in the apparatus reduces the possibility that these species will not be detected.

Measurement of deposition rates using a QCM to simulate a surface is a very accurate procedure and has been used to perform basic research on surface deposition kinetics. Deposition kinetics will, in general, be surface dependent, so strictly speaking, the data presented here apply only to the surface of the particular QCM crystal used. However, it is impractical to perform deposition tests for more than one type of QCM surface because of the cost. Also, most contamination deposition models currently used by industry do not account for differences in the deposition characteristics of different types of surface.

Mass spectrometry is the most practical way to identify gaseous species in vacuum in real time. The mass spectrometer was integrated into the test method with minimal impact, and proved to be very reliable and easy to use.

The QTA/MS technique, which combines mass spectrometry with the QTA test to separate the different outgassed species and determine their mass fragmentation patterns, is a new form of gas chromatography. Development of a new chromatography technique normally requires considerable dedicated research and development effort. The present program attempted to create, develop, and routinely implement the QTA/MS technique as a subtask of the overall test method development and database measurement program. Not surprisingly, evaluation of the QTA/MS technique took a large portion of the program effort, and the description of this evaluation in Section 5.2.2 created the largest single section of this report. It is shown in Section 5.2.2 that the QTA/MS technique has been demonstrated to a point at which its separation capability is adequate for supporting a manual determination of the mass fragmentation patterns and chemical identity of the outgassed species. It is believed that QTA/MS can be developed into a routine test with fully computerized data reduction if the minor hardware changes listed in Section 7.1.2 are made, and if the appropriate algorithms and data interfaces referred to in Section 7.1.5 are

established.

The test plan called for determination of the outgassing rates of each individual outgassed species by computerized deconvolution of the mass fragmentation patterns measured at each point in time in the isothermal outgassing test using mass fragmentation pattern data for the individual species obtained from the QTA/MS test. Although this was feasible in principle, it required many factors such as mass spectrometer gain, ionization constants, individual species fragmentation patterns, etc., to remain constant over the duration of a test in order for meaningful quantitative results to be obtained. Also, it required the mass spectrometer to have a high dynamic range in order to track the less abundant species. These quantitative performance requirements could not be met by the current mass spectrometer system, which is best used in a mainly qualitative mode. Hence, even if QTA/MS had been able to provide clean fragmentation pattern data, quantitative performance limitations on mass spectrometry would have prevented the goal of determining individual species outgassing rates using fully computerized data reduction from being reached. However, the current limitations are not basic to mass spectrometry, and conversations with the mass spectrometer hardware and software suppliers indicate that many improvements can be made using existing technology to improve the quantitative performance of the system. This is discussed further in Section 7.1.2.

It has proven to be a good idea to include GC/MS tests in the test method. Although the species evolved and detected in GC/MS are not exactly the same as those evolved in the vacuum outgassing test because of the different pressures, temperatures, and test durations, they are sufficiently similar for the GC/MS species identification and relative proportion data to be a very useful addition to the test. GC/MS will thus be retained in the test method for the foreseeable future.

7.1.2 Test Apparatus

The basic design of the apparatus was very satisfactory. The apparatus was easy to use and was able to function automatically for long periods with a high degree of reliability. Three years operational experience with the apparatus has shown that the main test failure modes are external mechanisms such as building electrical power or cooling water failure. The apparatus measurement accuracy was satisfactorily demonstrated in Phase II. The few modifications that seem desirable in the light of experience are discussed in the following paragraphs, and are evolutionary rather than fundamental.

The temperature controllers originally selected and used for the program employ on-off control of the 110 ac line voltage to modulate power to the QCMs and the sample holder. These controllers were selected because of their lower price and because they had been used successfully before at Lockheed. However, in the previous application the

QCMs had been mounted in holders with substantial thermal mass which reduced the heat flow transients experienced by the QCM crystals during power cycling. In the present apparatus, the QCMs are heated directly so the crystals experience a larger heat flux transient and show significant power modulation induced noise. This noise source can be eliminated by using more expensive dc voltage modulation to control power. This modification is already in progress.

The heat leak into the liquid nitrogen reservoirs, and hence the liquid nitrogen consumption rate, could be reduced considerably by better use of multilayer insulation and shields, and by using structural supports and service wires and tubing with smaller cross sections, longer lengths, and different materials. Reducing the liquid nitrogen consumption rate would lower the cost per test, and would also reduce the fill frequency and hence the impact of fill transient noise in the data. It would also reduce the probability of test failure owing to problems with the liquid nitrogen supply control system and tanks.

The apparatus could, in principle, be kept cold using a mechanical refrigerator, and a cost analysis might show that this approach would be less expensive. However, a mechanical refrigerator would be less reliable and could introduce additional noise to the data. Use of a mechanical refrigeration system is, therefore, not recommended.

Because the entire QCM housing had to be heated in order to heat the sensing crystal, an excessive amount of power was required to raise a QCM to 400 K. The excessive power increased liquid nitrogen consumption and caused unnecessary thermal transients in other components. It should be possible to eliminate this problem entirely by using a newer design QCM such as the QCM Research Mark 16 in which only the measuring crystal is heated. This modification is in progress.

The major problem encountered in the QTA/MS test was that the mass spectrometer detected species evaporating from the QCM holder as well as the measuring crystal. This problem could be eliminated by using a QCM design in which the crystal can be heated independently of the housing, such as the QCM Research Mark 16. As noted in the previous paragraph, this modification is already in progress.

The mass spectrometer used represented more or less the state of the art in small computer controlled systems and was equipped with more software options for data manipulation than could usefully be exploited by the test method. However, the usable dynamic range of the mass spectrometer was limited by comparison with the QCMs. The dynamic range of the mass spectrometer at a constant electrometer range and multiplier gain setting is about four orders of magnitude. The dynamic range of the QCMs is about five or six orders of magnitude. There was a difference of about four orders of magnitude between the outgassing rates measured for high outgassing materials at the beginning of a

test and the rates measured for low outgassing materials at the end of a test, so the range capabilities of the mass spectrometer were clearly stressed. The dynamic range of the mass spectrometer was further stressed by the need to monitor minor ion peaks in the fragmentation patterns of species whose abundance was less than ten percent. The high or low detection limit can be adjusted in the present system prior to a test, but it cannot be adjusted in the middle of a test without a major impact on the data collection format. Conversations with the mass spectrometer system hardware and software suppliers indicate that they are currently modifying the system to permit sensitivity changes to be made during a test, which would eliminate the system range problem. In fact, if the system is modified to allow automatic selection of the electrometer sensitivity during a test, the usable dynamic range of the mass spectrometer could be extended to about eight orders of magnitude.

7.1.3 Test Procedure

The basic test procedure worked very well, gave no problems, and no changes are recommended.

7.1.4 Data Acquisition

With the increasing availability of relatively low cost computerized data acquisition systems, it is possible to accumulate large amounts of high quality experimental data with little effort. This program took advantage of this technology, using two computers to control the test apparatus and acquire and store a very large amount of QCM and mass spectrometer data. The computer systems performed their control and data acquisition functions very well, due almost entirely to the availability of versatile software for both the QCM and mass spectrometer systems. The QCM system software was developed in house by Lockheed prior to this program, while the mass spectrometer system software was purchased commercially. It is frequently the case that solving a problem in one area creates a new problem in another area. In this case, the ability to acquire large amounts of data placed great demands on the data reduction, analysis, and presentation tasks. This problem is discussed in the following section.

7.1.5 Data Reduction, Analysis, and Presentation

The major overall conclusion regarding data reduction concerns the size of the problem, not the technical difficulty. The test method produced a very large amount of useful experimental QCM and mass spectrometer data and is capable of generating even more data per nominal test if so desired (such as cross peak data in the range 5 to 1024 ranges). The biggest obstacle to exploiting the full measurement capability of the test method is the lack of algorithms for performing the tedious manual data reduction procedures described in Section 5. The effort required to develop procedures for data reduction algorithms, or adapting existing commercially available mass spectrometer data conversion

algorithms for this test method was well outside the funding capacity of this program. Because of the size of this problem, it has not been possible to include any of the measured mass spectrometer data in this report, other than the R-2540 example given in Section 5.2.

The basic mass measurement was accumulation or evaporation of mass on or from a QCM surface. Reduction of these data to obtain sample total mass loss, total outgassing rate, and volatile condensable material involved simple unambiguous arithmetic, with the only complication being that there was more random and thermally-induced noise in the QCM frequency data than had been expected. The effect of this noise in the present data has been successfully reduced by several simple software modifications. Additional sophisticated data filtering and smoothing software can be developed or acquired if needed. Hardware modifications to eliminate noise at its source are discussed in Section 7.1.2. It should therefore be possible to remove most of the noise from the data in the future with no difficulty.

In the current apparatus configuration data acquisition and data reduction are performed using two separate algorithms, so data could not be reduced at the same time that a test was being conducted. To perform data reduction, the test program had to be interrupted or another compatible computer had to be located. The solution to this problem is to combine the two codes to permit real time viewing and printout of processed QCM data. It is also desirable to eventually merge the QCM and mass spectrometer data acquisition and reduction algorithms and use a single computer system for the entire apparatus.

The form of deposition data that the industry is most familiar with is Volatile Condensable Material (VCM) so the deposition data in the database are presented in this format. However, VCM data are a function of the apparatus dimensions as well as the outgassing material and the surface of deposition. Section 5.1 shows that it is technically simple to process the VCM data so as to remove this apparatus dependence. However, there was insufficient funding to make the necessary modifications to the data reduction software and to process all of the test data in this manner.

Computerized reduction of the QTA/MS data first requires successful development of the QTA/MS test so that the spurious peak is eliminated and the test adequately performs its chromatographic species separation function. Also, the dynamic range of the mass spectrometer must be extended so that the saturation problems encountered in the present tests are eliminated. Assuming that these problems can be eliminated, the algorithm to analyse the QTA/MS data and extract the mass fragmentation pattern for each species exists in the present system. This algorithm needs to be modified so as to output the data in a format suitable for entry into a deconvolution algorithm for removing the fragments of each

species in the total isothermal outgassing flux, and to the NBS fragmentation pattern library for species identification.

There is no incentive to use the GC/MS data in a quantitative manner because the mix of species evolved in the GC/MS test is not the same as that evolved in the vacuum outgassing test. Hence the GC/MS test presented no problem in data reduction, analysis, or presentation because the standard data provided by the GC/MS system were quite adequate. Indeed, if the test procedure and software described in the previous paragraph were successfully developed, there would be no need to include GC/MS in the test method since species identification would be performed using QTA/MS data and the built-in NBS library. Since development of this technology is not likely to occur in the near future it is planned to keep GC/MS in the test method, because it provides useful supporting information at minimal cost.

7.2 RECOMMENDATIONS

The following recommendations for future work address refinement and extension of the test method capability, extension of the database, and implementation of the data at the program level.

7.2.1 Test Method Refinement

7.2.1.1 Hardware Modifications

The 90 K QCM should be replaced by a QCM whose design permits the crystal to be heated without heating the housing. The other three QCMs should also be replaced if funding is available, but this modification is not as critical.

The current temperature controllers should be replaced by voltage modulated dc supplies.

The thermal design of the apparatus should be refined so as to minimize heat transfer from the ambient surroundings to the colder components. Reduction of heat leaks will reduce liquid nitrogen consumption and thermal cross talk between QCMs and structural components during QTA.

The mass spectrometer system controller software should be modified so that the electrometer sensitivity can be changed during a test so that the system does not saturate when measuring the more abundant peaks but is still able to monitor minor peaks. Also, the data acquisition software should be modified so that data measurement sensitivity changes are automatically adjusted for in the data reduction and presentation procedures.

To a practical extent, the test chamber should be modified to permit the test sample and the surfaces of the collector QCMs to be exposed to ultraviolet radiation, protons, electrons, and atomic oxygen to determine the effect of the total space environment on

outgassing and deposition kinetics.

7.2.1.2 Data Reduction and Presentation

A more sophisticated data filtering and smoothing subroutine should be added to the QCM data reduction algorithm. A curve fitting capability should also be added so that the data can be presented in a form more directly usable by the modeling community.

The QCM data acquisition and reduction algorithms should be combined so that reduced data can be viewed during a test, and test data can be made available immediately following a test.

The QCM and mass spectrometer data acquisition and reduction software should be integrated to permit single computer control and closure of the complete data reduction loop without the need for manual intervention.

7.2.1.3 QTA/MS Development

When the recommended changes to the QCM, temperature control power supplies, and mass spectrometer dynamic range are implemented, the QTA/MS test should be revaluated to determine the degree of improvement that they make to the species separation capability of QTA/MS.

The development of the QTA/MS test as an analytical chemistry tool should be further investigated, independently of its use in the outgassing/deposition test.

7.2.1.4 Individual Species Outgassing Rates

If the recommended development of QTA/MS successfully provides adequate mass fragmentation pattern data for the individual species, an algorithm should be developed for deconvoluting the isothermal outgassing test mass spectrometer data so as to resolve the outgassing rates of the individual species. Commercially available deconvolution algorithms may possibly be used for this purpose, either directly or with minor modifications.

7.2.2 Database Extension

7.2.2.1 Consolidation of Existing Data

The existing database should be consolidated by reducing the data that were measured under the present program but which could not be reduced because of funding limitations. This includes the following tasks:

(i) Further process the 150 K, 220 K, and 298 K deposition rate data to express them in an apparatus geometry-independent form, such as instantaneous evaporation rate as described in Section 5.1.2.2.2.

(ii) Reduce and present the QTA/MS data for all materials and tests in a manner similar to that performed for R-2560 and described in Section 5.2 .

(iii) Reduce and present the individual species outgassing rate data for all materials

and test temperatures in a manner similar to that performed for R-2560 at 125°C and described in Section 5.3 .

7.2.2.2 Extension of Database Parameters

An exploratory program should be established to assess the effects of the space radiation, particle, and atomic oxygen environments on material outgassing and deposition kinetics. The objective of the exploratory program would be to determine whether the magnitude of these effects is sufficient to make it advisable to establish an extended data measurement program to characterize them, and to help define a logical, practical measurement program. The exploratory program should be coordinated with other programs currently addressing this general area, such as the Aerospace Corporation program to study photolytic effects.

If the exploratory program indicates that space environmental effects on outgassing and/or deposition are significant enough to make formal characterization necessary, an appropriate systematic measurement program should be established.

7.2.3 Technology Insertion

The outgassing/deposition database supports a systematic approach to contamination control. A typical example of the systematic approach was described in Section 1.2 and Fig. 1-1. Incorporation of the database into a systematic approach should be performed as part of a comprehensive effort to complete and consolidate all of the technology needed to establish such a methodology. The following actions are recommended for insertion of the database into a comprehensive systematic contamination control methodology, and for establishing the methodology.

7.2.3.1 Industry Workshop

An industry workshop should be held on modeling the generation, transport, deposition, and optical effects of outgassing products; its purpose would be to present the results of this and other Air Force programs to the contamination modeling community and to give guidance on how best to present and extend the database. The workshop should be scheduled soon after the completion of this report.

7.2.3.2 Consolidation of Prediction Technology

The Air Force should establish a program to correlate and, where possible, consolidate all existing on orbit molecular contamination prediction technology. This effort should be undertaken jointly with NASA. The scope would cover characterization of material outgassing, plume, and liquid dump sources; transport modeling codes for plume flow, free molecular flow, molecular backscatter, etc.; impinging flux deposition models and data; and optical effects of contaminants, including reflectance, transmittance, and scatter, at all relevant wavelengths and at ambient and cryogenic temperatures. Such an

effort would identify deficiencies in the technology, prevent duplication, and help identify a future unified course of action to complete the needed technology development. One of the recommended courses of action should be to establish the program described in the following paragraph.

7.2.3.3 Standard Model Development and Verification

The molecular transport models used by the industry are, in general, proprietary and are not standardized. Hence, different organizations will predict different rates of contamination accumulation for the same system even though they use input data from the same database. It is highly desirable that these models either be standardized, or, as a minimum, be compared with each other. One possible way to compare models is via a type of round robin prediction test. A typical set of spacecraft specifications could be prepared and organizations could be invited to predict accumulation on various surfaces. If the differences between the various predictions are serious, then the need to develop a single standard model would be demonstrated.

The major deficiency in prediction technology is the almost complete absence of comparisons between predicted and actual on-orbit contamination levels. A program should be established to systematically compare prediction with measurement. The first phase of the program would perform measurements on a mockup satellite in a vacuum chamber. After model verification on the ground, a second phase would measure on orbit accumulation rates. On orbit rates are currently measured on some spacecraft, but the number of sensors used is invariably small, and no comparisons are made with preflight predictions.

7.2.3.4 Insertion Into Programs

The Air Force should require analyses of system contamination sensitivity, predictions of contamination levels anticipated from all sources, and contamination control developed to a level of detail TBD to be provided as a CDRL item at PDR and/or CDR. The CDRL requirement could call for use of specific computer models and databases. The currently imposed requirement that materials must have TML and VCM values less than 1.0 and 0.1 percent, respectively, establishes the precedent for placing contamination control requirements in a contract statement of work.

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Appendix

MATERIAL DATABASE

This Appendix contains outgassing/deposition data for the 20 sample materials tested during the Air Force Wright Aeronautical Laboratories contractual program F33615-82-C-5025, entitled "Characterization of Contamination Generation Characteristics of Satellite Materials". Section A.1 describes the contents and presentation of the database. Section A.2 contains the database itself. The database is preceded by an index describing where the test data for these materials are located in the Appendix. The Appendix and the material test matrix are discussed in more detail in Section 6 of the final report text.

A.1 DATABASE PRESENTATION AND CONTENTS

A.1.1 Materials Tested

Table A-1 describes the materials tested and their manufacturer or other source.

A.1.2 Test Summary

With minor exceptions as noted in context the following measurements were conducted on each material as part of the outgassing/deposition test.

(i) Material samples were weighed ex situ on a laboratory balance before and after the isothermal outgassing test.

(ii) The outgassing rate and mass loss of an isothermal sample were measured as a function of time by collecting outgassing products on a liquid-nitrogen-cooled QCM. All samples were tested at 125°C and 75°C, while some materials were also tested at a third temperature of either 25°C or 100°C.

(iii) The outgassing flux was monitored by mass spectrometer during the isothermal outgassing/deposition test.

(iv) The deposition rates of outgassing products from the isothermal sample on surfaces at 150 K, 220 K, and 298 K were measured by simulating these surfaces with QCMs.

(v) Following the isothermal test. QCM thermal analyses (QTA) were consecutively made on the outgassed products condensed on each of the QCMs.

(vi) The flux evaporating from the QCMs during QTA was monitored by a mass spectrometer (QTA/MS).

(vii) Ex situ gas chromatography/mass spectrometry (GC/MS) analyses of the materials were performed for sample temperatures of 125°C and 200°C.

Table A-1
Sample Material Data

MATERIAL FAMILY	COMMON NAME	DESCRIPTION	MANUFACTURER OR OTHER SOURCE
Adhesives	R-2560	Elastomer, silicone, room temperature vulcanizing	McGhan NuSil Corporation
	RTV 566	Compound, silicone, controlled volatility, low temperature	General Electric Corporation
	DC 93-500	Silicone, two component, room temperature vulcanizing, controlled volatility	Dow Corning Corporation
	DC 6-1104	Sealant, controlled volatility, silicone	Dow Corning Corporation
Films	Kapton	Polyimide plastic film, 0.001 in thick x 18 in wide	E. I. Dupont de Nemours
	Mylar	Polyethylene terephthalate film, 0.005 in thick x 48 in wide	E. I. Dupont de Nemours
	FEP Teflon	Fluorinated ethylene propylene plastic film, 0.001 in thick x 48 in wide	E. I. Dupont de Nemours
Oils and Greases	Brayco 815Z	Oil, perfluorinated, polyether, low volatility	Bray Oil Company
	Braycote 600	Grease, perfluorinated, polyether, low volatility	Bray Oil Company
	Krytox 143AD	Lubricant, oil, perfluoroalkylpolyether	E. I. Dupont de Nemours
	Vakote MLD73-91	Oil, hydrocarbon	USAF/AFWAL/MLBT
Paints and Thermal Control Coatings	S/13G/LO-V10	Paint, thermal control, low outgassing, white, SWS V-10 silicone binder, ZnO pigment	IIT Research Institute/ Univ. of Dayton Res. Inst.
	Chemglaze Z306	Coating, polyurethane, one component, flat black	Lord Corporation
	DC Q9-6313	Thermal control coating, polysiloxane resin, silver flake	Dow Corning/Lockheed, developed under USAF/AFWAL/MLBT contract
	Aremco 569	Thermal control coating, inorganic, Al_2O_3 pigment, K_2SiO_3 binder	Aremco Corporation
	LMSC 1170	Thermal control coating, transparent silicate, Al_2O_3 pigment, K_2SiO_3 binder	Lockheed Corporation
Carbon-Reinforced Composites	AS4/PEEK	AS4 carbon fiber, Victrex polyetheretherketone thermoplastic matrix	Imperial Chemical Industries Ltd
	AS4/PPS	AS4 carbon fiber, polyphenylene disulphide thermoplastic matrix	Phillips Petroleum Company
	AS4/3501-6	AS4 carbon fiber, DEGBA resin (MY 720) thermoset epoxy matrix	Source A: Hercules/Ciba Geigy Source B. USAF/AFWAL/MLBT

A.1.3 Test Data

The test data for each material consist of a Test Information Sheet followed by a set of graphical and tabular data.

A.1.3.1 Test Information Sheet

The Test Information Sheet (TIS) contains the following information pertinent to the testing of a particular material.

- **Material Tested:** The material tested is identified by its commonly used name. A more detailed description of the material is given in Table A-1. Additional material information is provided in the Comments section of the TIS.
- **Date Test Started:** The date on which the test was started is provided for historical and traceability purposes.
- **GC/MS Data Files:** The codes identifying the computer files on which the GC/MS data are permanently stored are given.
- **Material Sample Data:** The test sample surface area, the pre-test sample weight, and the ex situ total mass loss determined from the difference between pre- and post-test weighings are given.
- **Isothermal Test Data:** The duration of the isothermal outgassing and deposition portion of the test, and the codes identifying the computer files in which the QCM mass accumulation and mass spectrometer ion count data are stored are given. Where the test duration given is less than five days the outgassing rate reached a virtually constant or negligible value by the time indicated.
- **QCM Thermal Analysis Data:** The codes are given which identify the computer files in which the QCM thermogravimetric analysis (QTGA) and mass spectrometer ion count data obtained during QCM thermal analysis (QTA/MS) are stored.
- **Comments:** This section contains additional data and comments unique to the specific material tested, the test sample, or the conduct of the test. If the required comment is lengthy or if a comment is common to more than one material test, this section will refer the reader to a numbered comment in Section A.1.4. In the absence of an industry standard numbering system, the Lockheed Engineering Purchase Specification (EPS) number is given for the test material when available in order to establish material source traceability. The EPS number is part of the Lockheed Raw Material Convenience Number System, which identifies a material by a seven-digit number describing its peculiar characteristics (type, class, dimension, supplier, etc.). Lockheed EPS numbers exist for most materials in current use in the aerospace industry, but are not assigned to developmental materials.

A.1.3.2 Graphical and Tabular Data

The following test data are presented in grapnical or tabular form for each material.

- **Mass Loss/Deposition Data:** The following QCM measured outgassing and deposition kinetics data are presented for each sample temperature:
  - Total Mass Loss as a function of test time during the isothermal outgassing test as determined by the total mass accumulation on the 90 K QCM.
  - Total Outgassing Rate as a function of test time during the isothermal outgassing test as determined by the rate of accumulation on the 90 K QCM.
  - Volatile Condensable Material as a function of test time during the isothermal outgassing test as determined by the mass accumulation on the 150 K QCM.
  - Volatile Condensable Material as a function of test time during the isothermal outgassing test as determined by the mass accumulation on the 220 K QCM.
  - Volatile Condensable Material as a function of test time during the isothermal outgassing test as determined by the mass accumulation on the 298 K QCM.
  - Mass Remaining on the 90 K QCM (Fractional Condensable Material) as a function of QCM temperature during the QCM thermogravimetric analysis.
  - Evaporation Rate from the 90 K QCM as a function of QCM temperature during the QCM thermogravimetric analysis.

GC/MS Data: The following GC/MS data are presented for sample temperatures of 125°C and 200°C:

- Quantitation Report including the percentage of each species found in the GC/MS, the scan time at which the species was detected, and the chemical identity of the species when possible.
- Plot of the Amount of Collected Volatiles Remaining in the GC/MS Column as a function of scan time.

A.1.4 Test Information Sheet Annotations

The following notes are referred to in the Comments section of the TIS.

- Note 1: The initial and final ex situ weights of the Krytox 143 AD oil sample were not measured at the time of testing. In the early stages of the measurement program it was felt that, since the rate of mass loss of liquids depended upon free surface area rather than mass, reporting of percent mass loss would not be relevant for these materials. Later in the program it was decided that percent mass loss data should be presented for all materials in the interest of data consistency. At this later time the absolute weight loss for Krytox 143AD could be determined from the QCM accumulation data, but the initial weight had to be estimated since the original sample had been disposed of by that time. An estimated weight was determined based on the density of the material and the volume of the holder, and was checked by refilling the sample holders with Krytox oil and weighing. The accuracy of this weight estimate is believed to be about ±10 percent.

- Note 2: The DC Q9-6313, Aremco 569 and LMSC 1170 thermal control coatings were supplied by Lockheed Space Systems Division (SSD) Materials and Processes Engineering. The coatings were supplied already sprayed on aluminum substrates, whose weights were unknown. In order to measure the substrate weights, and hence determine the initial weight of the coating alone, the substrates were cleaned by chemically and mechanically removing the coatings after the outgassing tests had been performed. Because of the destructive manner of coating removal there are uncertainties in the original substrate weights determined in this manner, which decrease the certainty in the initial coating weights to ±10 percent.

- Note 3: Accurate ex situ mass loss data are not available for some oils or greases because of spillage from the sample holders. This problem was eliminated in later tests by using more stable sample holders. The test was not repeated because the ex situ mass loss was not considered to be a critical data item for oils. (See also Note 1)

- Note 4: Film material absorb water vapor very rapidly upon post-test exposure to the atmosphere. Equilibration of these films to the ambient humidity after removal from the vacuum chamber prevented meaningful post-test weights from being obtained.

- Note 5: GC/MS test results are not available for Brayco 815Z oil, Braycote 600 grease, DC Q9-6313 thermal control coating, Aremco 569 thermal control coating, and LMSC 1170 thermal control coating. GC/MS tests were performed on these samples between July 1986 and July 1987 concurrently with the outgassing tests. At that time the manner in which the GC/MS test data would be incorporated in the test method had not been finally established so the data were stored in the GC/MS computer for later retrieval. By the time the utility of the GC/MS data had been better defined some data had been inadvertently discarded during the chemistry department annual computer storage housekeeping. Since representative samples of these materials listed were no longer available the tests could not be repeated. The data from the original GC/MS test on Krytox 143AD was also lost in this manner, but a sufficient quantity of the original sample of this material was still available for retest.

- Note 6: This program was the first field application of the newly-developed Teknivent software for controlling the Balzers mass spectrometer with an IBM PC computer, and so some developmental problems were encountered. Because of these problems the mass spectrometer was inoperative at the time that Brayco 815Z, Braycote 600 and Krytox 143AD were scheduled to be tested. GC/MS analysis of these materials prior to the outgassing test had shown that their outgassed products consisted of fluorocarbon (C_xF_y) species with a wide and essentially continuous range of molecular weights, with no uniquely identifiable species. Because of the absence of clearly identifiable species it was felt that minimal additional useful data would be gained by delaying the test schedule until the mass spectrometer system was fully operational, and so these materials were tested without the mass spectrometer.

- Note 7: DC Q9-6313, Aremco 569 and LMSC 1170 thermal control coatings were tested during the early part of the test program while familiarity with capabilities of the mass spectrometer and its software was still being gained. As a result, the system sensitivity was not fully utilized during these three material tests. (See also Note 6)

- Note 8: A formal QCM thermogravimetric analysis (QTGA) was not performed on all of the higher temperature QCMs (i.e. 150 K, 220 K, and 298 K) if there was minimal or no deposit on them at the end of the isothermal outgassing test. However, all QCMs were always heated to 125°C at the end of a test to ensure that there was no contaminant residue on them before starting the next test.

- Note 9: Malfunctions in the automatic controllers used to maintain liquid nitrogen levels in the reservoirs and failures in the liquid nitrogen supply dewars have been been responsible for occasional test interruption or truncation. These events have been noted in the Test Information Sheets under the generic description of "liquid nitrogen failure".

- Note 10: In early July 1987, a bearing failure caused the internal destruction of the turbomolecular pump used for evacuating the effusion cell interlock chamber. A replacement for this pump was not available until October 1987. During the interim the interlock chamber was evacuated using only the mechanical pump. The materials tested during this period including LMSC 1170 thermal control coating, DC Q9 6313 thermal control coating, VacKote MLD 73-91 oil, RTV 566 adhesive and DC 93-500 adhesive.

A.2 MATERIAL DATA

This section contains the graphical and tabular outgassing and deposition data for the materials described in Table A-1. The page locations are as follows:

TEST INFORMATION

MATERIAL TESTED : R 2550 adhesive

DATE TEST STARTED : December 11, 1987

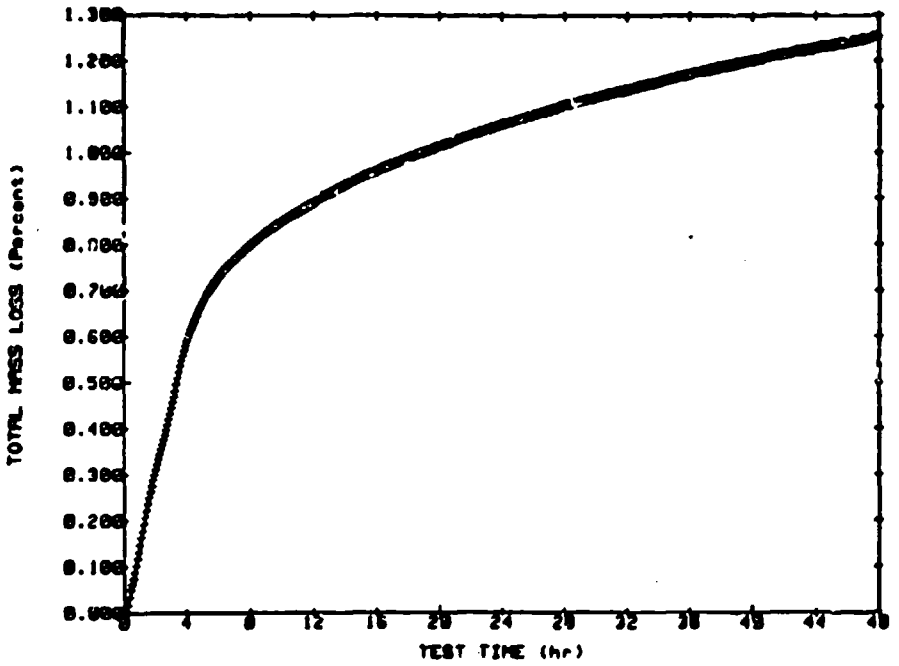
GC/MS DATA FILES :

125°C Test	JG18DI.GC*B
200°C Test	JG21DI.GC*B

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	1.43	1.43
Weight, pretest (g)	2.40841	2.38749
Total mass loss (%)	1.53	1.58
ISOTHERMAL TEST DATA :		
Test duration (h)	48	48
QCM/Temperature Data File	G1215	G1219
Mass Spectrometer Data File	-	-
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G1217Q	G1221Q
Mass Spectrometer Data File	-	-

COMMENTS :

- material is a room temperature vulcanizing (RTV) silicone elastomer produced by McGhan NuSil Corp
- LMSC LPS # 40 (Rev) (ECO 0004)
- samples purchased from McGhan NuSil Corp
- sample holders were Al tubes 1.0 inch long by 0.375 inch I.D.
- sample configuration (125°C test) : 1 Al tube filled with sample
- sample configuration (75°C test) : 1 Al tube filled with sample
- 90 K QCM shutter open - not aperture - during QTA after 125°C Isothermal Test
- mass spectrometer scanning m/e = 10 to 500



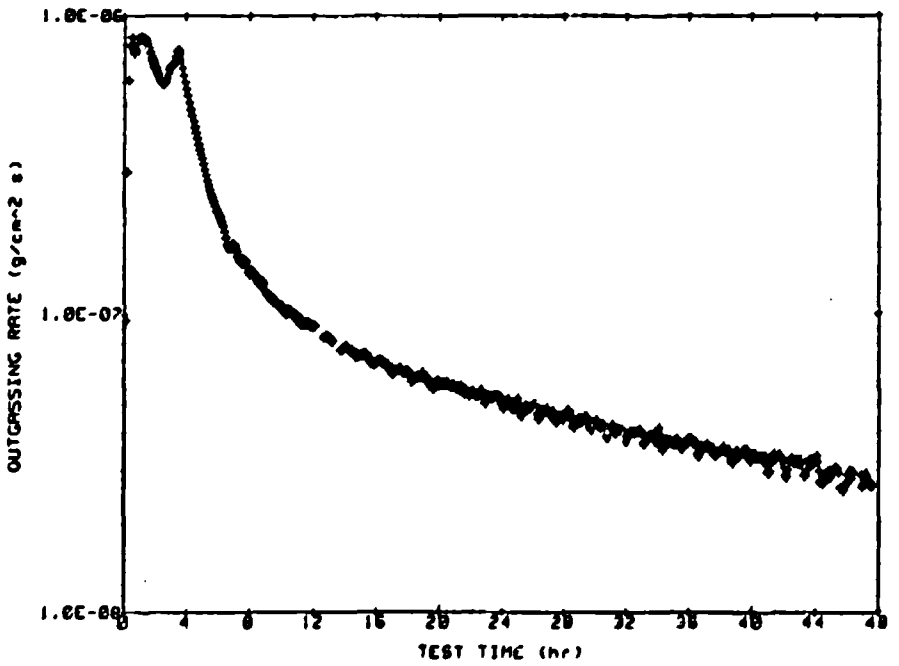
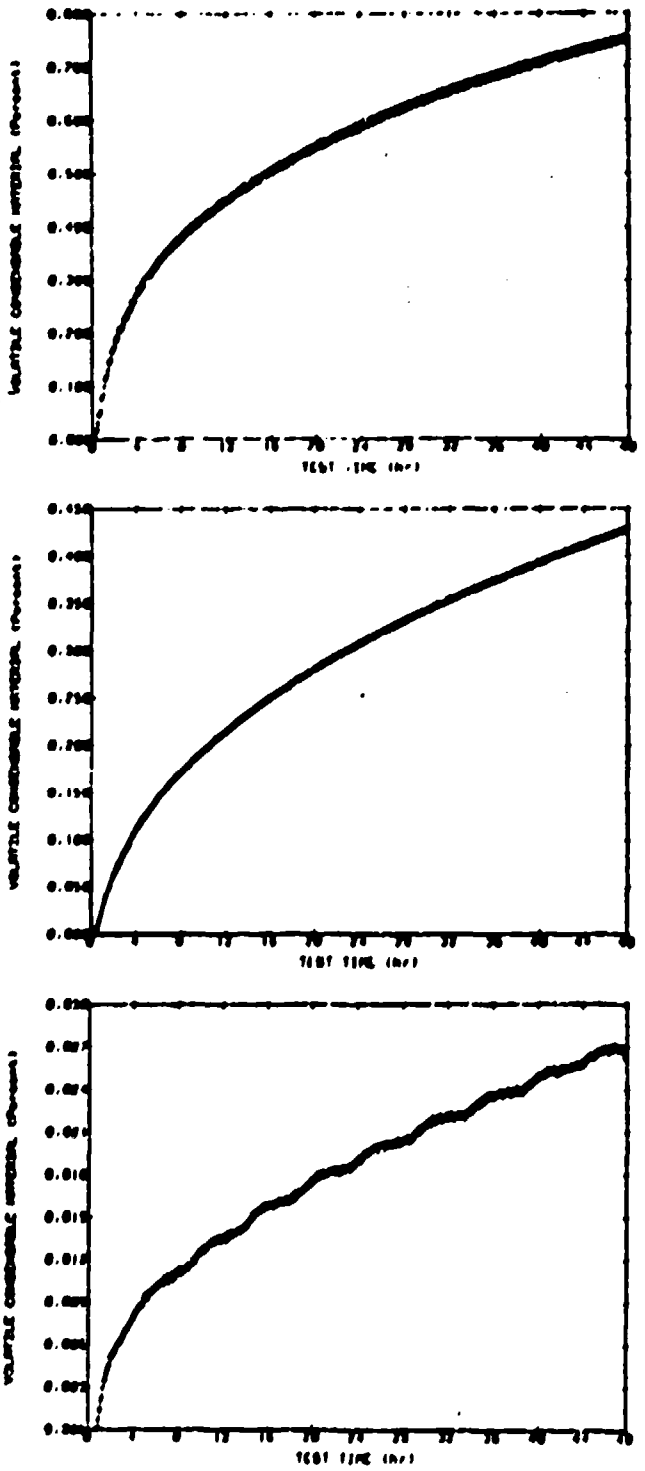


Fig. A-1 Total Mass Loss and Outgassing Rate as Functions of Time for an R-2560 Sample at 125°C.



150 K QCM

220 K QCM

298 K QCM

Fig. A-2 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an R-2560 Sample at 125°C.

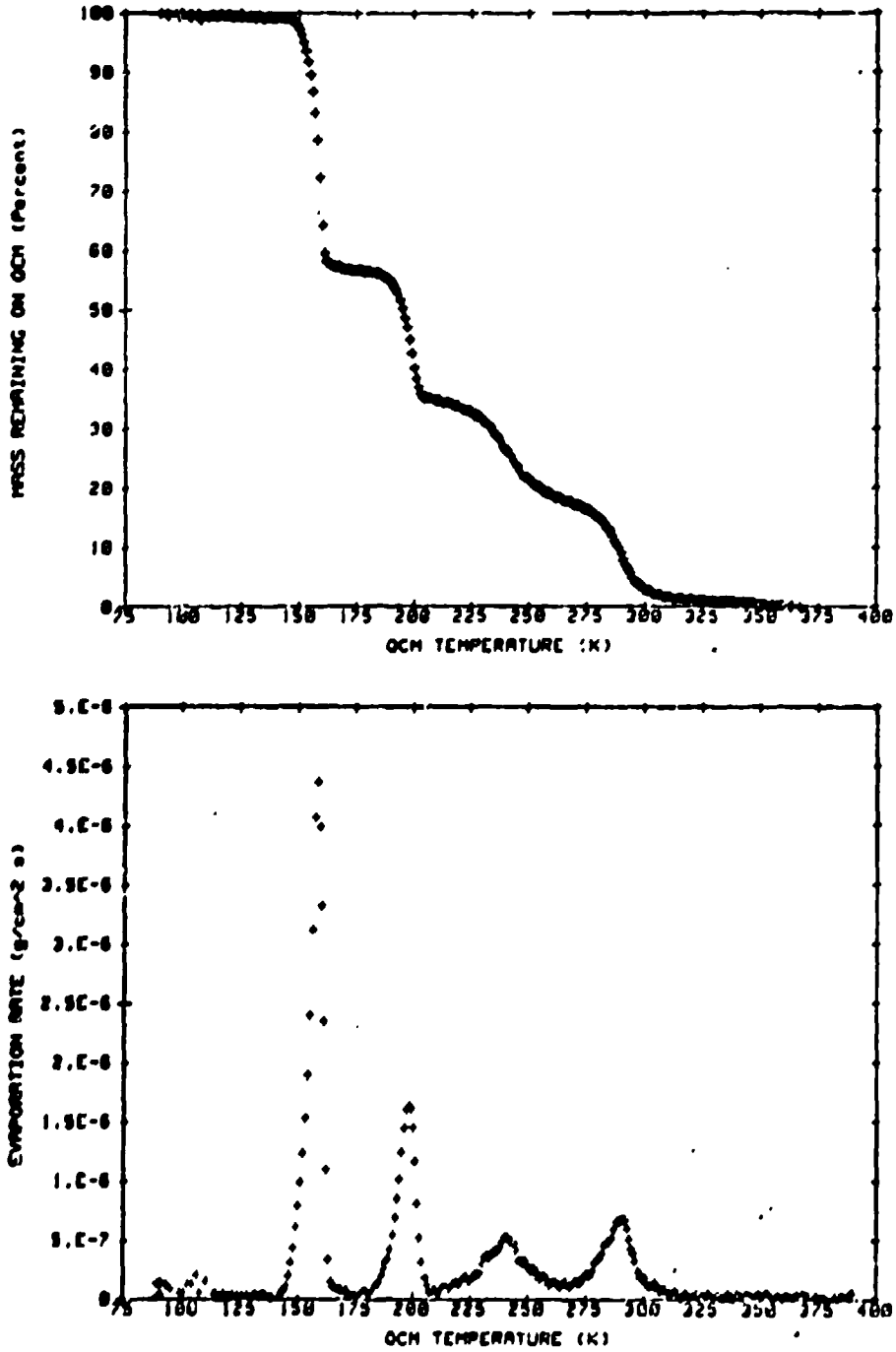


Fig. A-3 QTGA Data for Outgassing Products Collected on the 90 K QCM from an R-2560 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

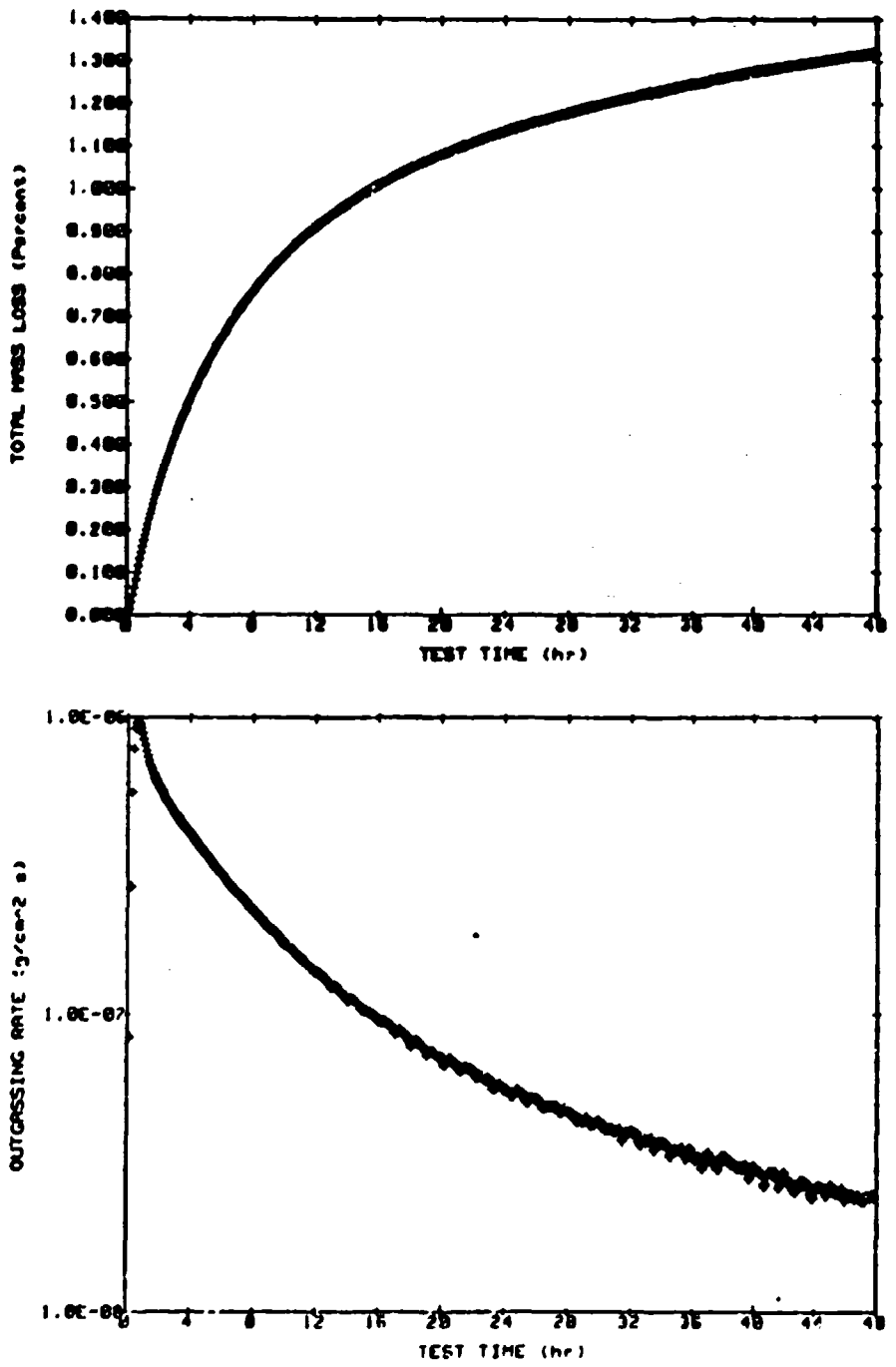


Fig. A-4 Total Mass Loss and Outgassing Rate as Functions of Time for an R-2560 Sample at 75°C.

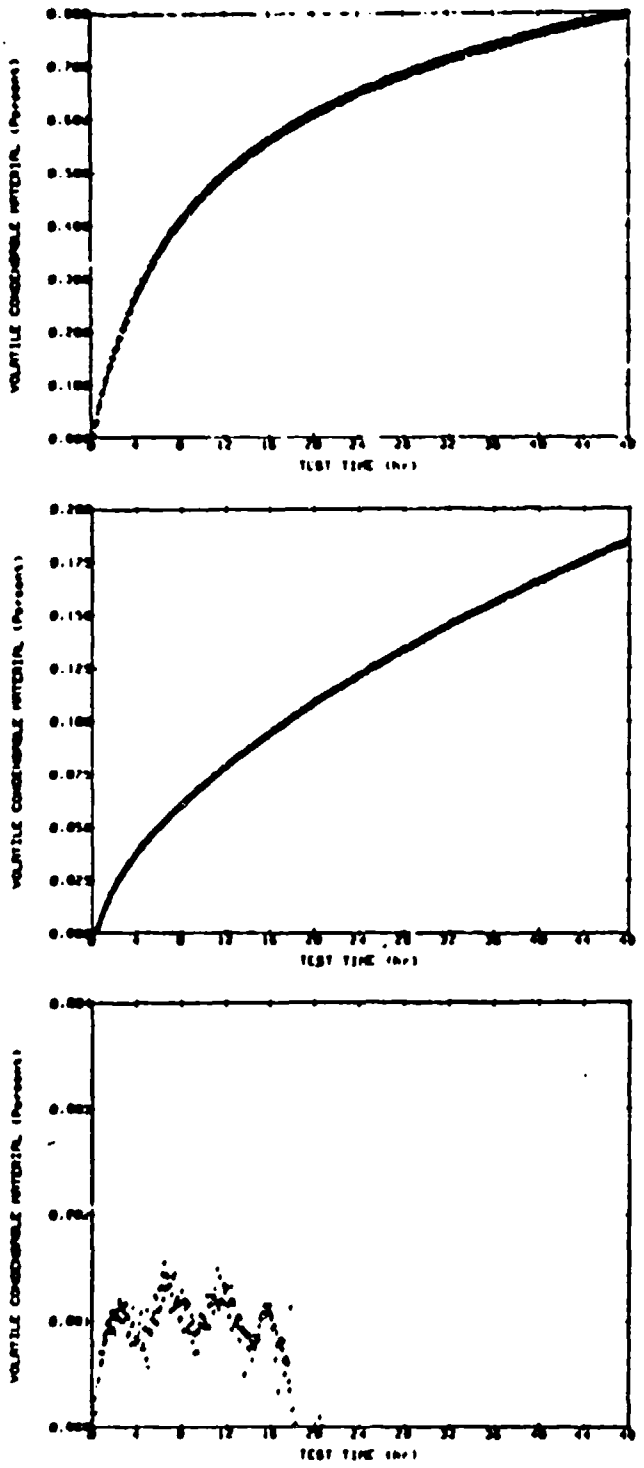


Fig. A-5 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an R-2560 Sample at 75°C.

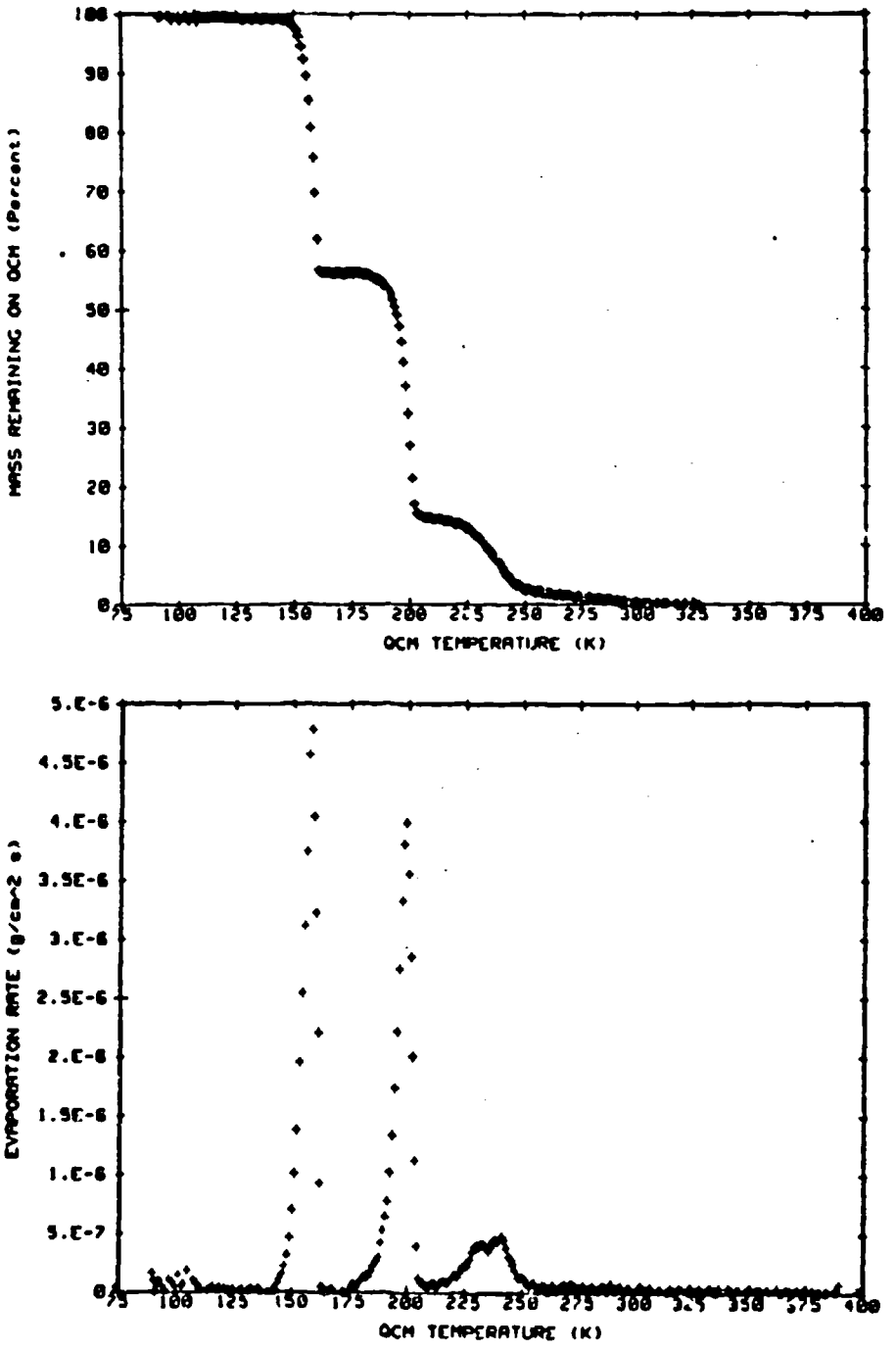


Fig. A-6 QTGA Data for Outgassing Products Collected on the 90 K QCM from an R-2560 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-2

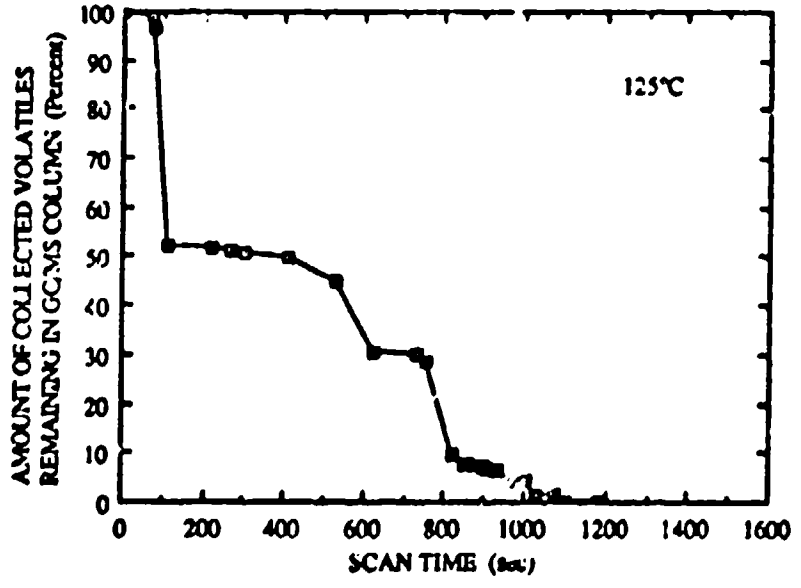
GC/MS Data for R-2560 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
73	1.14	CO_2 artifact
75	2.20	CF_2Cl_2
79	0.24	n-butane
111	44.40	n-propanol & benzene
222	0.21	toluene
269	0.74	hexamethyl cyclotrisiloxane
306	0.31	xylene isomer
410	1.07	octamethyl cyclotetrasiloxane
527	4.7*	decamethyl cyclopentasiloxane
622	14.58	octanoic acid & dodecamethyl cyclohexasiloxane
730	0.43	dibutyl diprepyl silicate
758	1.61	tetradecamethyl cycloheptasiloxane
821	18.82	dodecanoic acid
848	1.77	hexadecamethyl cyclooctasiloxane
862	0.28	similar to dodecanoic acid
897	0.39	siloxane
913	0.54	unspecified silicone (alkyl silicate ?)
933	0.60	octadecamethyl cyclononasiloxane
964	1.56	unspecified silicone (alkyl or aryl silicate ?)
1008	0.30	siloxane
1030	2.61	cosamethyl cyclodecasiloxane
1076	0.17	
1102	1.27	docosamethyl cycloundecasiloxane
1182	0.21	tetracosamethyl cyclododecasiloxane

Table A-3

GC/MS Data for P-2560 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
69	0.28	CO_2 artifact
75	2.13	n-butane
104	24.77	n-propanol
143	2.04	benzene
389	0.71	octamethyl cyclotetrasiloxane
500	2.39	decamethyl cyclopentasiloxane
521	0.35	siloxane
550	5.01	[illegible]anoic acid
596	30.25	alkyl silicate ?
657	1.05	decanoic acid
716	0.93	tetradecamethyl cycloheptasiloxane
768	10.86	dodecanoic acid
806	0.37	hexadecamethyl cyclooctasiloxane
870	2.33	tetradecanoic acid
919	2.54	phenyl methyl siloxane
962	0.72	eicosamethyl cyclodecasiloxane
980	3.29	phenyl methyl siloxane
1025	0.27	docosamethyl cycloundecasiloxane
1045	0.27	phenyl methyl siloxane
1049	1.36	phenyl methyl siloxane
1086	0.30	tetracosamethyl cyclododecasiloxane
1127	1.01	phenyl methyl siloxane
1159	0.37	hexacosamethyl cyclotridecasiloxane
1226	1.10	phenyl methyl siloxane
1253	0.40	octacosamethyl cyclotetradecasiloxane
1354	0.79	phenyl methyl siloxane
1382	0.64	triacontamethyl cyclopentadecasiloxane
1484	2.65	MW 456 aromatic acid
1535	0.38	unknown
1565	0.44	unknown



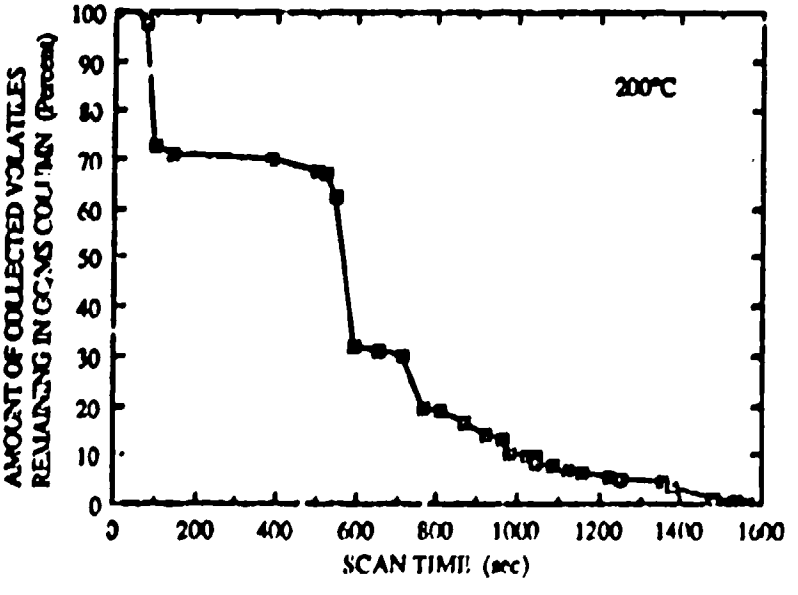


Fig. A-7 Amount of Collected Volatiles Remaining in GC/MS Column from R-2560 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : RTV 566 adhesive

DATE TEST STARTED : September 15, 1987

GC/MS DATA FILES :

125°C Test : JG27AUG87B
200°C Test : JG27AUG87C

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	8.55	8.55
Weight, pretest (g)	15.90798	15.67280
Total mass loss (%)	0.26	0.11
ISOTHERMAL TEST DATA :		
Test duration (h)	51	48
QCM/Temperature Data File	G0915	G0923
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0918Q	G0925Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a low-temperature, controlled-volatility silicone compound produced by General Electric Co.
- LMSC EPS # 40-203-0050161
- samples supplied by C.C. Chappell, LMSC Material & Process Laboratories (O/48-92)
- sample holders were aluminum tubes 1.0 inch long by 0.375 inch I.D.
- sample configuration (125°C test): 6 Al tubes filled with sample
- sample configuration (75°C test): 6 Al tubes filled with sample
- interlock chamber evacuated with mechanical pump (Note 10, Sec. A.1.4)
- mass spectrometer scanning m/e 10 to 400
- no QTA performed on 298 K QCM after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 298 K QCM after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- 125°C isothermal test teminated when chamber was accidentally vented to atmosphere
  effusion cell was removed and samples were weighed
  chamber remained in low vacuum condition with QCMs at correct temperatures for 4 hrs
  high vacuum was then restored and chamber was allowed to equilibrate for 15 hrs
  outgassing contaminants from isothermal test were still on QCMs
  500 Hz of contaminant (probably water) accumulated on QCM #1 during down-time
  essentially no change in frequency for the other three QCMs during down-time
  QCM thermogravimetric analysis proceeded as normal

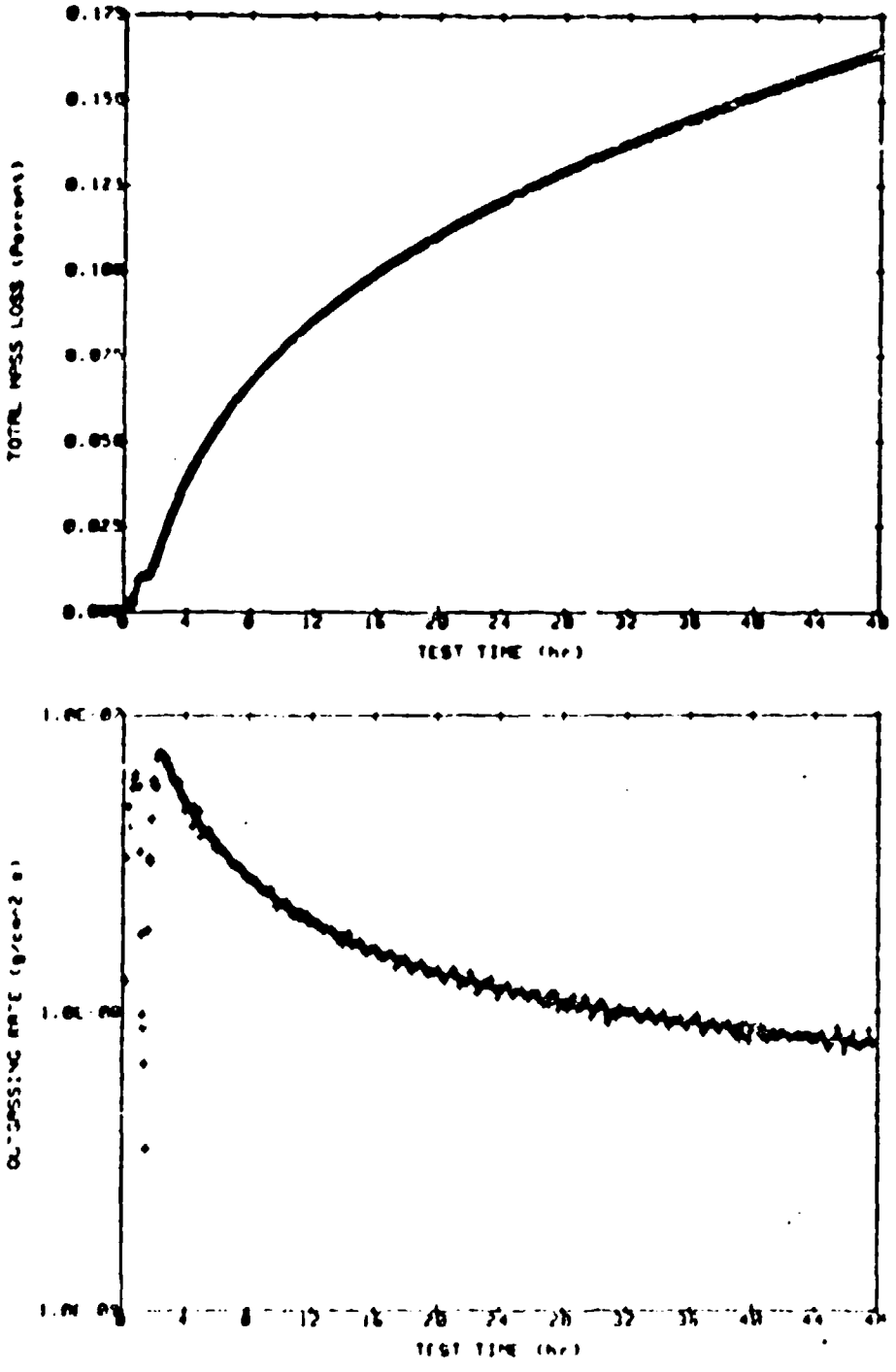


Fig. A-8 Total Mass Loss and Outgassing Rate as Functions of Time for an RTV 560 Sample at 125° C.

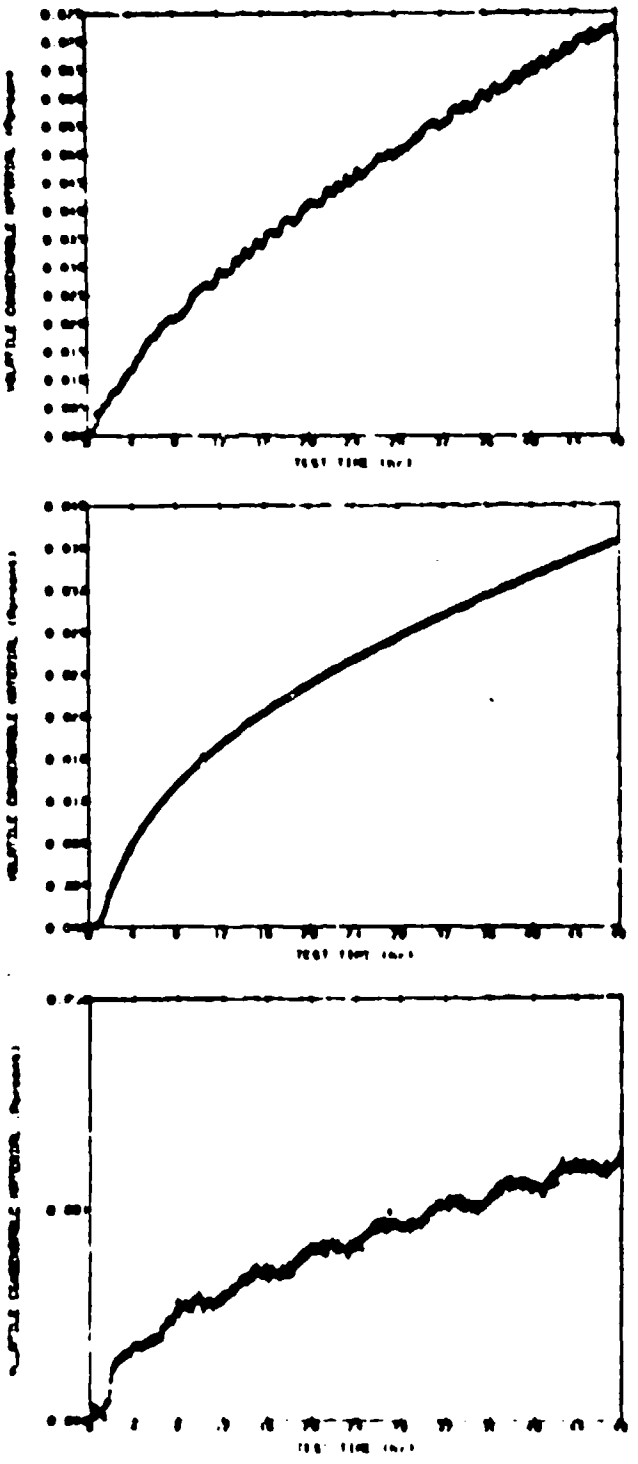


Fig. A-9 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an RTV 566 Sample at 125°C.

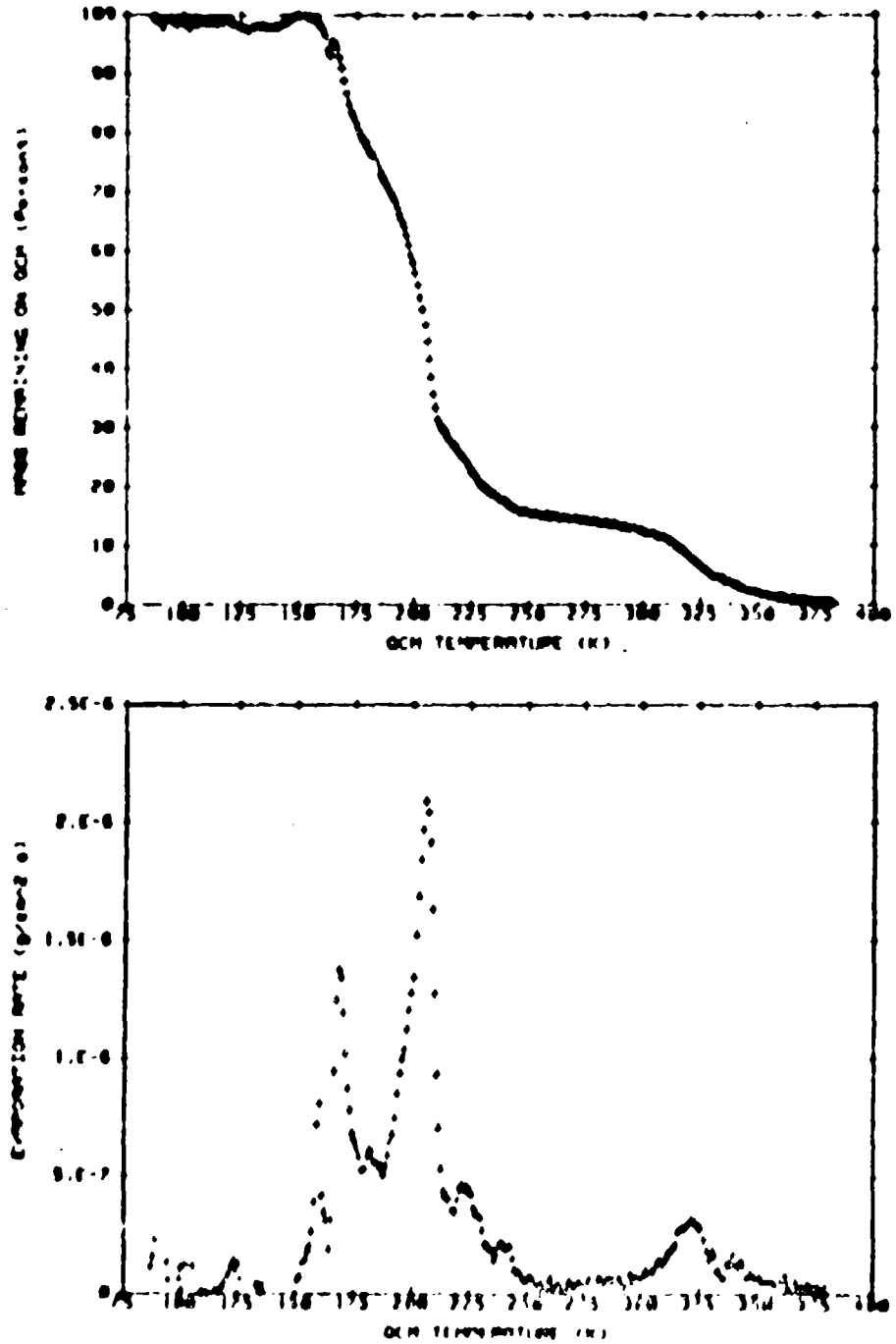


Fig. A 10 QTGA Data for Outgassing Products Collected on the 90 K QCM from an RTV 567 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

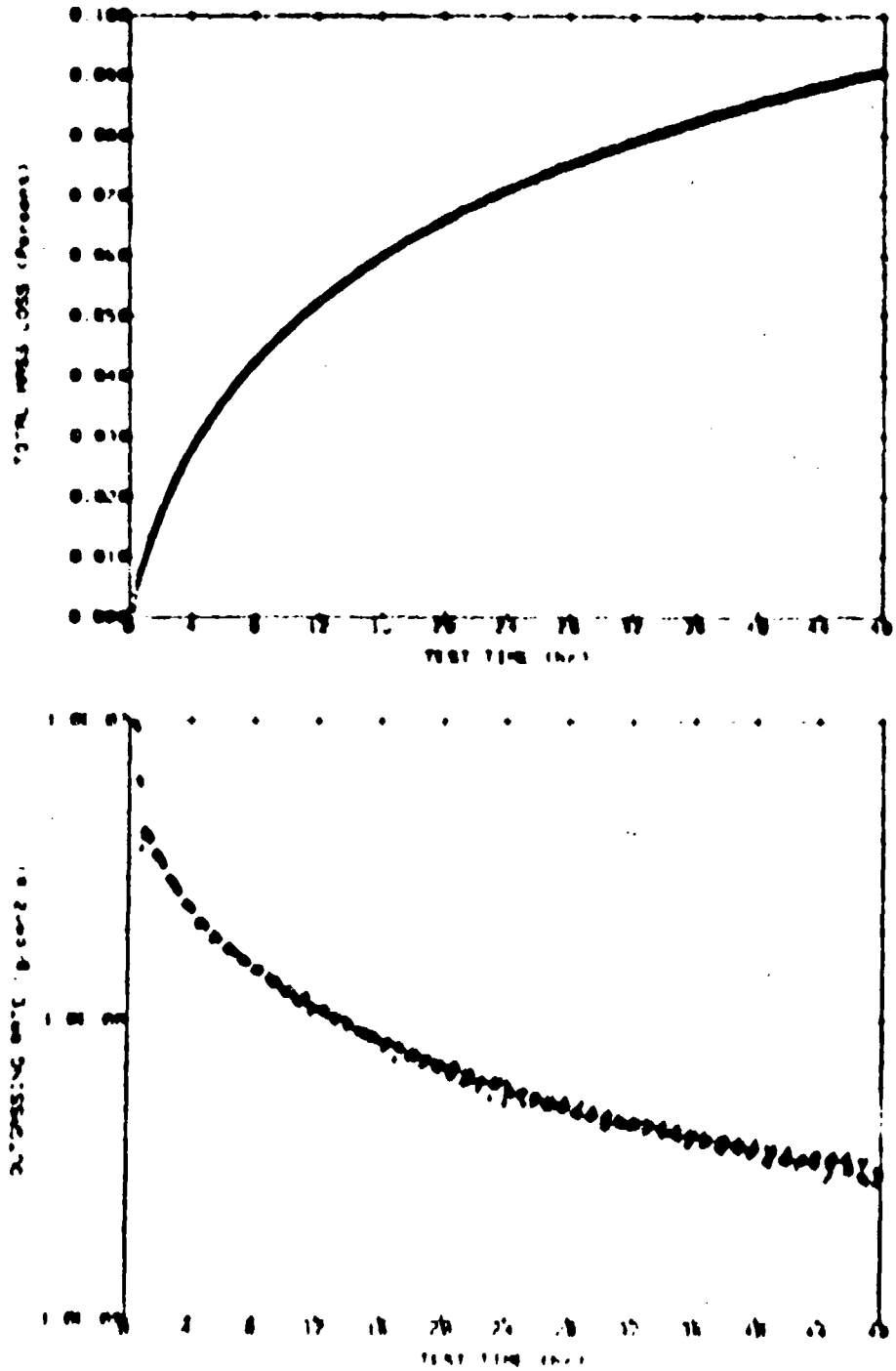
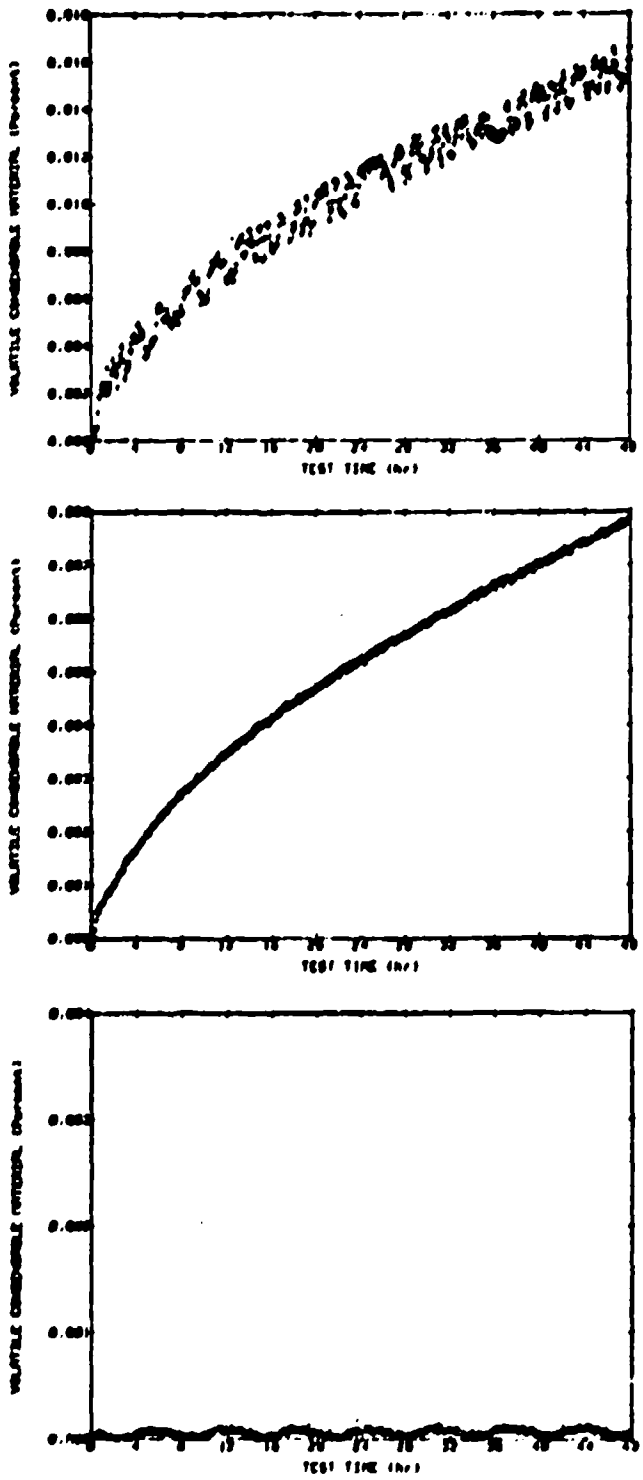


Fig. A.11 Total Mass Loss and Outgassing Rate as Function of Time for an RTV 566 Sample at 75°C



150 K QCM

220 K QCM

298 K QCM

Fig. A-12 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an RTV 566 Sample at 75°C.

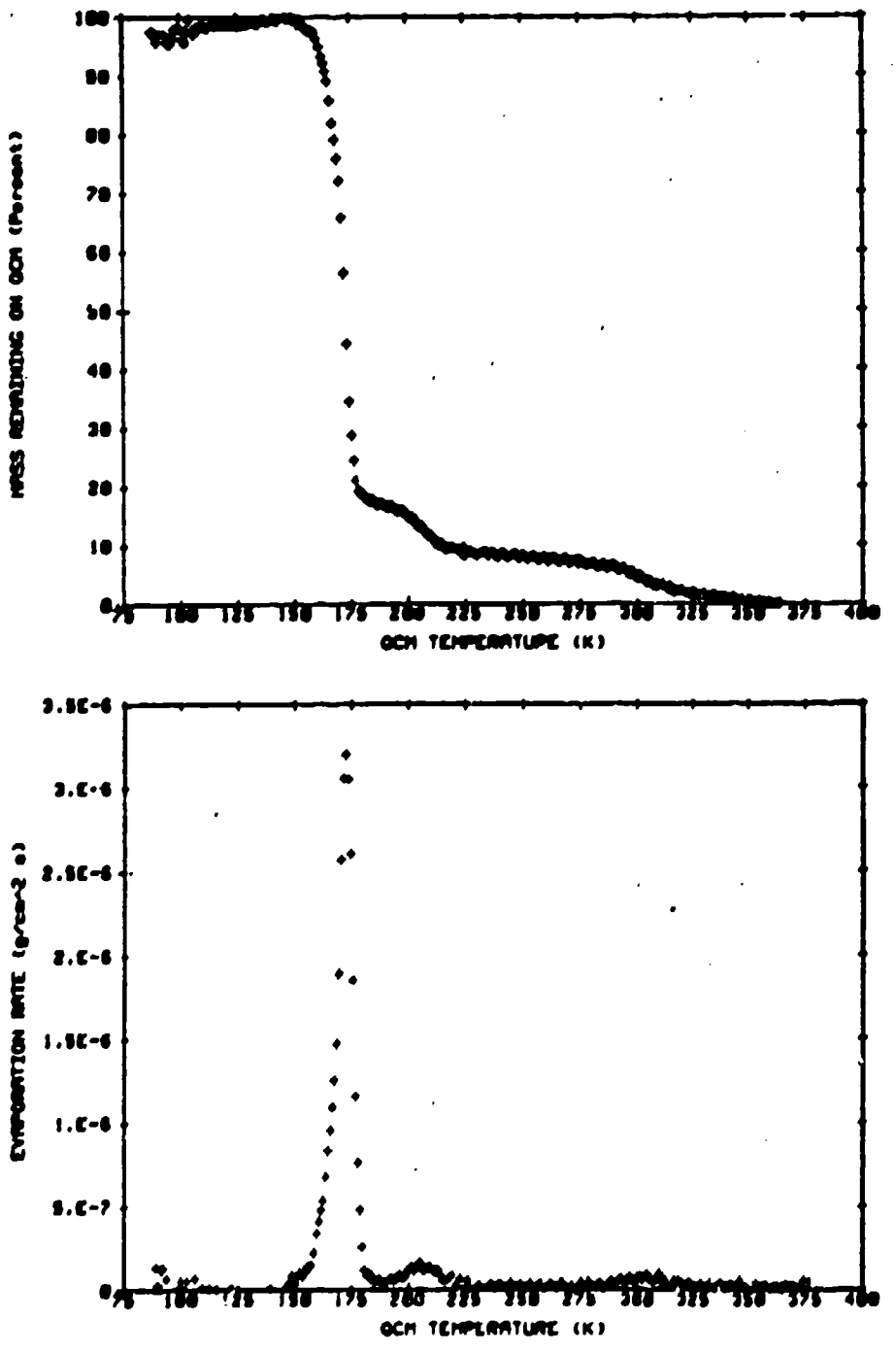


Fig. A-13 QTGA Data for Outgassing Products Collected on the 90 K QCM from an RTV 566 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-4

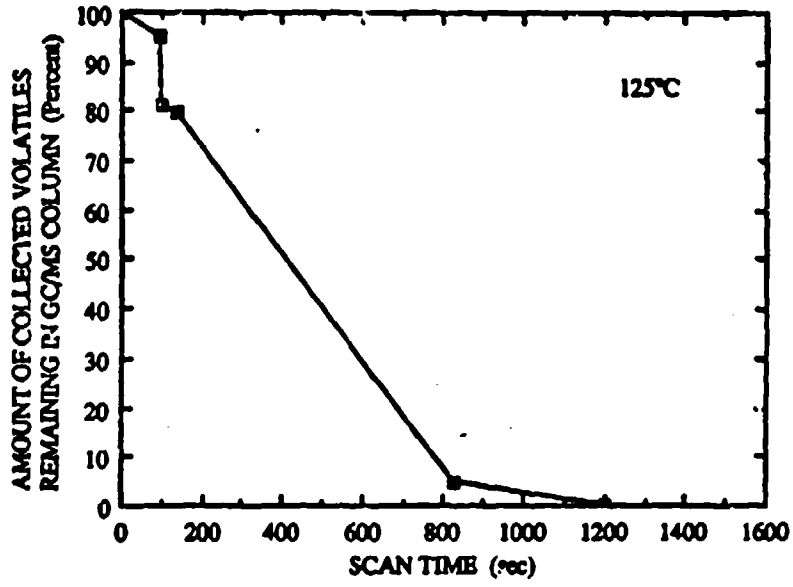
GC/MS Data for RTV 566 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
93	4.91	CO_2 artifact
100	13.73	ethanol
136	1.62	butanol
825	74.96	unknown
1199	4.78	artifact

Table A-5

GC/MS Data for RTV 566 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
138	0.78	butanol
179	1.09	1-butanol
295	0.58	hexamethyl cyclotrisiloxane
405	0.26	
510	0.58	
523	0.65	
569	0.90	octanoic acid
648	0.24	
693	12.05	decanoic acid
815	56.14	dodecanoic acid
825	11.45	unknown
830	0.17	
913	1.00	
919	4.52	tetradecanoic acid
1030	0.86	
1200	0.50	
1214	0.24	



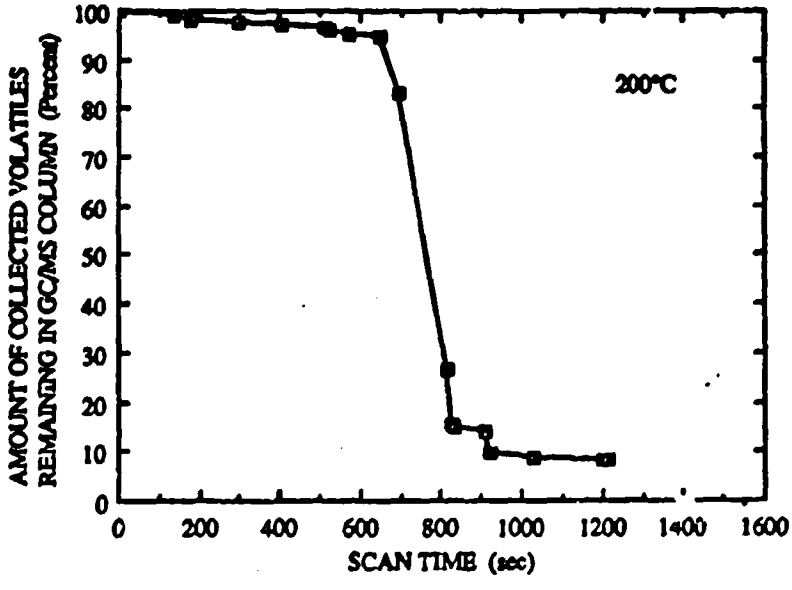


Fig. A-14 Amount of Collected Volatiles Remaining in GC/MS Column from RTV 566 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : DC 93-500 adhesive

DATE TEST STARTED : September 28, 1987

GC/MS DATA FILES :

125°C Test : KN28SEP87B
200°C Test : KN28SEP87D

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	8.55	8.55
Weight, pretest (g)	11.40281	11.34696
Total mass loss (%)	0.08	0.07
ISOTHERMAL TEST DATA		
Test duration (h)	48	49
QCM/Temperature Data File	G0928	G1001
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0930Q	G1003Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a two-component, controlled volatility, room temperature vulcanizing (RTV) silicone adhesive produced by Dow Corning Corp.
- LMSC EPS # 40-188-0010245
- samples supplied by C.C. Chappell, LMSC Material & Process Laboratories (O/48-92)
- sample holders were aluminum tubes 1.0 inch long by 0.375 inch I.D.
- sample configuration (125°C test): 6 Al tubes filled with sample
- sample configuration (75°C test): 6 Al tubes filled with sample
- interlock chamber evacuated with mechanical pump (Note 10, Sec. A.1.4)
- no QTA performed on the 298 K QCM after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

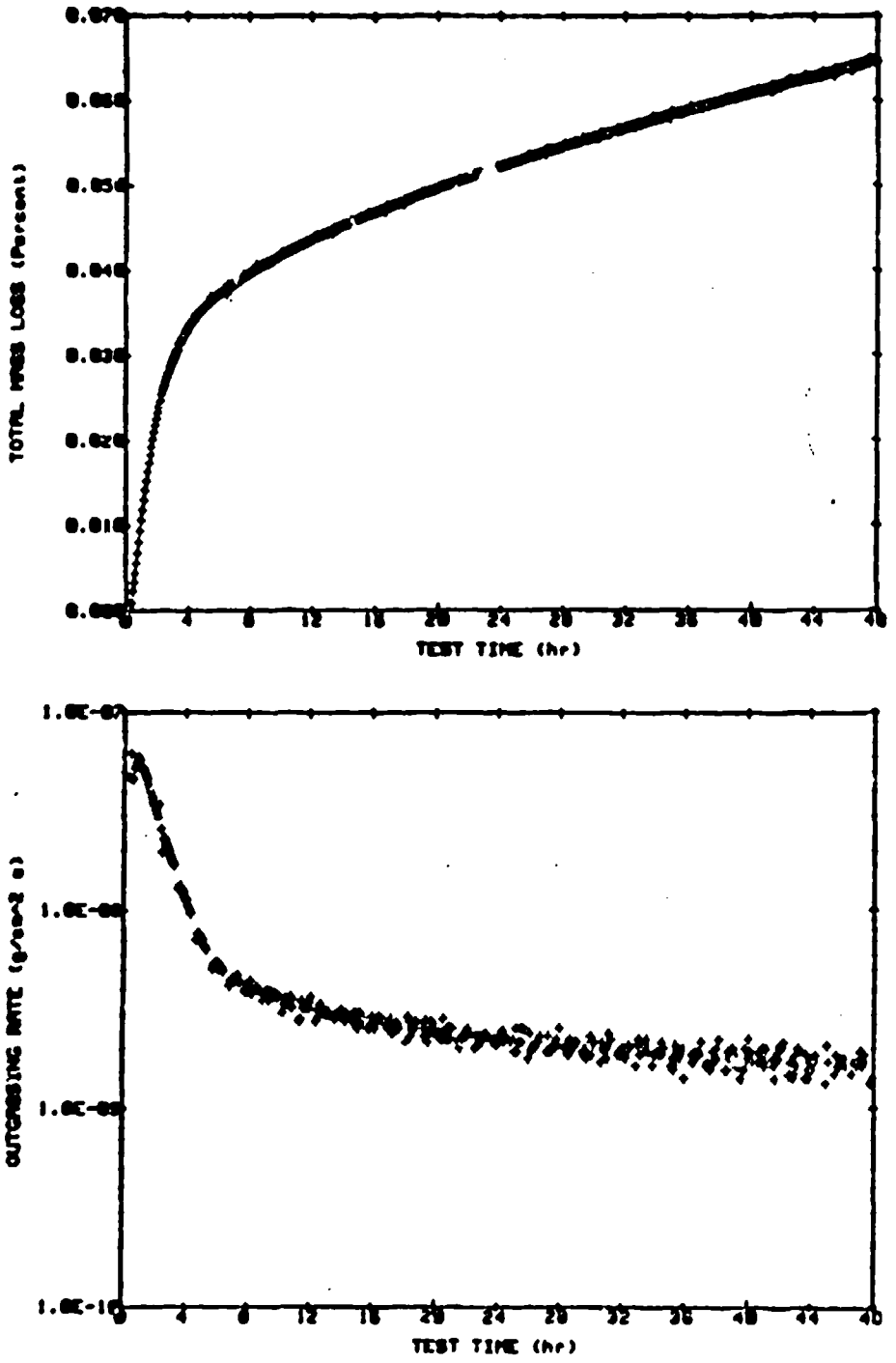


Fig A-15 Total Mass Loss and Outgassing Rate as Functions of Time for a DC 93-500 Sample at 125°C.

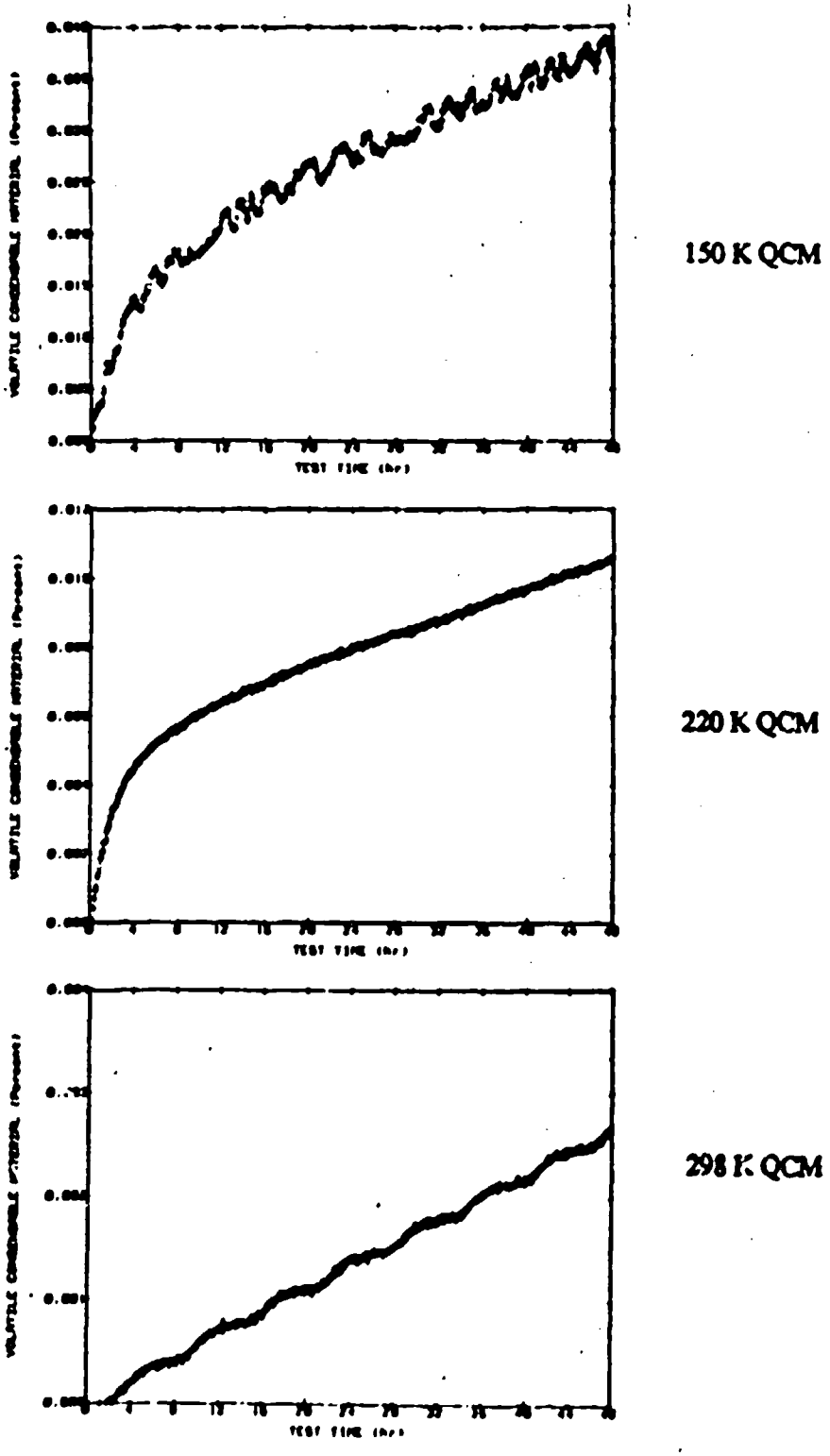


Fig. A-16 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC 93-500 Sample at 125°C.

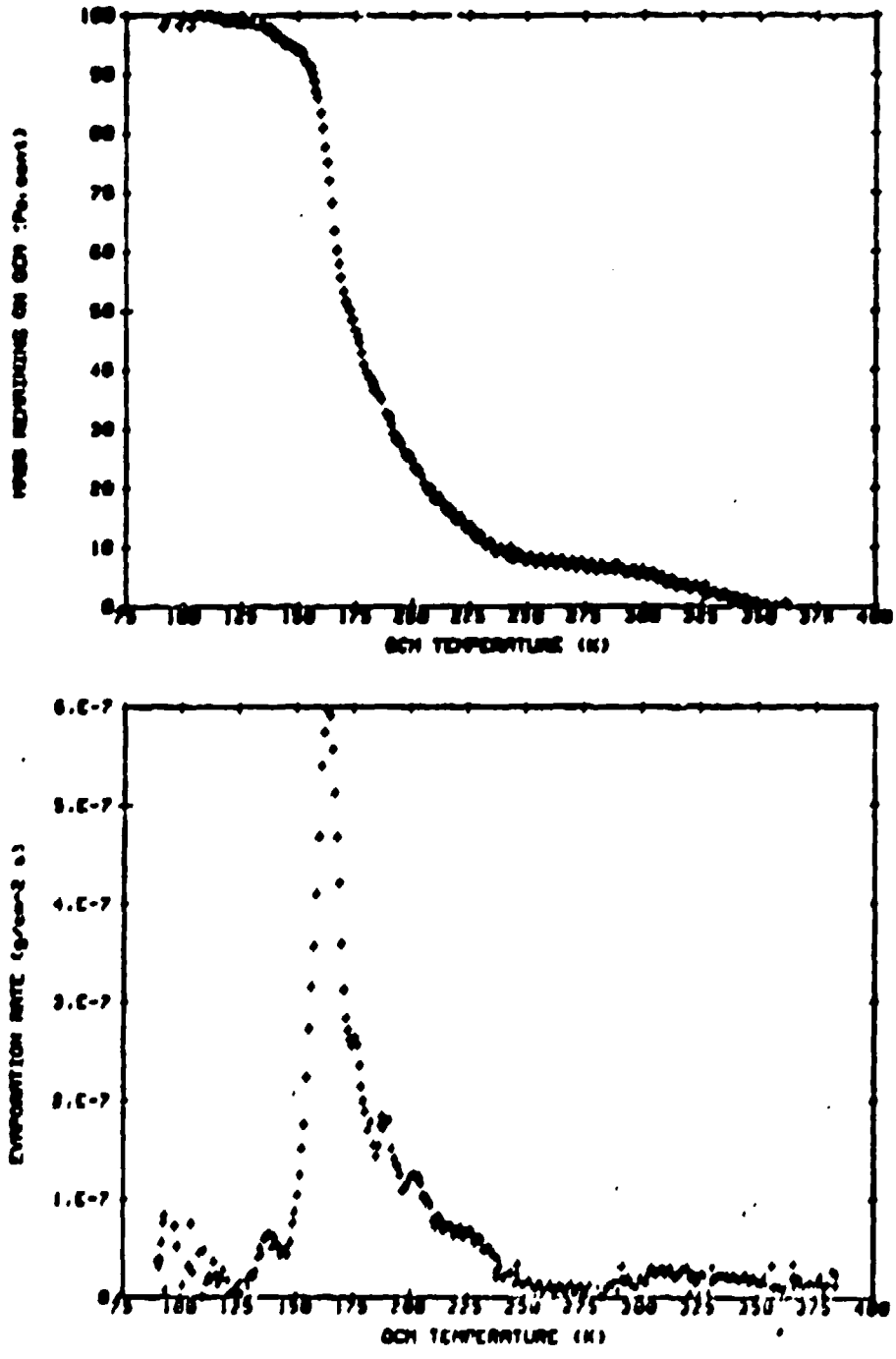


Fig. A-17 QTGA Data for Outgassing Products Collected on the 90 K QCM from a 3M 93-500 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

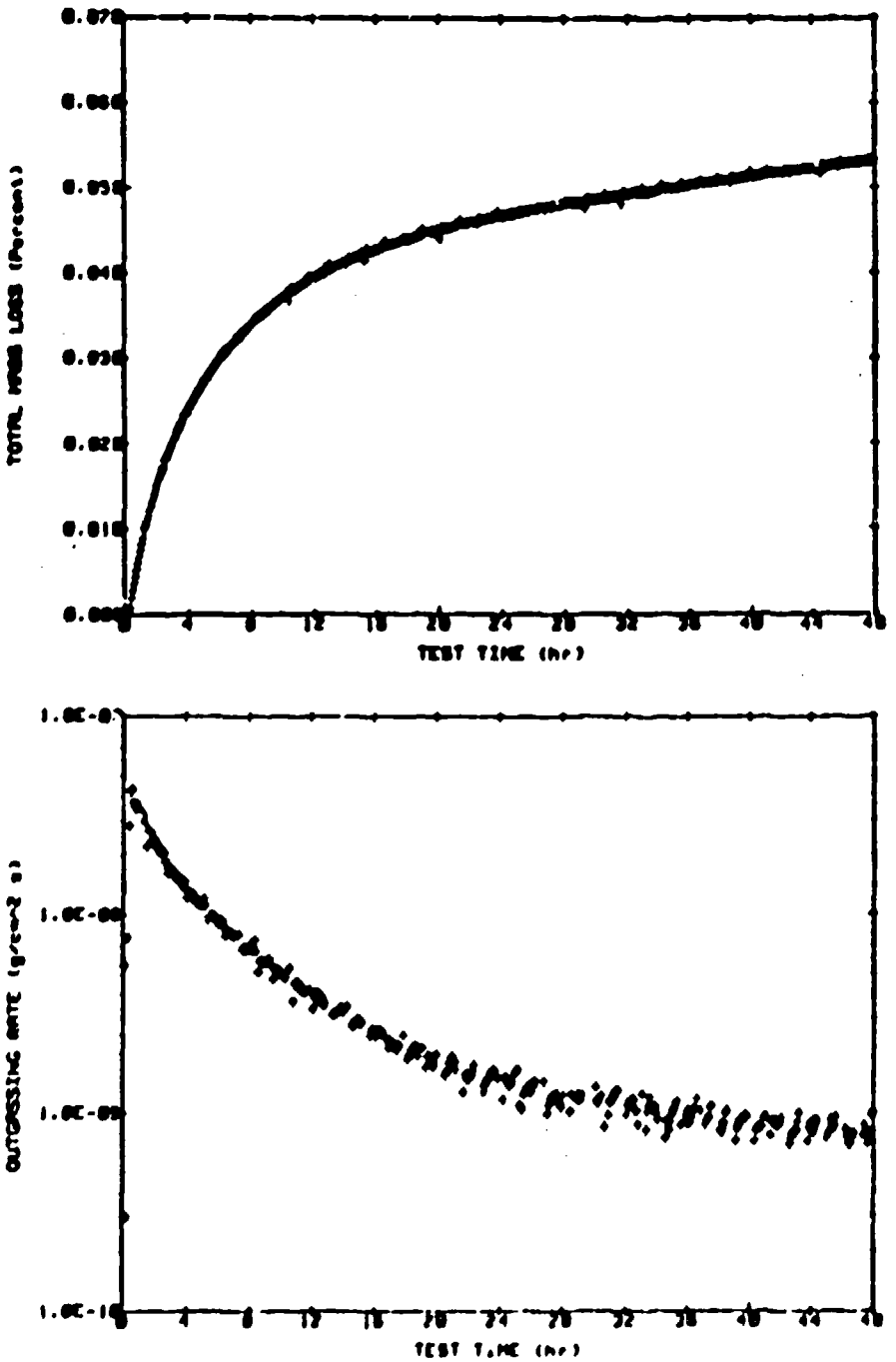


Fig. A-18 Total Mass Loss and Outgassing Rate as Functions of Time for a DC 93-500 Sample at 75°C.

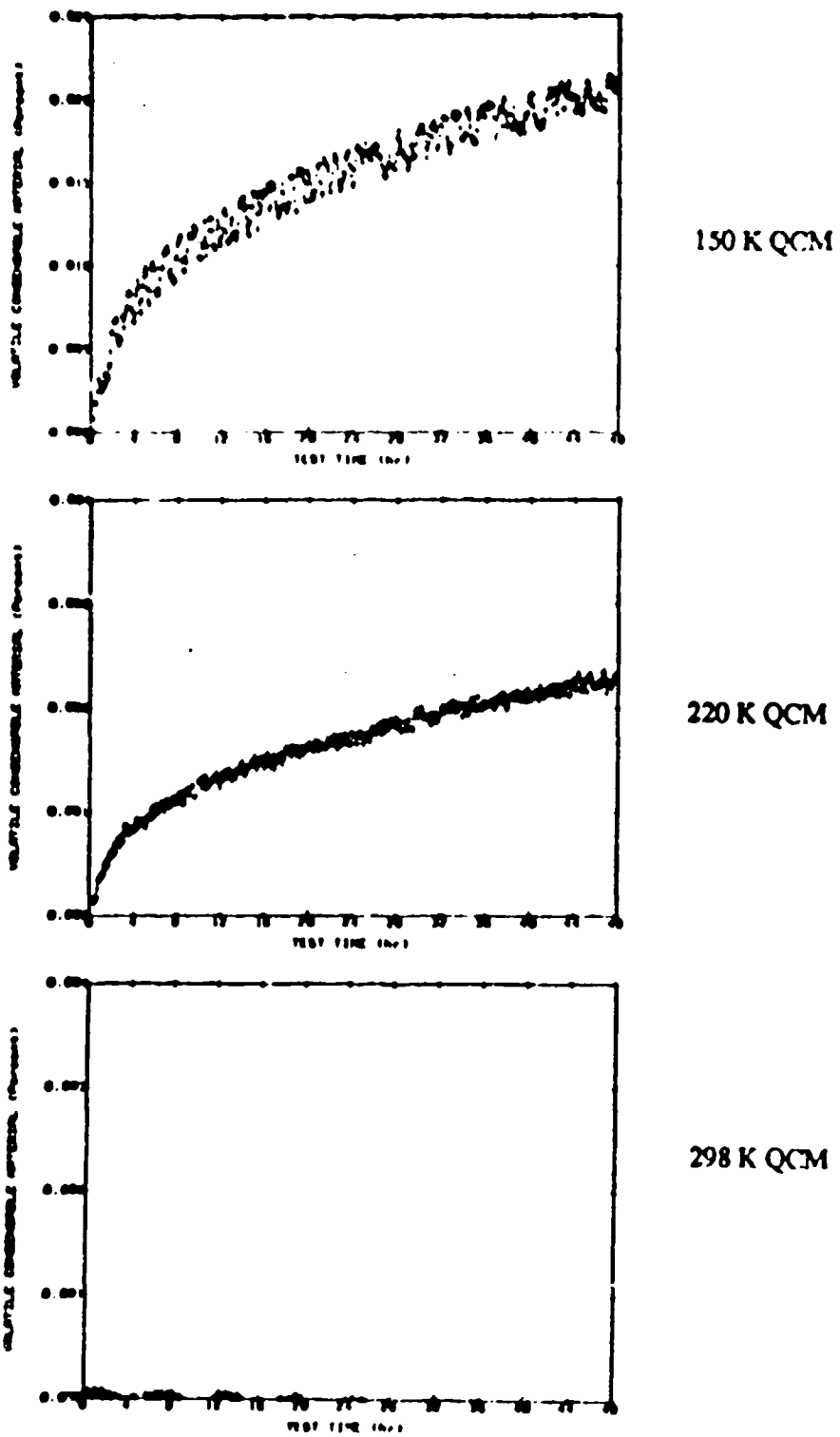


Fig. A-19 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC 93-500 Sample at 75°C.

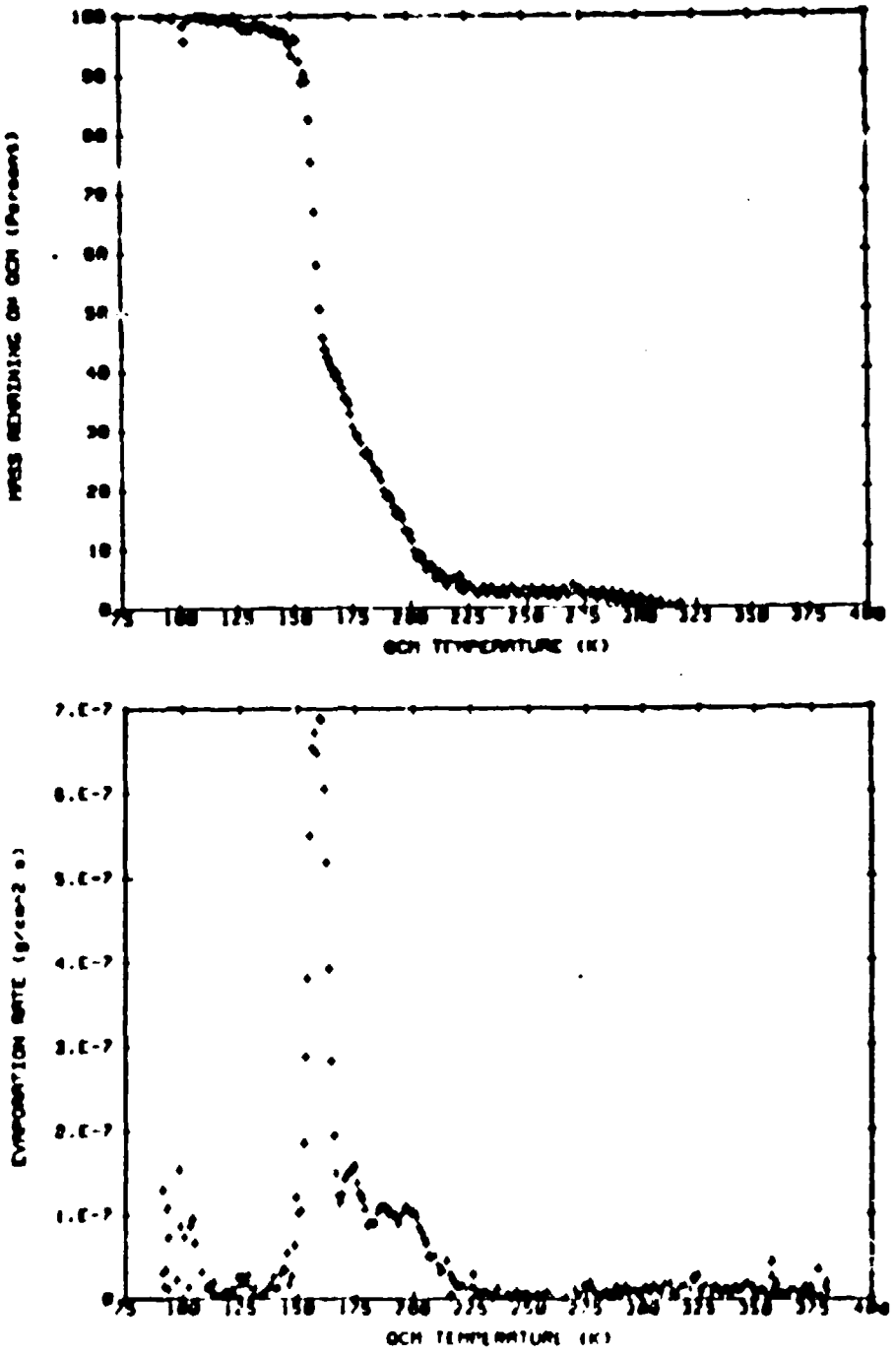


Fig. A-20 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC 93-500 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-6

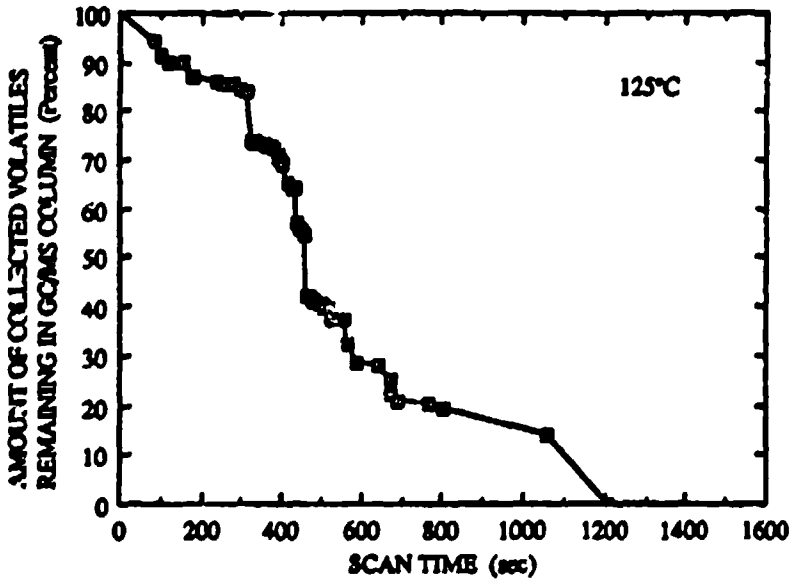
GC/MS Data for DC 93-500 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF ECTED SPECIES (percent)	SPECIES IDENTIFICATION
81	5.85	CO_2 artifact
101	2.08	
120	1.14	trimethyl silanol
177	2.92	hexamethyl disiloxane
237	1.04	
258	0.35	
298	1.04	siloxane
317	0.37	
327	9.97	siloxane
336	0.15	
365	0.37	
372	0.29	
383	0.21	
390	1.37	siloxane
395	0.54	
400	0.52	
406	0.85	
414	4.22	siloxane
428	0.55	
432	0.26	
440	7.23	siloxane
445	1.16	hydrocarbon
460	1.13	hydrocarbon
466	12.24	siloxane
475	0.54	hydrocarbon
482	0.45	hydrocarbon
491	0.46	hydrocarbon
503	0.54	siloxane
508	0.29	
519	0.23	
526	2.02	siloxane
561	4.76	siloxane
586	4.01	siloxane
640	0.22	siloxane
670	2.84	siloxane
670	2.97	siloxane
692	1.49	siloxane
765	0.20	siloxane
807	0.84	siloxane
1081	5.22	artifact
1205	14.23	artifact

Table A-7

GC/MS Data for DC 93-500 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
81	1.57	CO_2 artifact
88	7.94	trimethyl silane
93	1.49	tetramethyl silane
120	1.86	trimethyl silanol
150	3.12	
178	0.81	hexamethyl disiloxane
245	0.37	
280	0.35	
295	1.61	siloxane
299	4.01	siloxane
327	4.90	siloxane
387	1.96	siloxane
398	0.33	trimethyl benzene
404	0.55	
414	2.05	siloxane
417	0.31	
436	2.11	siloxane
441	5.94	siloxane
445	0.66	hydrocarbon
460	1.01	hydrocarbon
462	0.43	
466	8.99	siloxane
475	0.48	hydrocarbon
491	0.49	hydrocarbon
503	1.76	siloxane
516	0.60	
526	3.30	siloxane
559	0.30	
563	5.23	siloxane
587	5.66	siloxane
618	0.36	siloxane
640	0.68	siloxane
670	5.27	
692	4.53	siloxane
744	0.44	
769	2.99	siloxane
785	1.92	siloxane
806	7.86	siloxane
850	1.17	siloxane
870	0.59	siloxane
977	0.17	siloxane
1011	0.82	



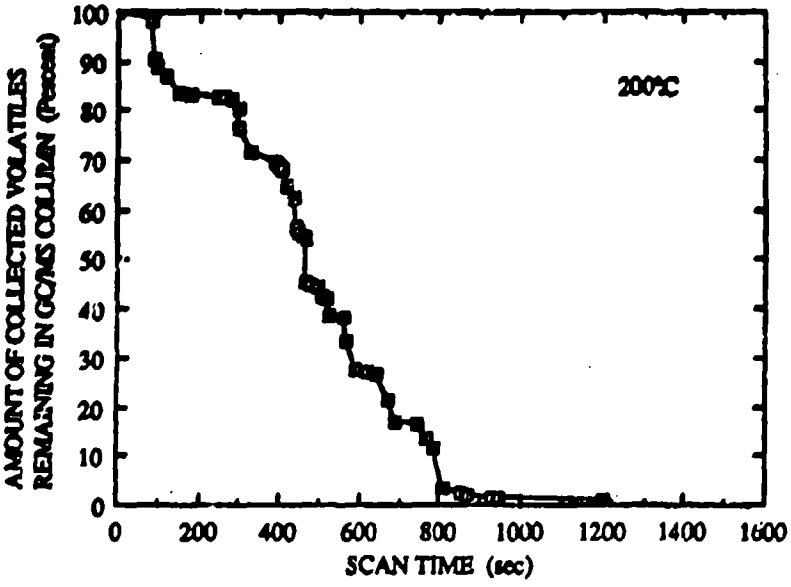


Fig. A-21 Amount of Collected Volatiles Remaining in GC/MS Column from DC 93-500 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : DC 6-1104 adhesive

DATE TEST STARTED : February 11, 1988

GC/MS DATA FILES :

125°C Test : JG8APR88C
200°C Test : JG6APR88C

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	8.55	8.55
Weight, pretest (g)	11.43941	11.36444
Total mass loss (%)	0.58	0.29
ISOTHERMAL TEST DATA :		
Test duration (h)	48	29
QCM/Temperature Data File	G0211	G0214
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0213Q	no data
Mass Spectrometer Data File	"	no data

COMMENTS :

- material is a controlled-volatility, silicone sealant produced by Dow Corning Corp.
- LMSC EPS# 40-191-0050169
- samples supplied by C.C. Chappell, LMSC Material & Process Laboratories (O/48-92)
- sample holders were aluminum tubes 1.0 inch long by 0.375 inch I.D.
- sample configuration (125°C test): 6 Al tubes filled with sample
- sample configuration (75°C test): 6 Al tubes filled with sample
- 75°C Isothermal Test terminated after 29 hours due to liquid nitrogen failure (Note 9, Sec. A.1.4)
- no QTA performed after 75°C Isothermal Test due to liquid nitrogen failure (Note 9, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

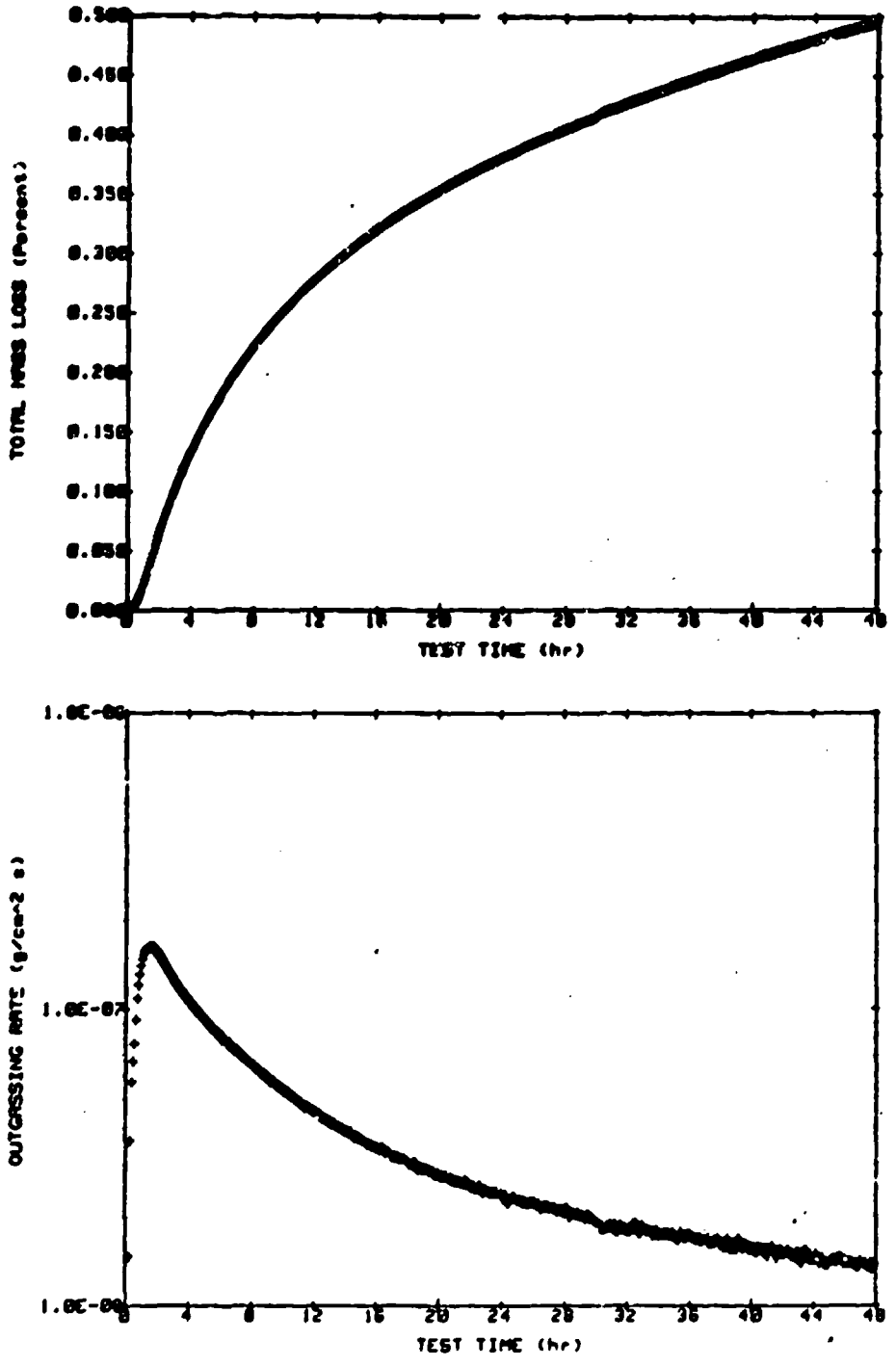
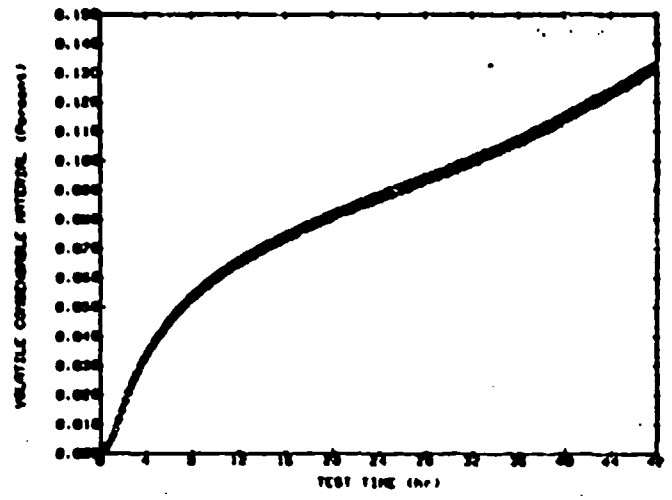
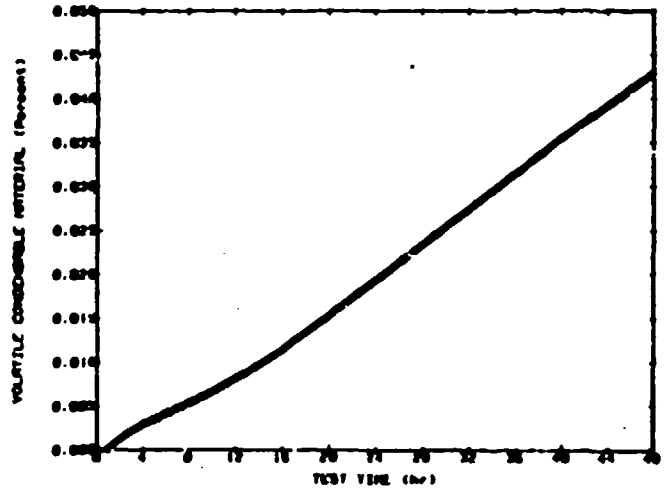


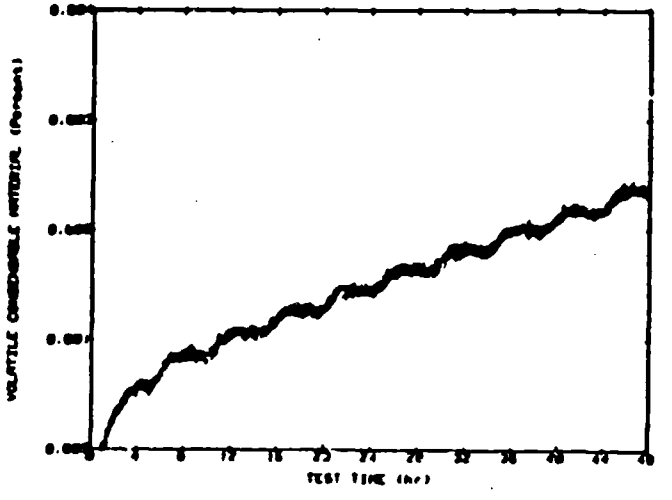
Fig. A-22 Total Mass Loss and Outgassing Rate as Functions of Time for a DC 6-1104 Sample at 125°C.



150 K QCM



220 K QCM



298 K QCM

Fig. A-23 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC 6-1104 Sample at 125°C.

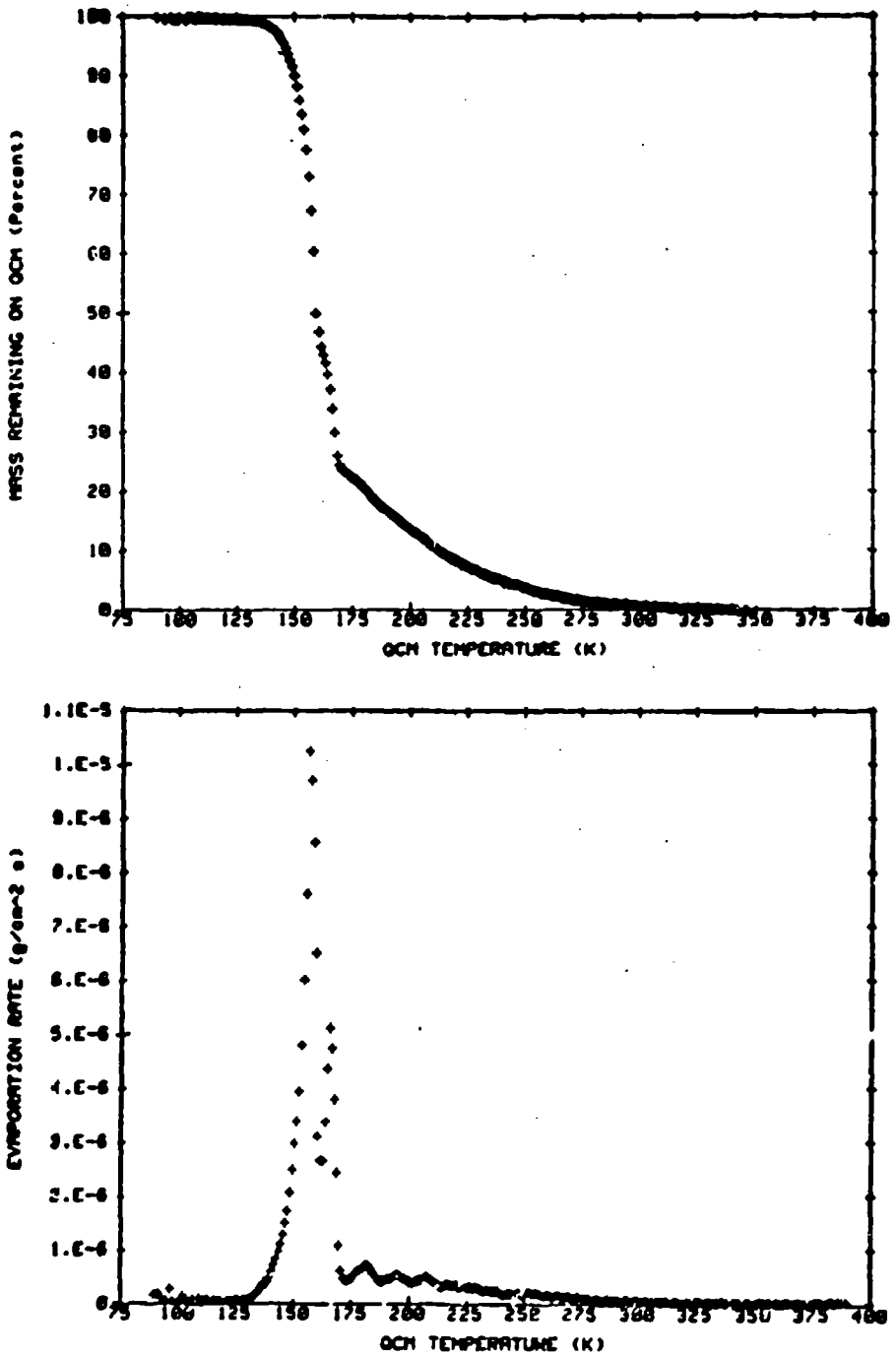


Fig. A-24 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC 6-1104 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

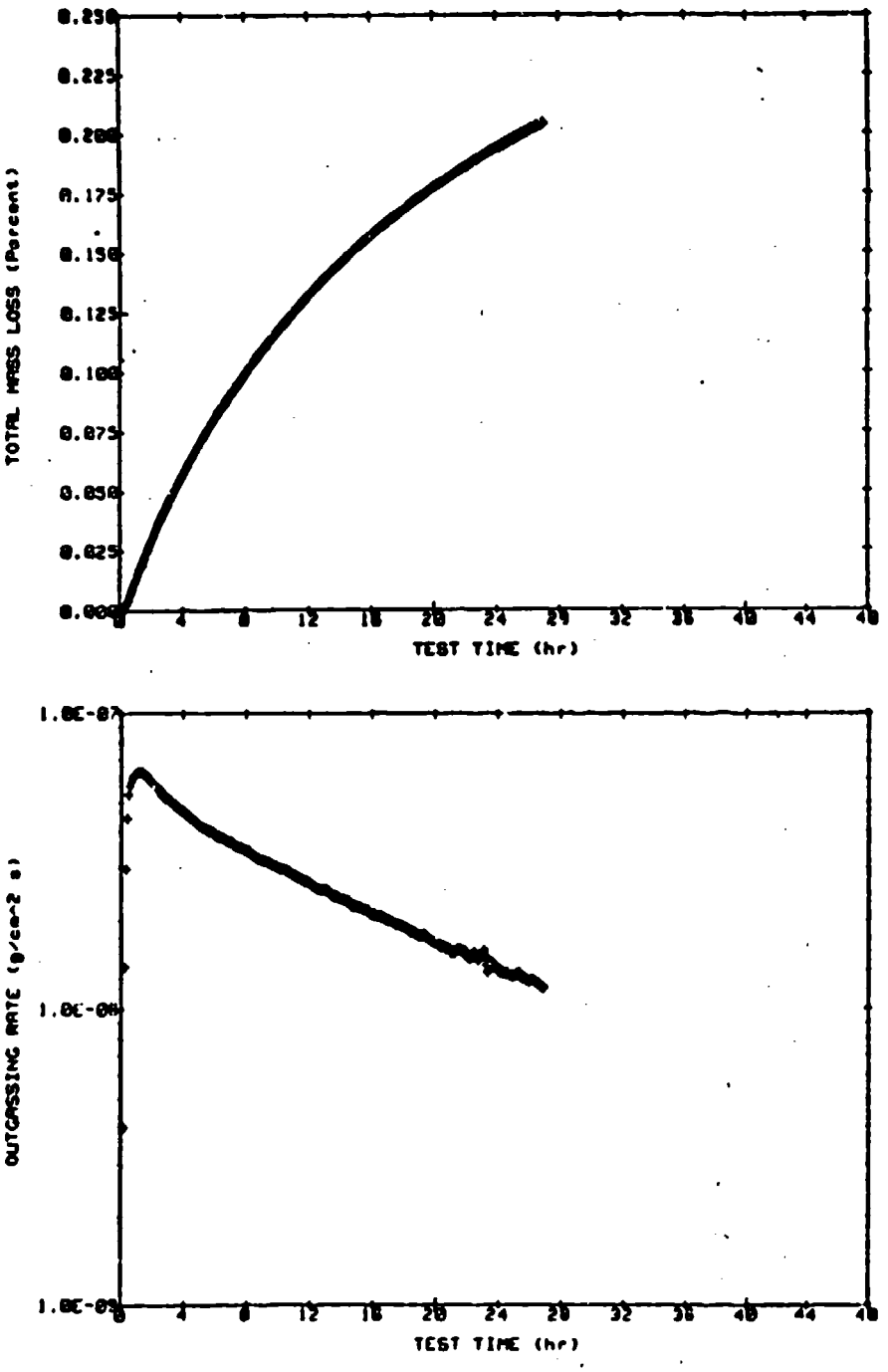


Fig. A-25 Total Mass Loss and Outgassing Rate as Functions of Time for a DC 6-1104 Sample at 75°C.

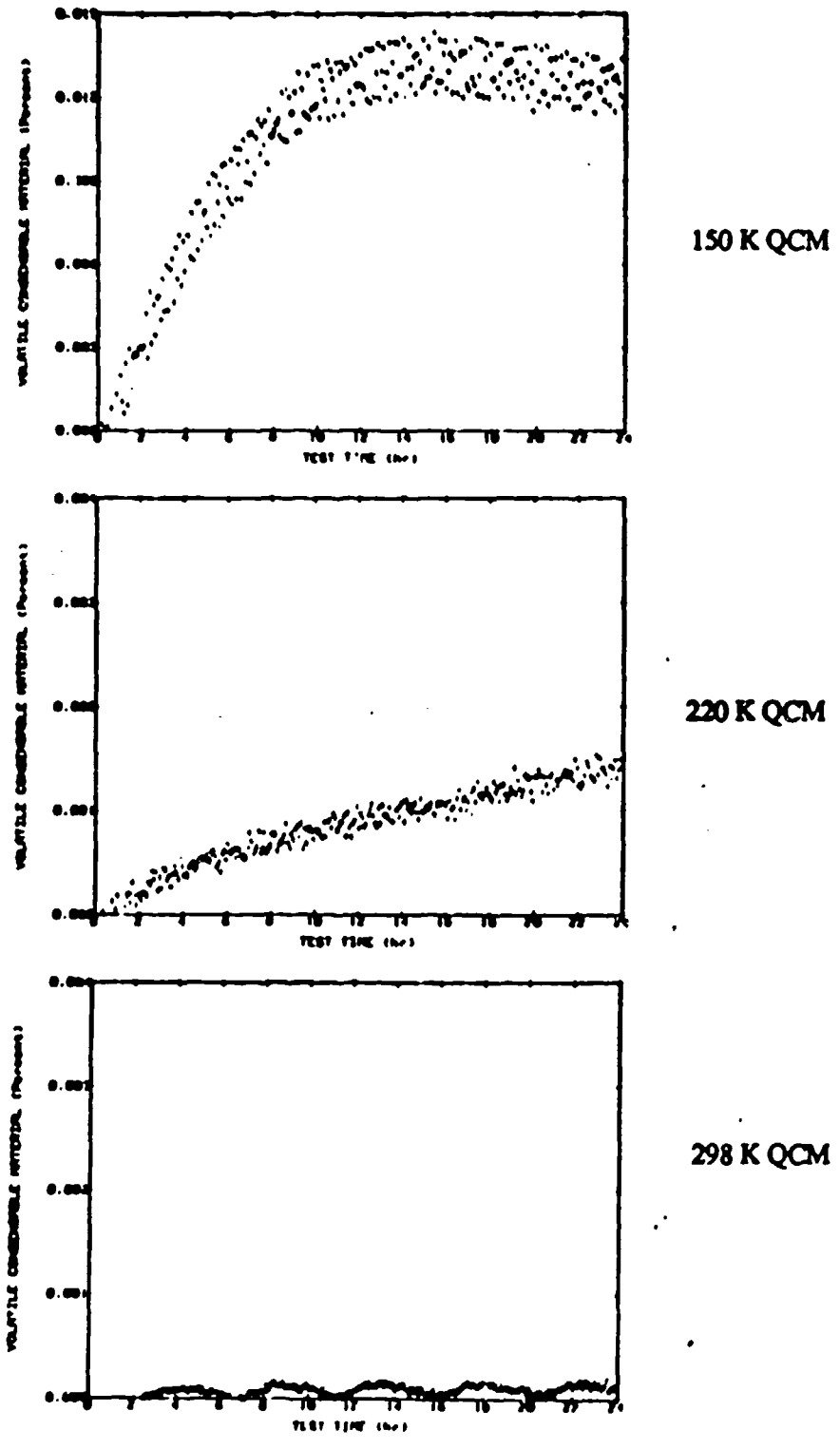


Fig. A-26 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC 6-1104 Sample at 75°C.

No Data Available - QCM Thermal Analysis Not Performed

Fig. A-27 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC 6-1104 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-8

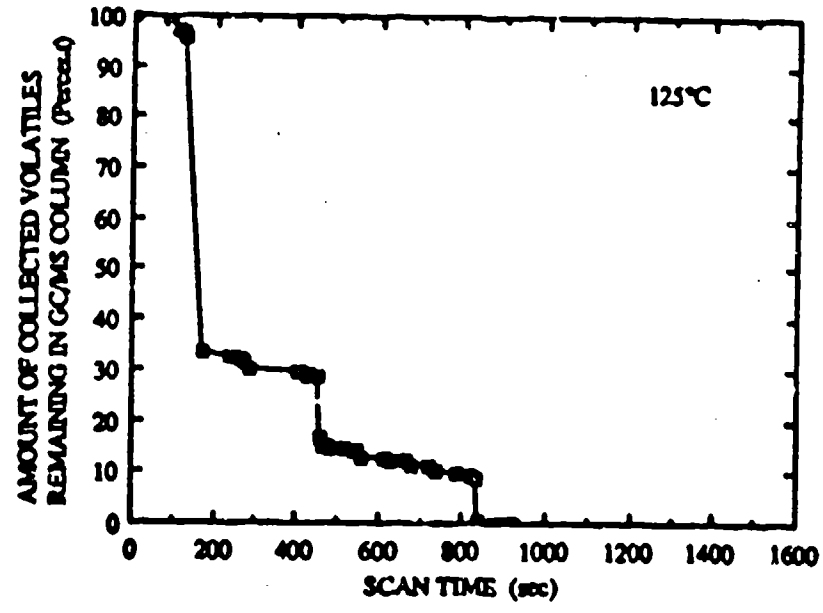
GC/MS Data for DC 6-1104 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
84	0.63	CO_2 artifact
92	0.25	
105	2.16	isopropanol
118	0.27	
123	0.94	trimethyl silanol
175	62.54	1-butanol
240	0.74	toluene artifact
250	0.13	
267	0.25	
271	0.49	
288	1.73	hexamethyl cyclotrisiloxane
403	0.25	
408	0.13	
426	0.57	
431	0.22	
453	0.17	
456	12.33	2-ethyl-1-hexanol
463	1.06	
478	0.38	
484	0.20	
516	0.11	
543	0.23	
545	0.20	
560	1.24	unspecified silicone compound
612	0.22	
629	0.36	
665	0.12	
678	0.75	
720	0.16	
722	0.12	
735	0.79	
784	0.65	
823	0.27	
832	0.55	
840	4.31	artifact
878	0.31	
921	0.17	

Table A-9

GC/MS Data for DC 6-1140 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
83	4.69	CO_2 artifact
98	0.41	
103	3.00	isopropanol
120	0.73	
122	3.14	trimethyl silanol
172	58.86	1-butanol
184	0.78	
244	1.05	toluene artifact
274	0.43	
291	3.92	hexamethyl cyclotrisiloxane
428	0.36	
458	9.46	2-ethyl-1-hexanol
562	0.76	
680	0.46	
736	0.75	
786	0.79	
834	0.61	
842	9.08	artifact seen in blank run
880	0.4	
923	0.33	



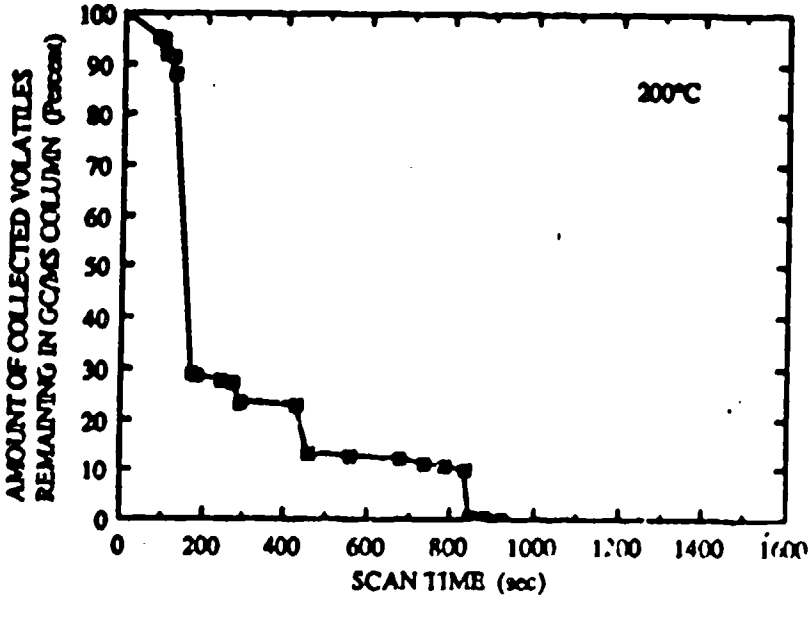


Fig. A-28 Amount of Collected Volatiles Remaining in GC/MS Column for DC 6-1104 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Kapton film (1 mil)

DATE TEST STARTED : February 19, 1988

GC/MS DATA FILES :

125°C Test : JG8APR88F
200°C Test : JG6APR88G

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	2090.32	2090.32
Weight, pretest (g)	3.758	3.770
Total mass loss (%)	no data	no data
ISOTHERMAL TEST DATA :		
Test duration (h)	24	24
QCM/Temperature Data File	G0219	G0221
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0220Q	G0222Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a polyimide plastic film (0.001 inch by 18 inch roll) produced by E.I. du Pont de Nemours & Co., Inc.
- LMSC EPS# 22-527-0000000
- samples supplied by J.J. Spaulding, LMSC Materials & Processes Engrg (O/62-92)
- sample configuration (125°C test): 2 sheeets - each 9.00 inch by 9.00 inch by 1 mil
- sample configuration (75°C test): 2 sheets - each 9.00 inch by 9.00 inch by 1 mil
- final sample weights very questionable - unable to confirm (Note 4, Sec. A.1.4)
- no QTA performed on the 298 K QCM after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

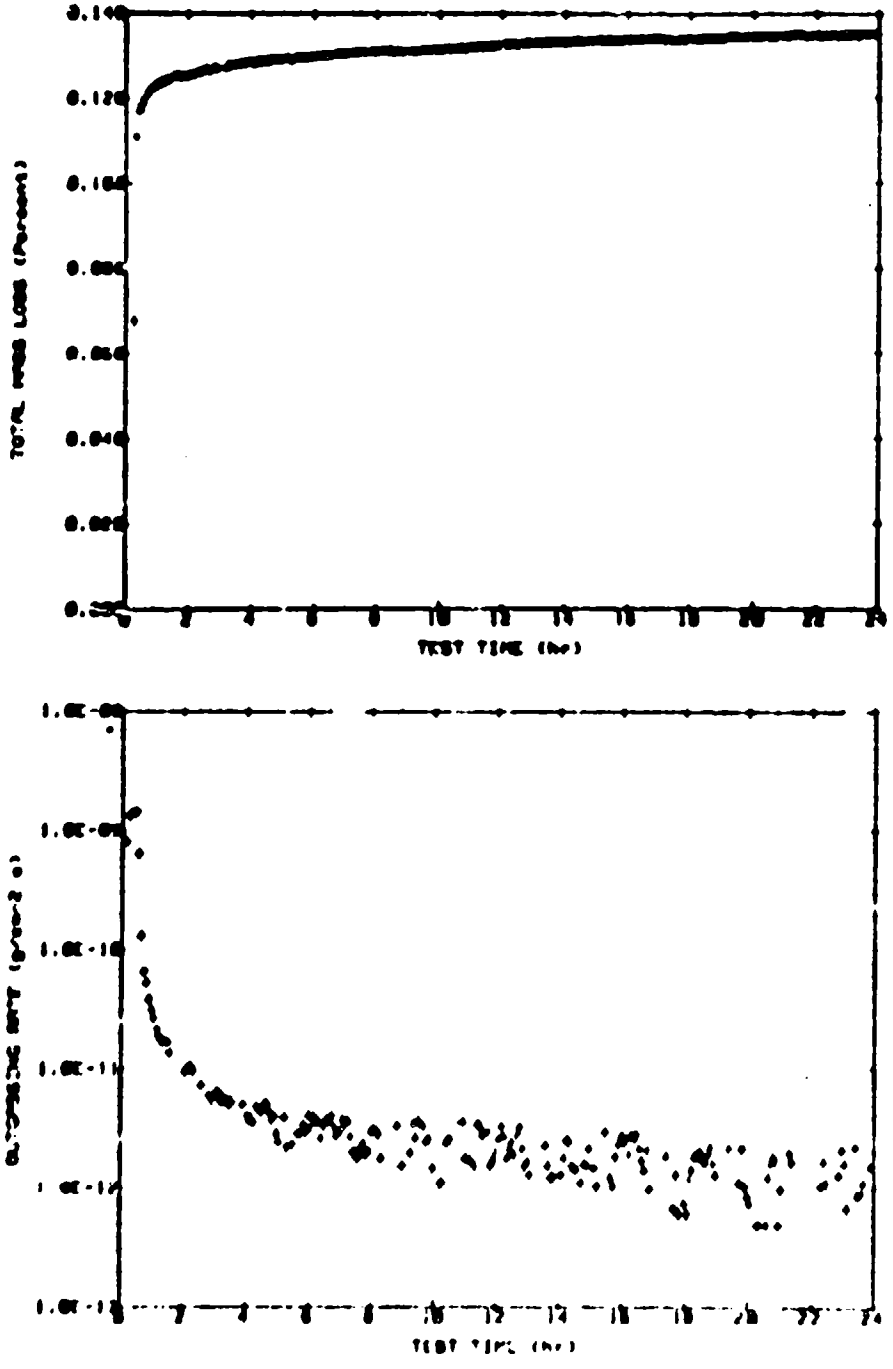


Fig. A-29 Total Mass Loss and Outgassing Rate as Functions of Time for a Kapton Sample at 125°C

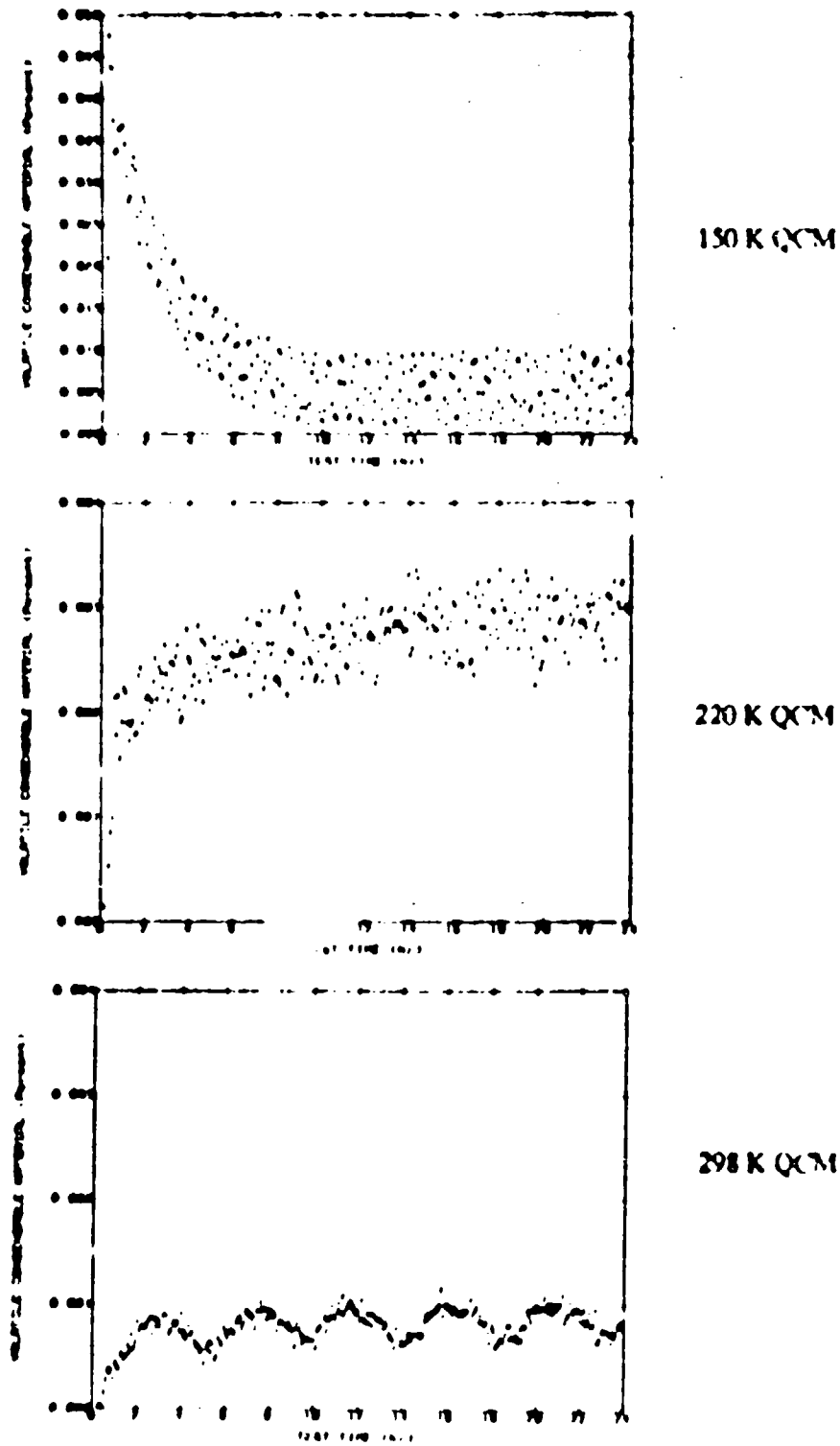


Fig. A-30 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Kapton Sample at 125°C.

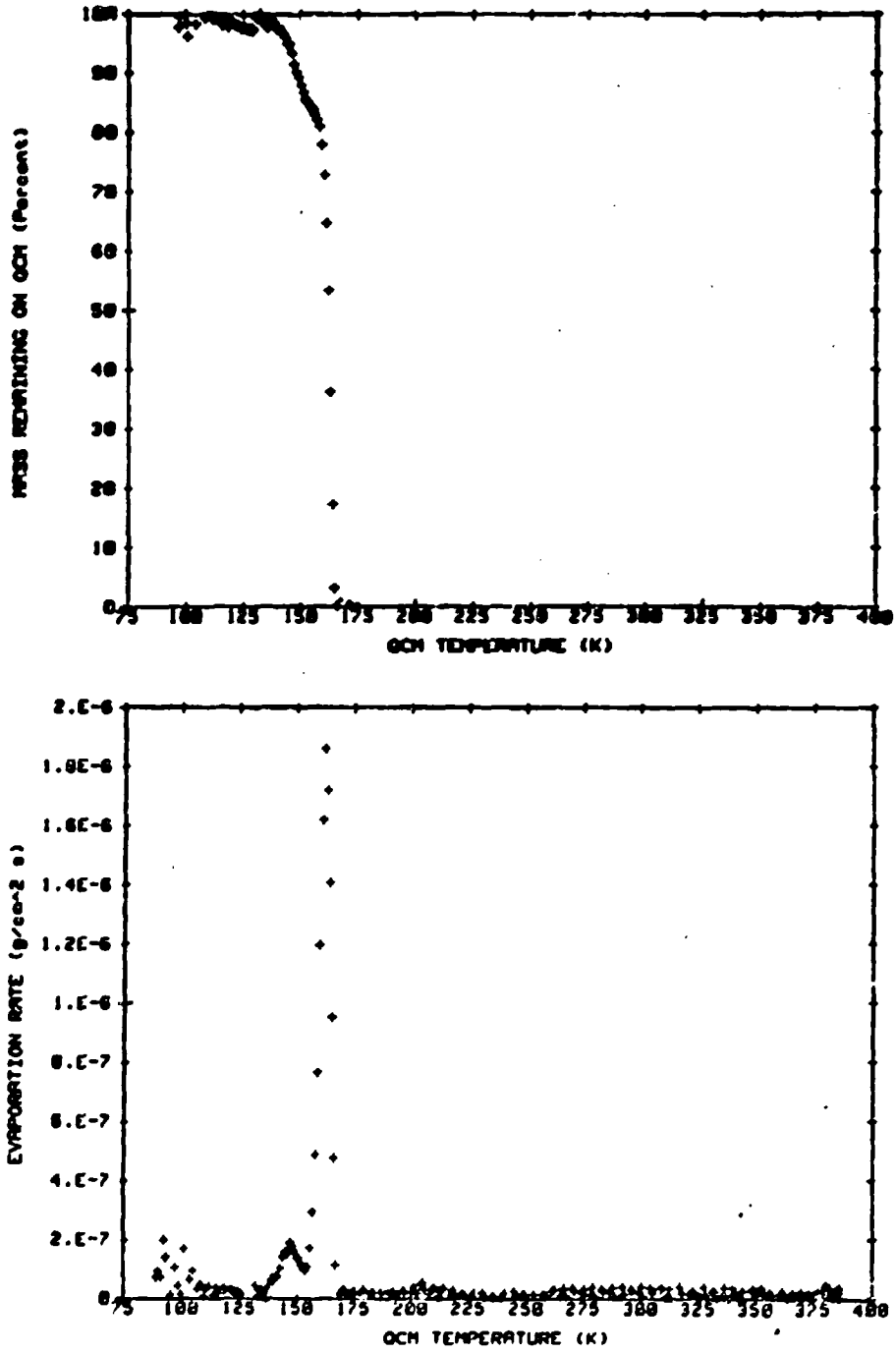


Fig. A-31 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Kapton Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

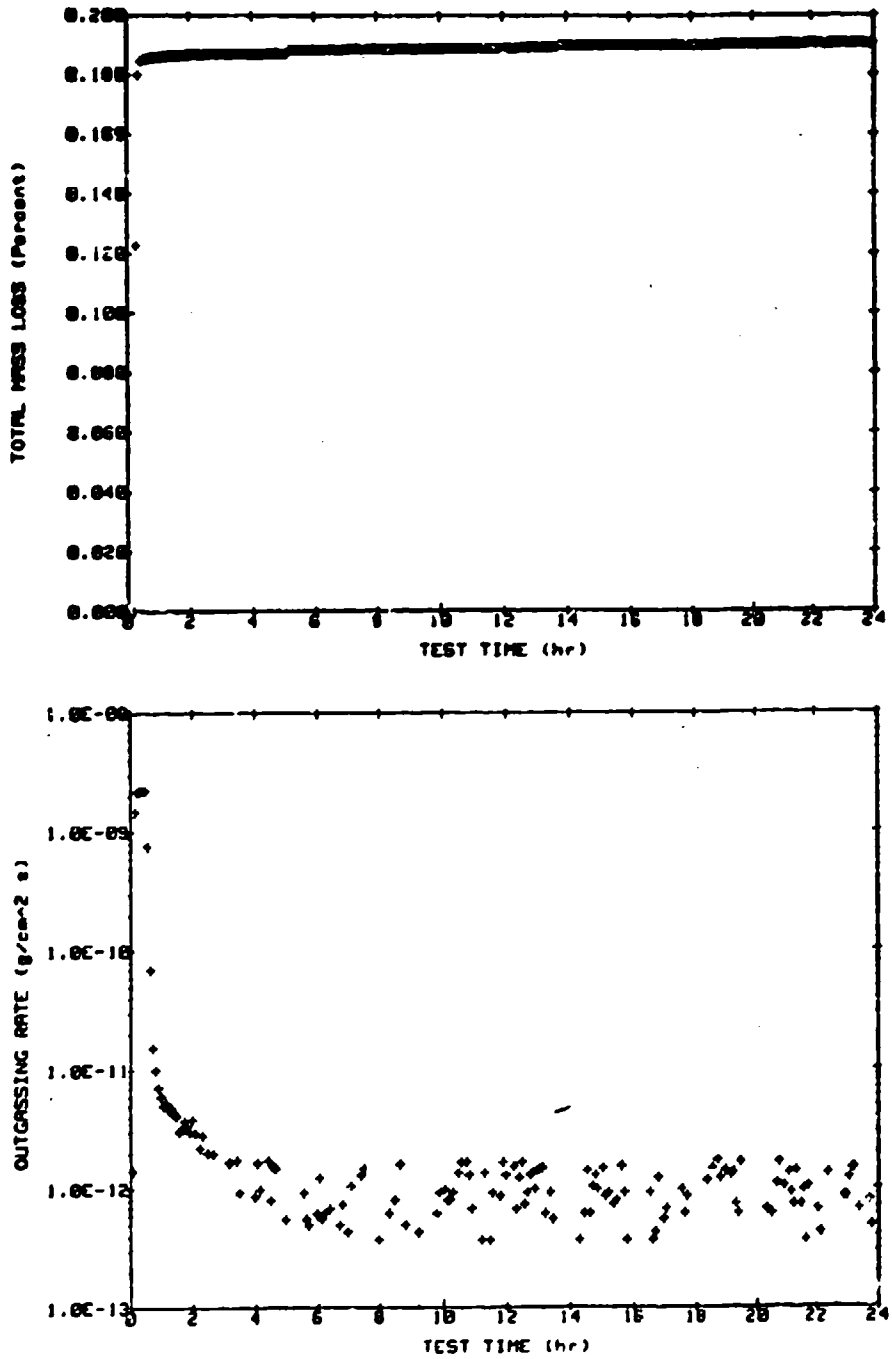


Fig. A-3 Total Mass Loss and Outgassing Rate as Functions of Time for a Kapton Sample at 75°C.

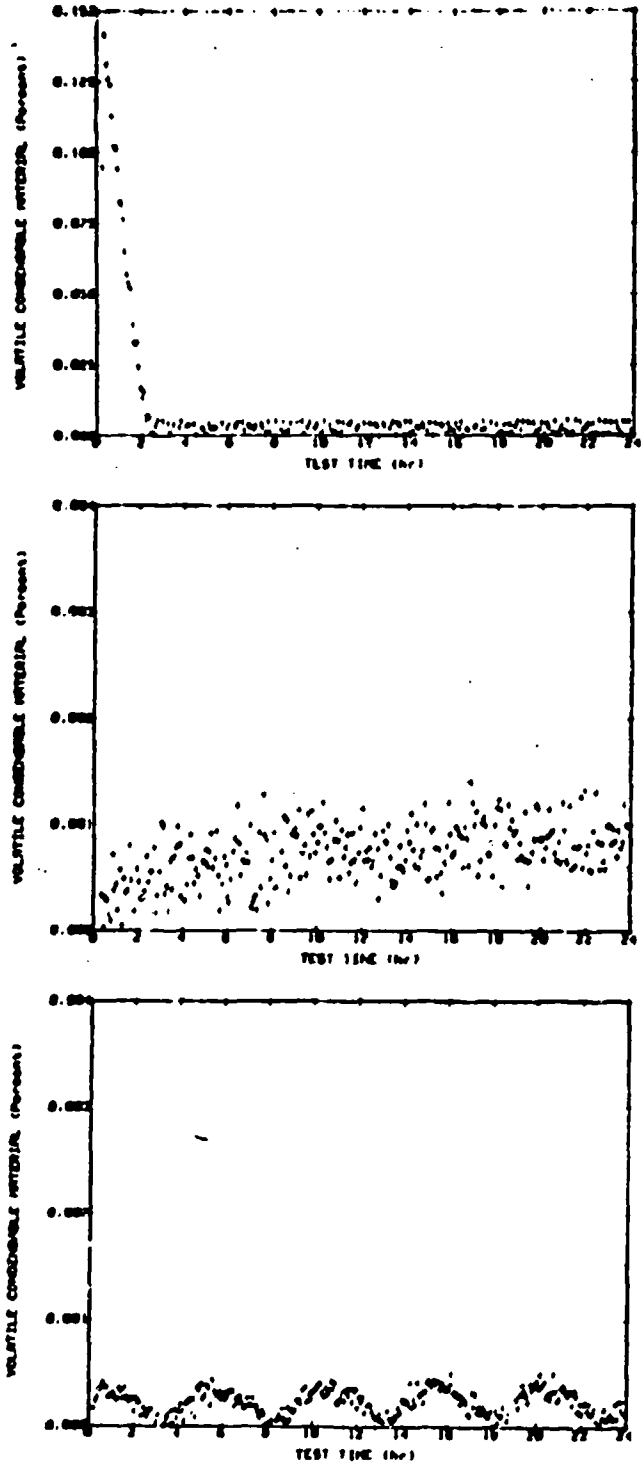


Fig. A-33 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Kapton Sample at 75°C.

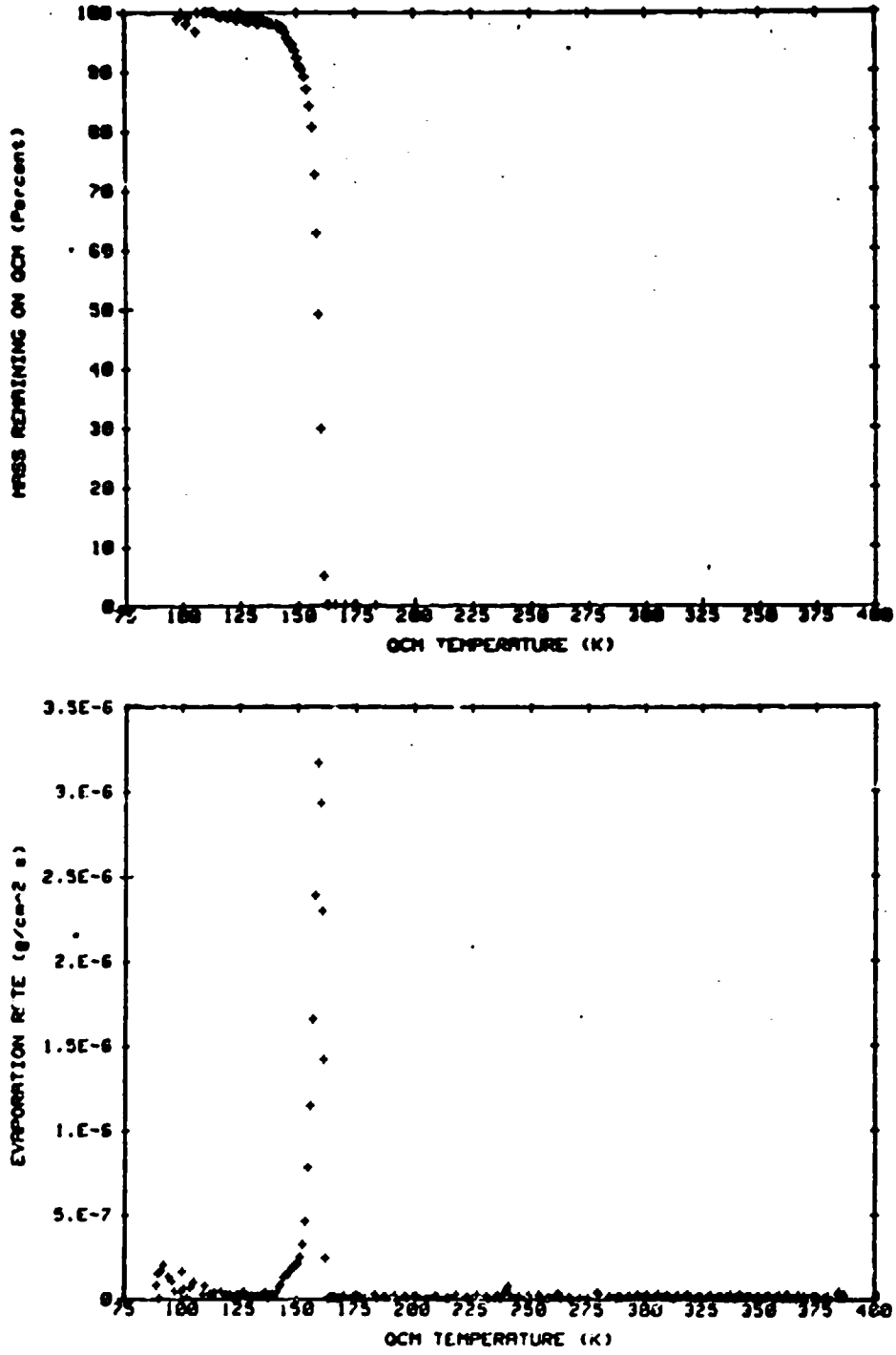


Fig. A-34 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Kapton Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-10

GC/MS Data for Kapton at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

NO CONTAMINANT SPECIES FOUND IN THIS SAMPLE AT THIS TEMPERATURE

Table A-11

GC/MS Data for Kaptop at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
84	36.65	CO_2 artifact
90	1.11	propane
98	1.16	
104	6.19	acetone isopropanol
108	0.61	
111	0.87	
121	2.24	C_6H_{14}
127	0.85	
134	2.27	
148	1.05	
161	14.69	acetic acid
167	2.46	benzene artifact
170	1.22	aliphatic hydrocarbon artifact
184	2.88	
231	0.80	
244	3.29	toluene artifact
405	0.81	
422	8.16	phenol
842	12.71	artifact seen in blank run

NO CONTAMINANT SPECIES FOUND IN THE 125°C SAMPLE

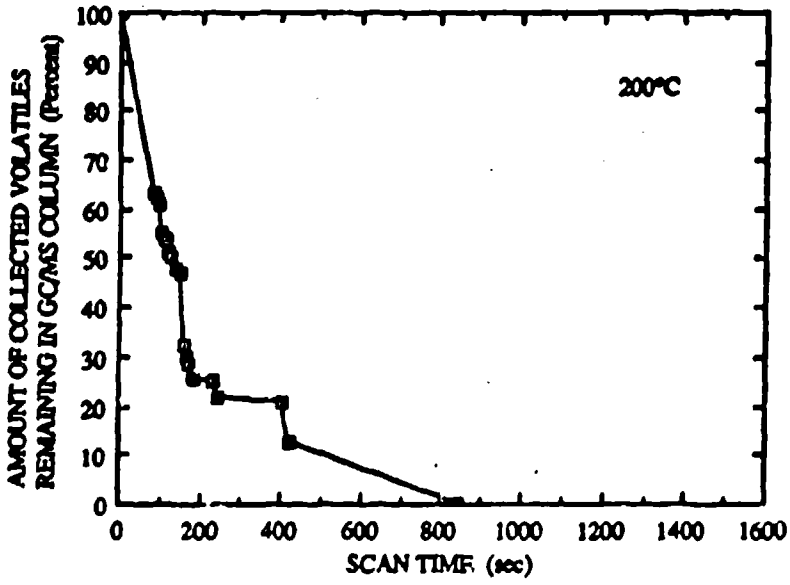


Fig. A-35 Amount of Collected Volatiles Remaining in GC/MS Column from Kapton at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Mylar film (5 mil)

DATE TEST STARTED : February 27, 1988

GC/MS DATA FILES :

125°C Test : JG8APR88D
200°C Test : JG6APR88D

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	522.58	522.56
Weight, pretest (g)	4.58020	4.64210
Total mass loss (%)	no data	no data
ISOTHERMAL TEST DATA :		
Test duration (h)	24	24
QCM/Temperature Data File	G0227	G0229
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0228Q	G0301Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a polyethylene terephthalate film (0.005 inch by 48 inch roll) produced by E.I. du Pont de Nemours & Co., Inc.
- LMSC EPS# 22-501-0005694
- samples supplied by J.J. Spaulding, LMSC Materials & Processes Engrg (O/62-92)
- sample configuration (125°C test): 1 sheeet - 9.00 inch by 4.50 inch by 5 mil
- sample configuration (75°C test): 1 sheeet - 9.00 inch by 4.50 inch by 5 mil
- final sample weights very unstable - unable to confirm (Note 4, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

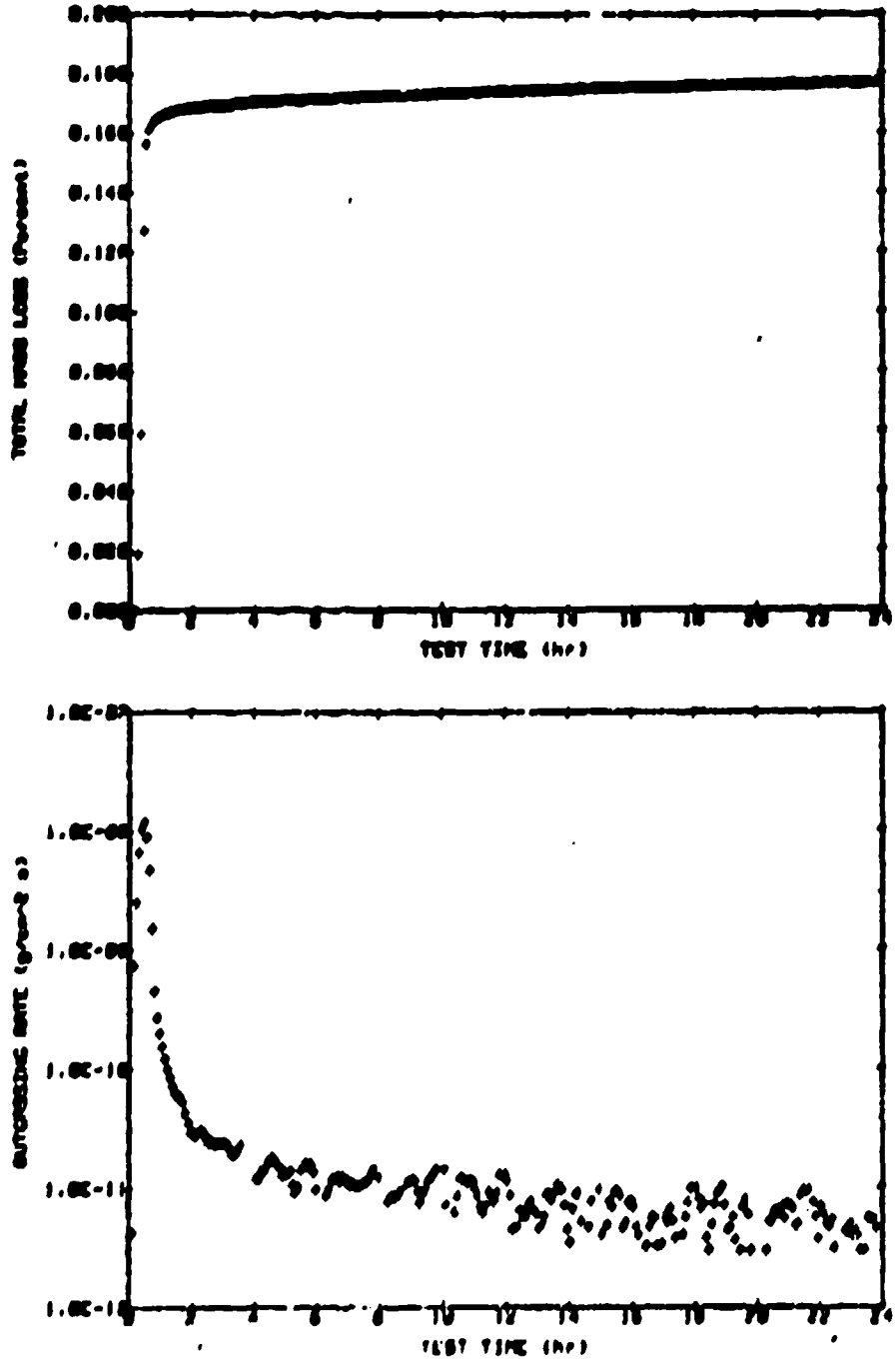


Fig. A-36 Total Mass Loss and Outgassing Rate as Functions of Time for a Mylar Sample at 125°C.

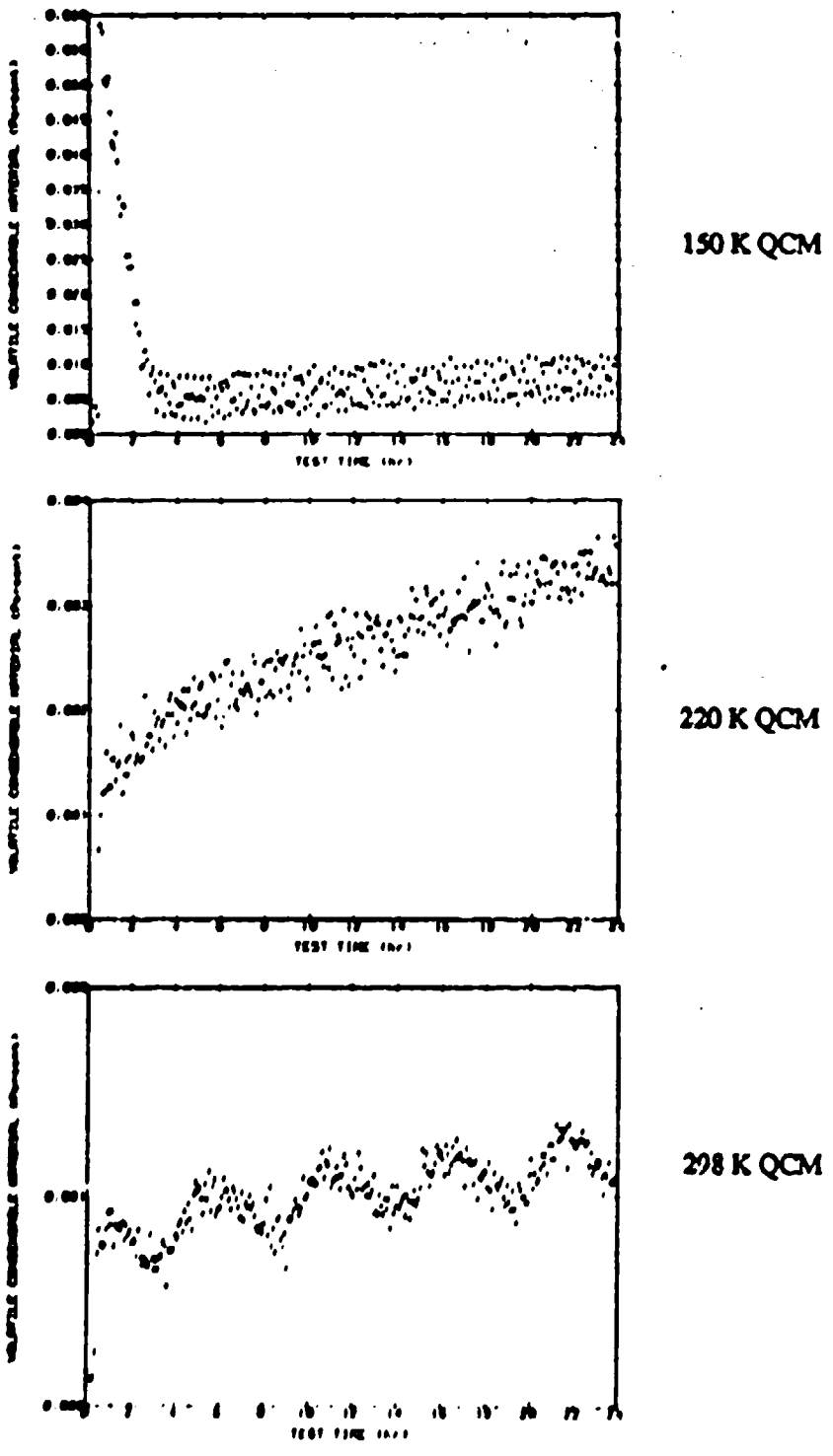


Fig. A-37 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Mylar Sample at 125°C.

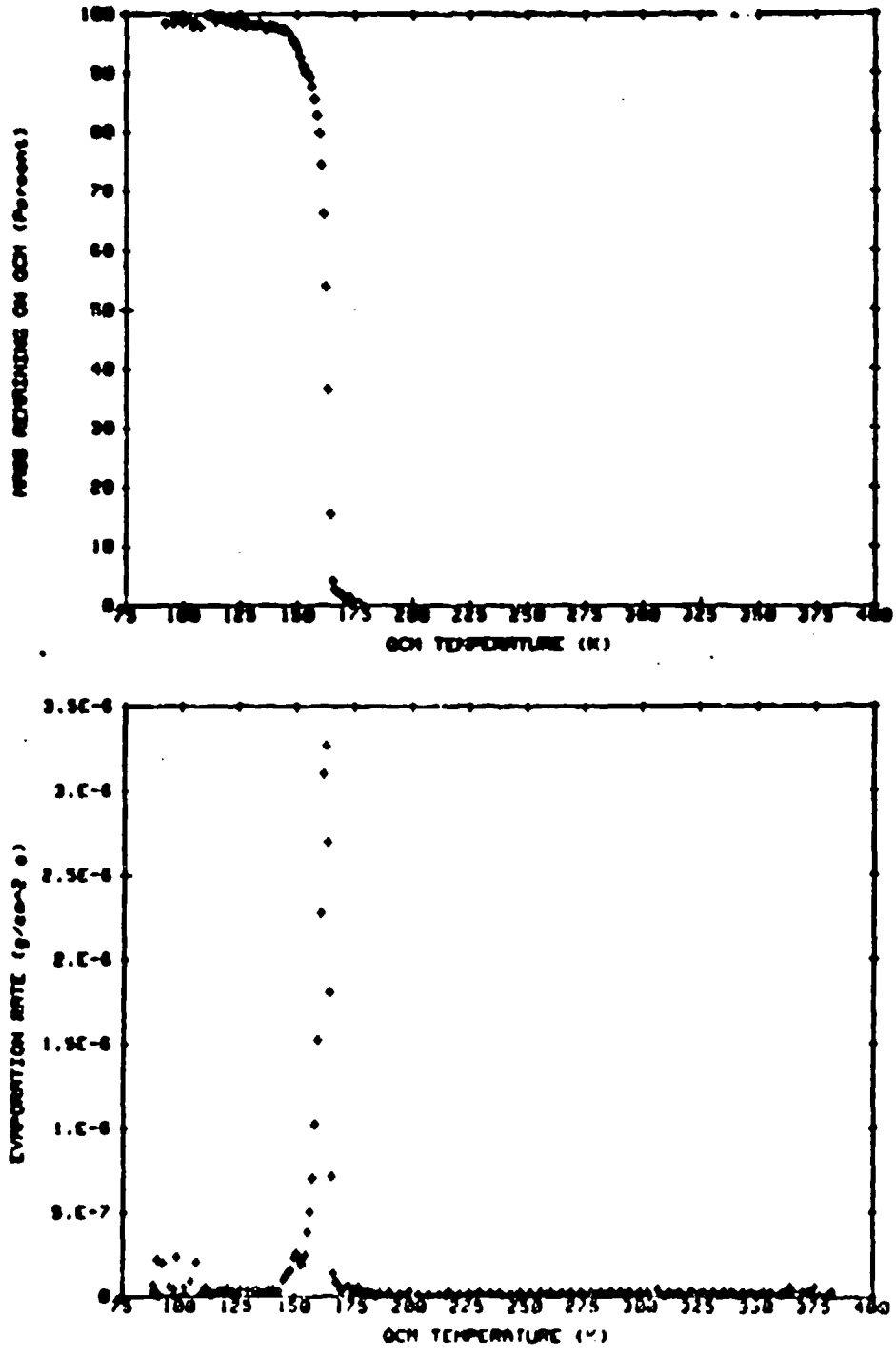


Fig. A-38 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Mylar Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

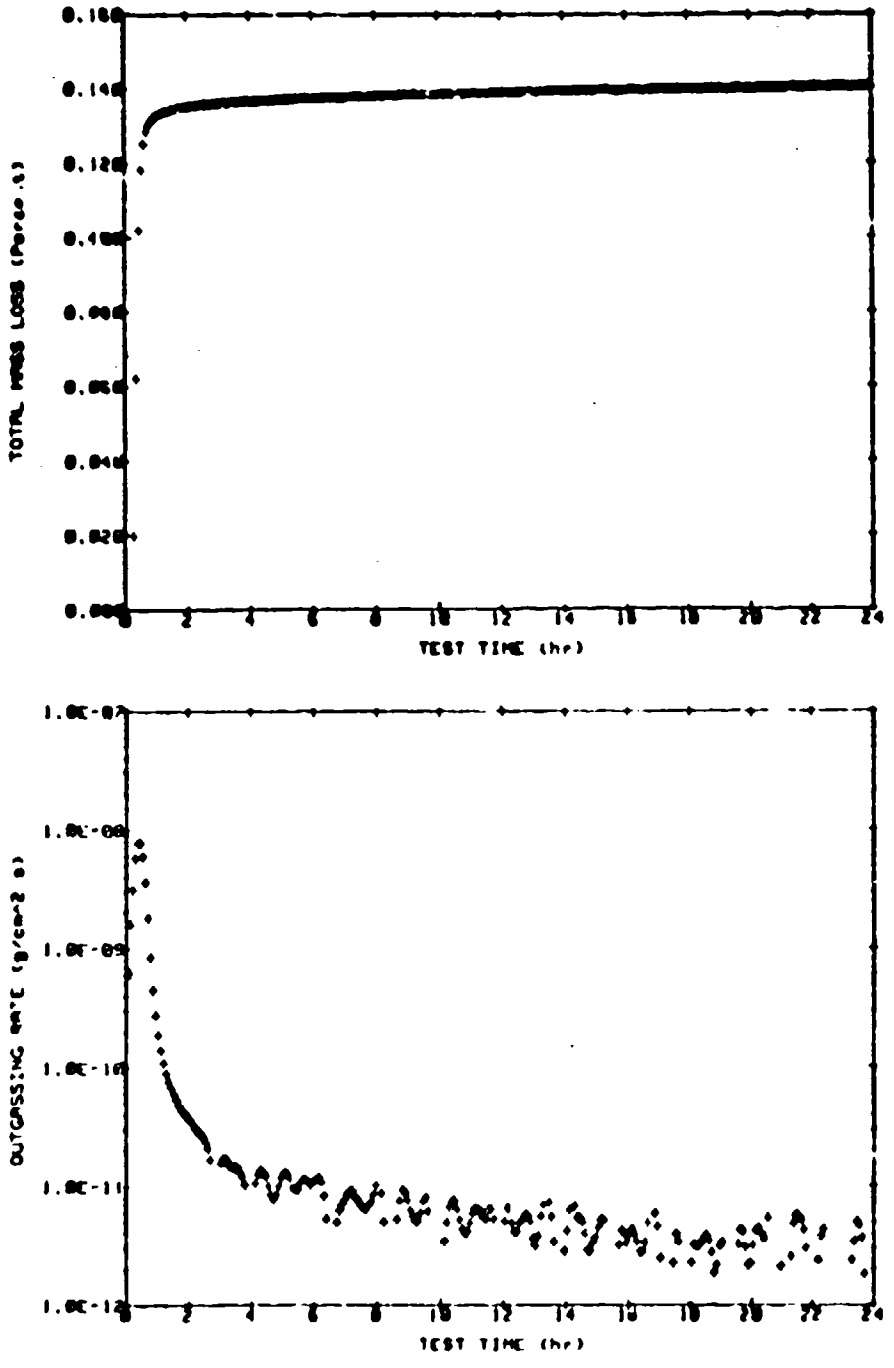


Fig. A-39 Total Mas Loss and Outgassing Rate as Functions of Time for a Mylar Sample at 75°C.

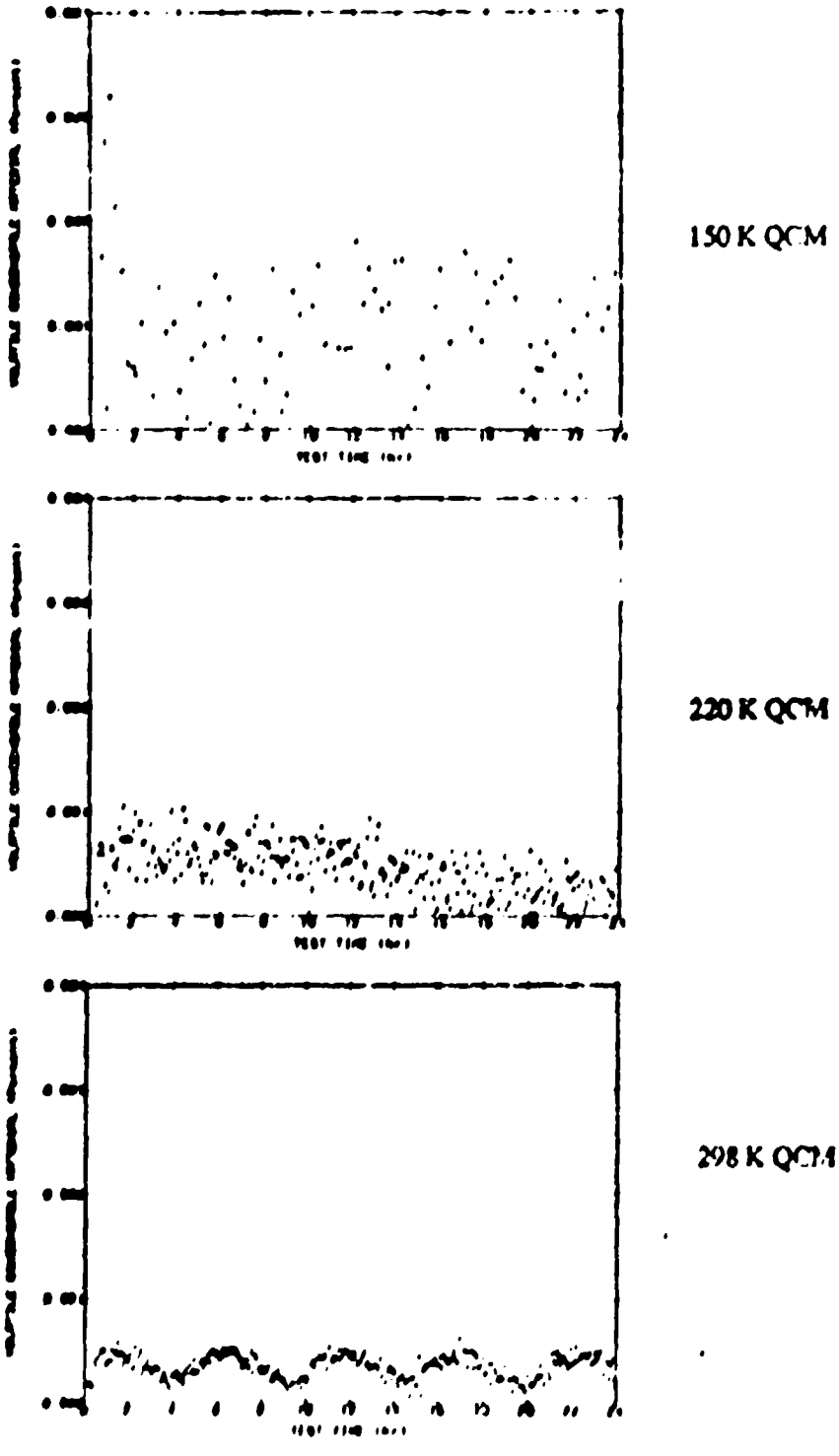


Fig. A-40 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Mylar Sample at 75°C.

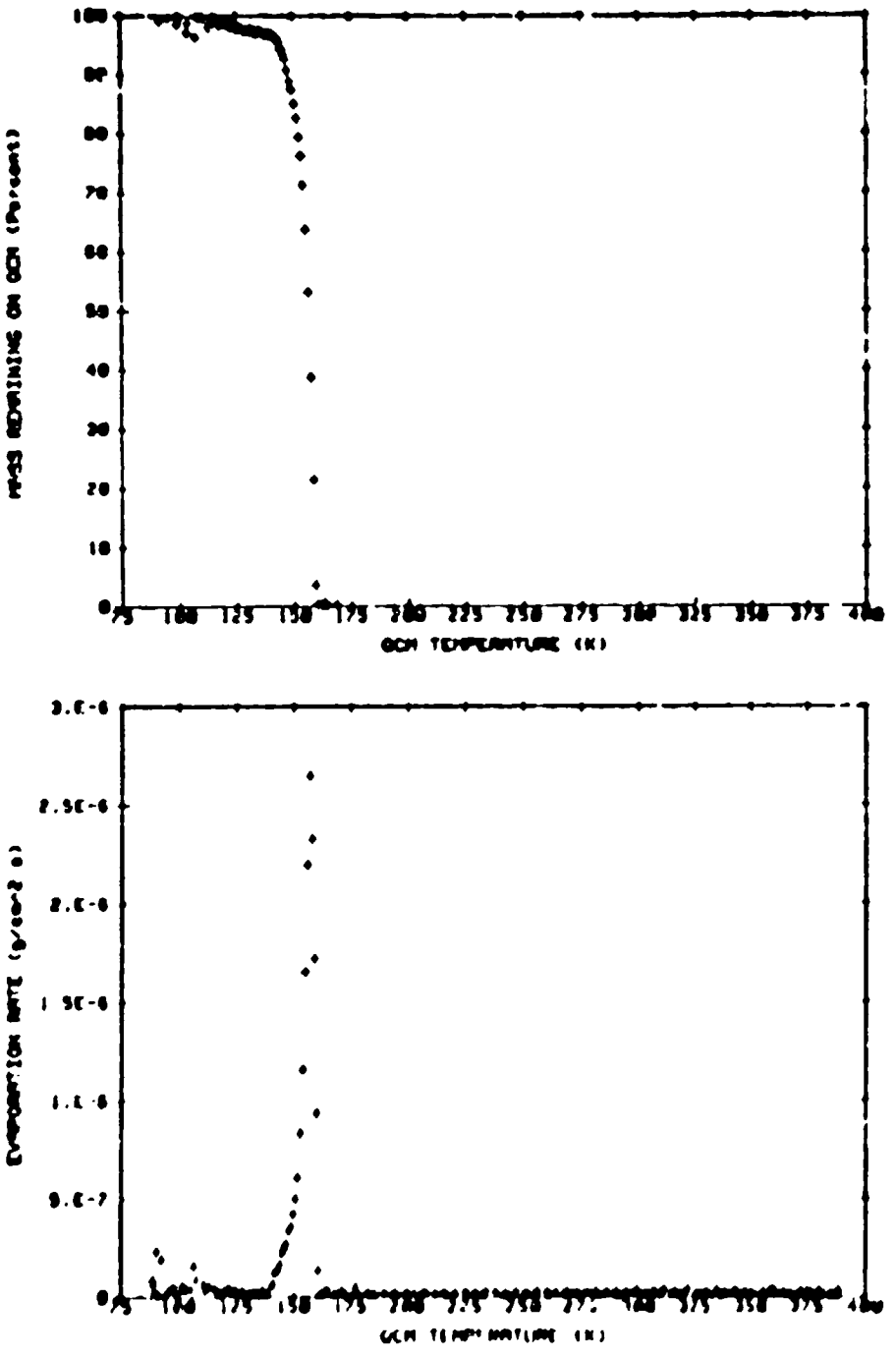


Fig. 41 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Mylar Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-12

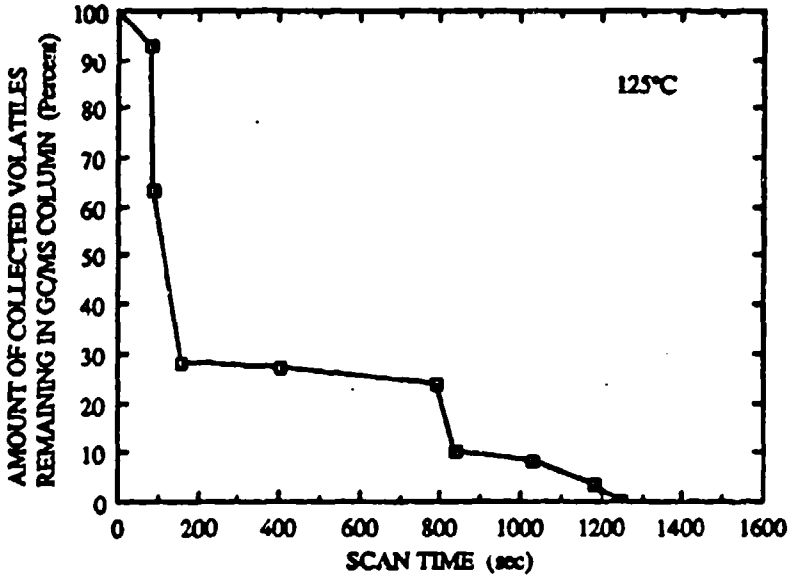
GC/MS Data for Mylar at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
82	7.16	CO_2 artifact
88	29.50	propane
159	35.47	2-methyl-2-propenol & unknown
404	0.77	artifact
791	3.57	
840	13.28	artifact
1030	2.08	phthalate ester
1183	4.62	
1247	3.56	

Table A-13

GC/MS Data for Mylar at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
87	40.94	CO_2 artifact
95	5.66	propane
105	1.60	2-methyl butane
111	1.17	
130	1.95	C_6H_{14}
170	41.08	2-methyl-1, 3-dioxolane
179	0.82	
193	3.38	aliphatic hydrocarbon artifact
238	0.91	
251	1.36	toluene artifact
408	1.12	artifact



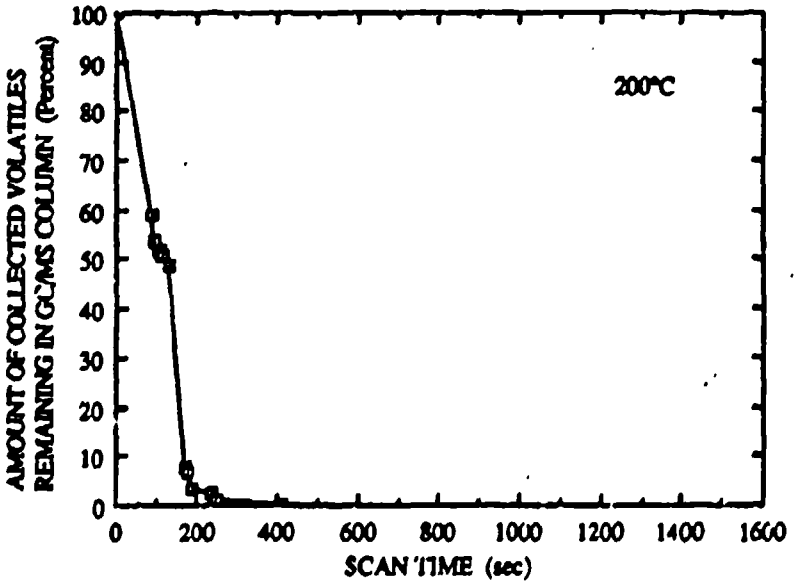


Fig. A-42 Amount of Collected Volatiles Remaining in GC/MS Column from Mylar at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : FEP Teflon film (1 mil)

DATE TEST STARTED : February 23, 1988

GC/MS DATA FILES :

125°C Test : JG8APR88E
200°C Test : JG6APR88E

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	2090.32	2090.32
Weight, pretest (g)	5.6330	5.60420
Total mass loss (%)	no data	no data
ISOTHERMAL TEST DATA :		
Test duration (h)	24	24
QCM/Temperature Data File	G0223	G0225
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0224Q	G0226Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a fluorinated ethylene propylene plastic film (0.001 inch by 48 inch roll) produced by E.I. du Pont de Nemours & Co., Inc.
- LMSC EPS# 22-304-0000000
- samples supplied by J.J. Spaulding, LMSC Materials & Processes Engrg (O/62-92)
- sample configuration (125°C test): 2 sheeets - each 9.00 inch by 9.00 inch by 1 mil
- sample configuration (75°C test): 2 sheeets - each 9.00 inch by 9.00 inch by 1 mil
- final sample weights very unstable - unable to confirm (Note 4, Sec. A.'.4)
- mass spectrometer scanning m/e = 10 to 500

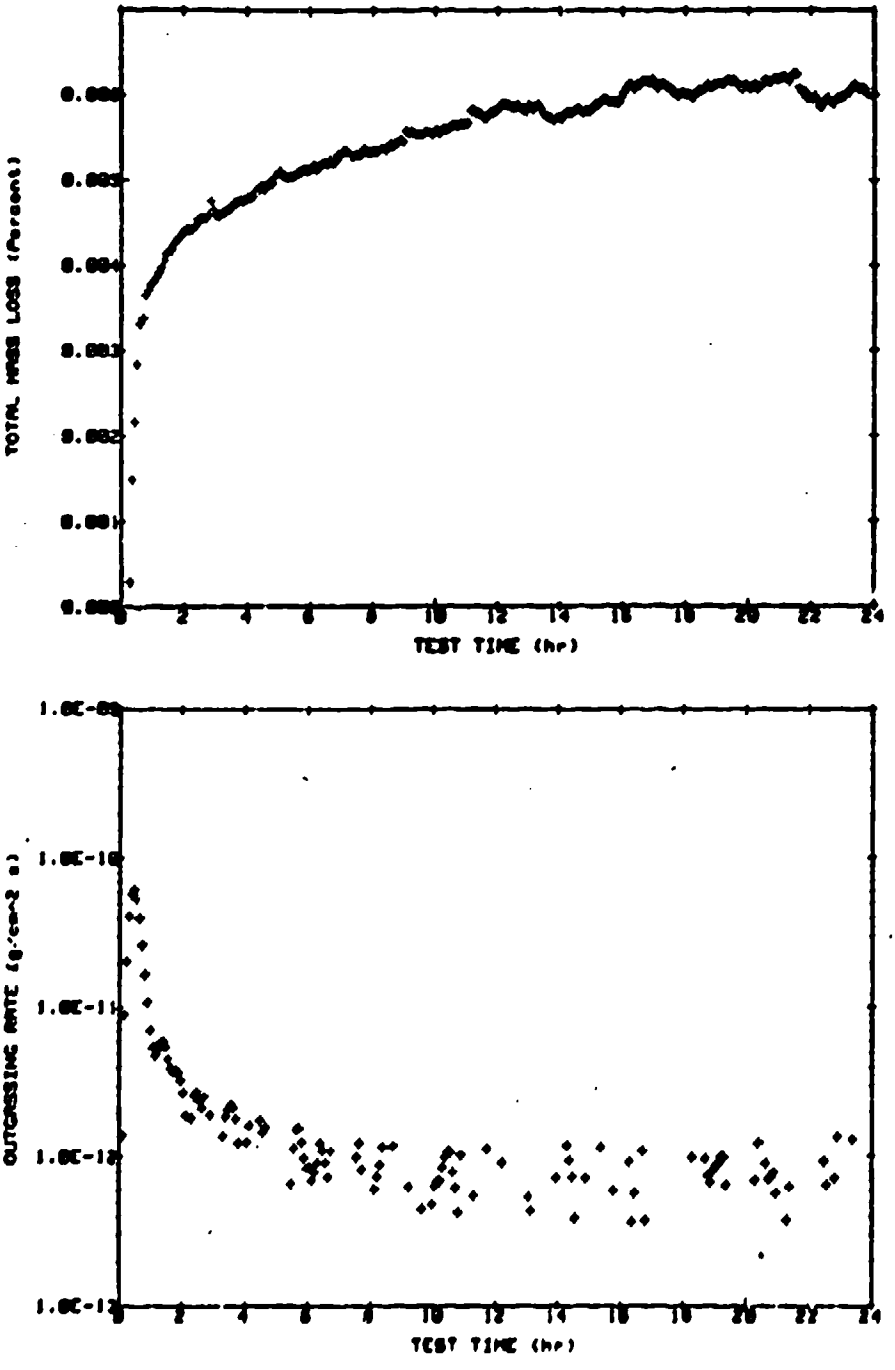


Fig. A-43 Total Mass Loss and Outgassing Rate as Functions of Time for an FEP Teflon Sample at 125°C.

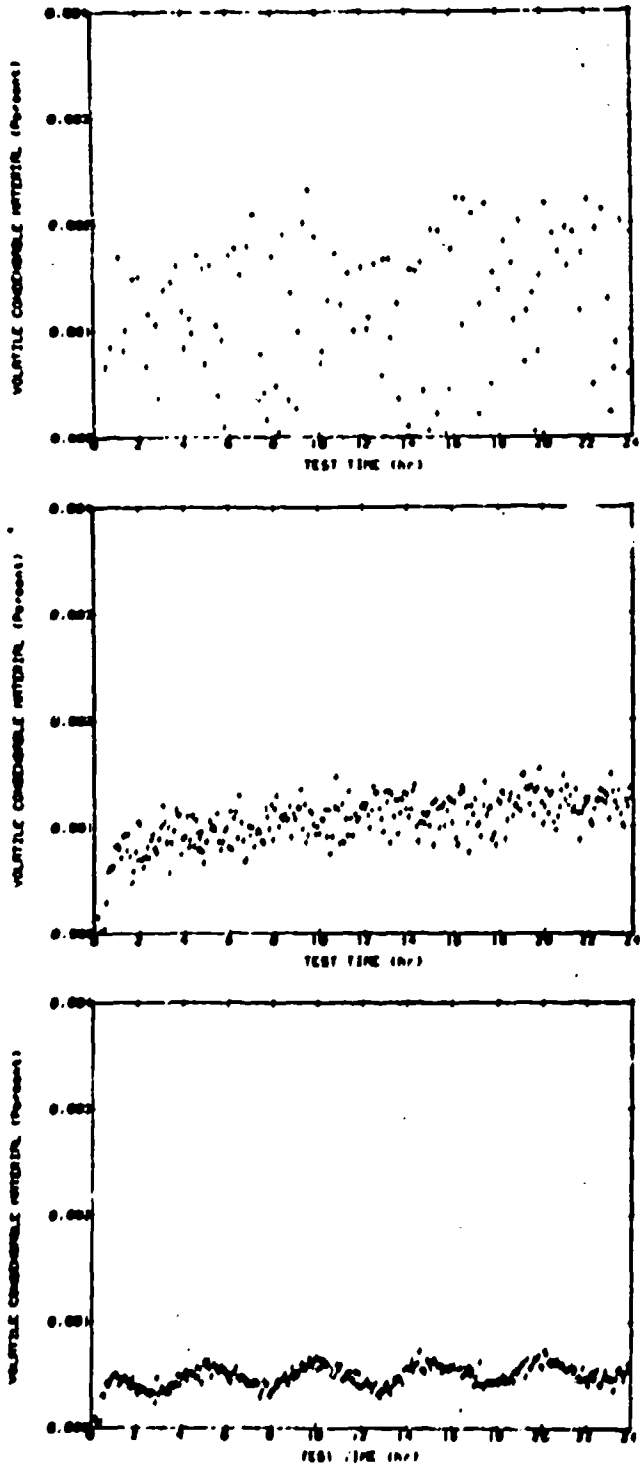


Fig. A-44 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an FEP Teflon Sample at 125°C.

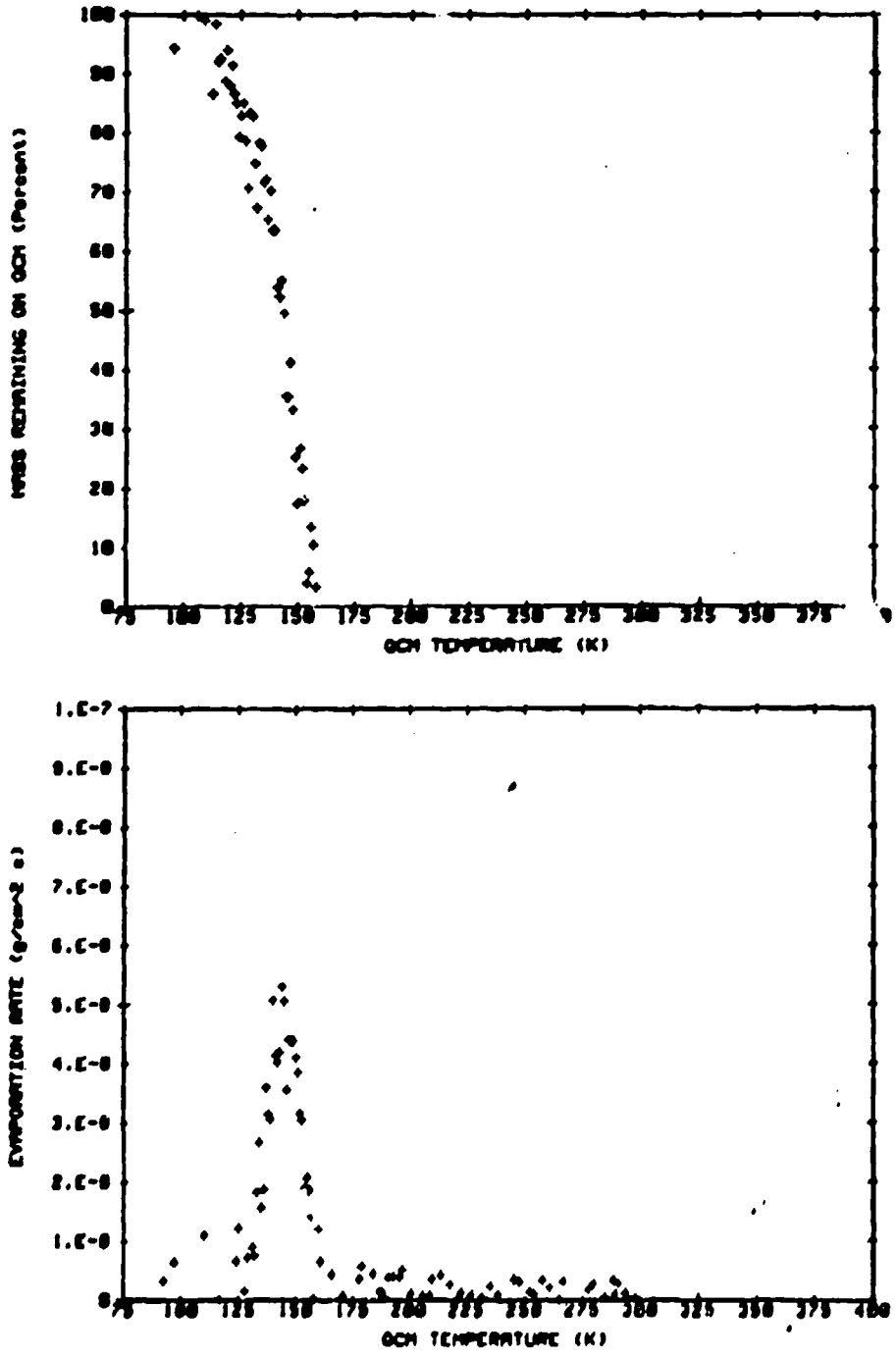


Fig. A-45 QTGA Data for Outgassing Products Collected on the 90 K QCM from an FEP Teflon Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

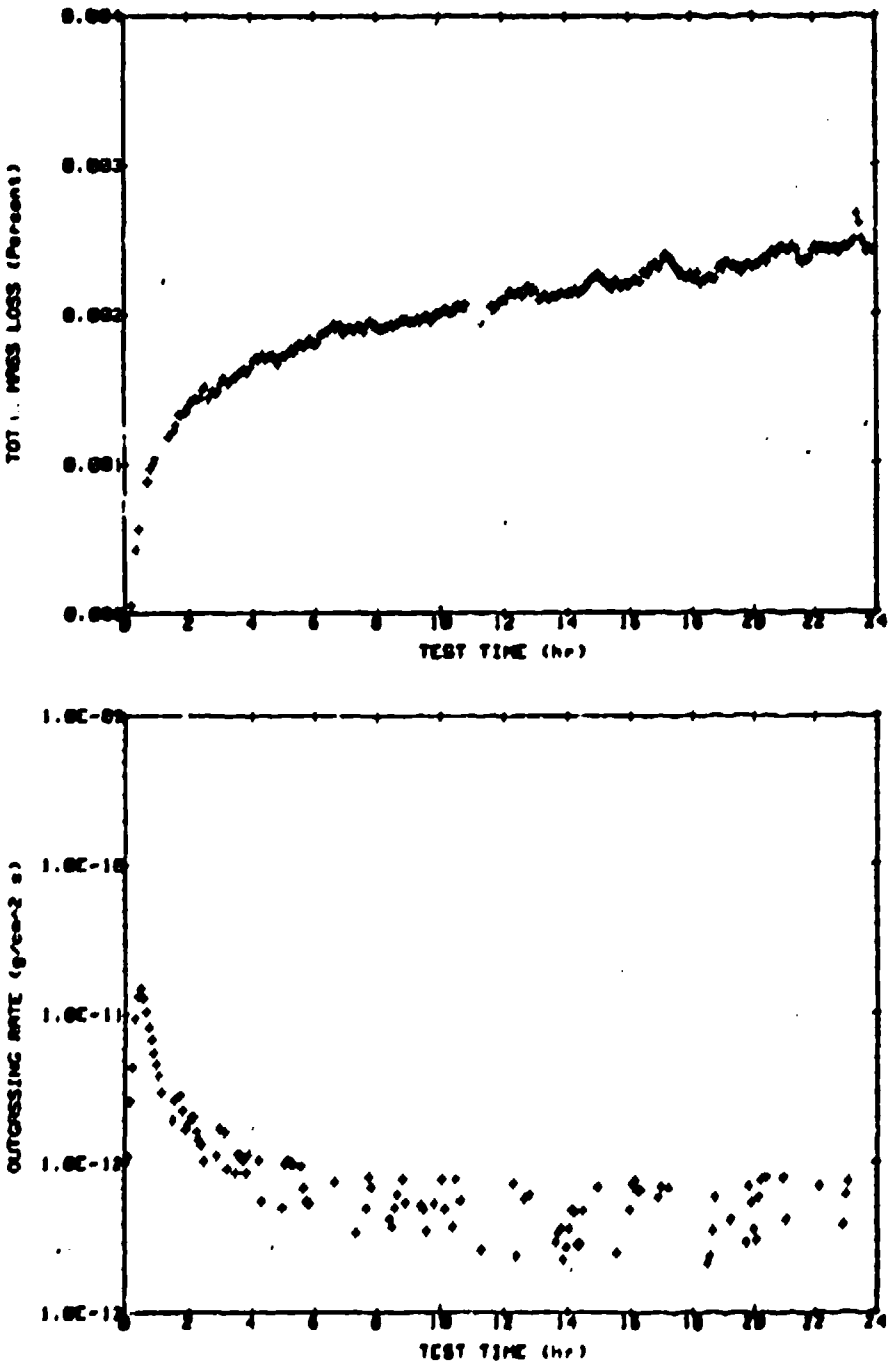


Fig. A-46 Total Mass Loss and Outgassing Rate as Functions of Time for an FEP Teflon Sample at 75°C.

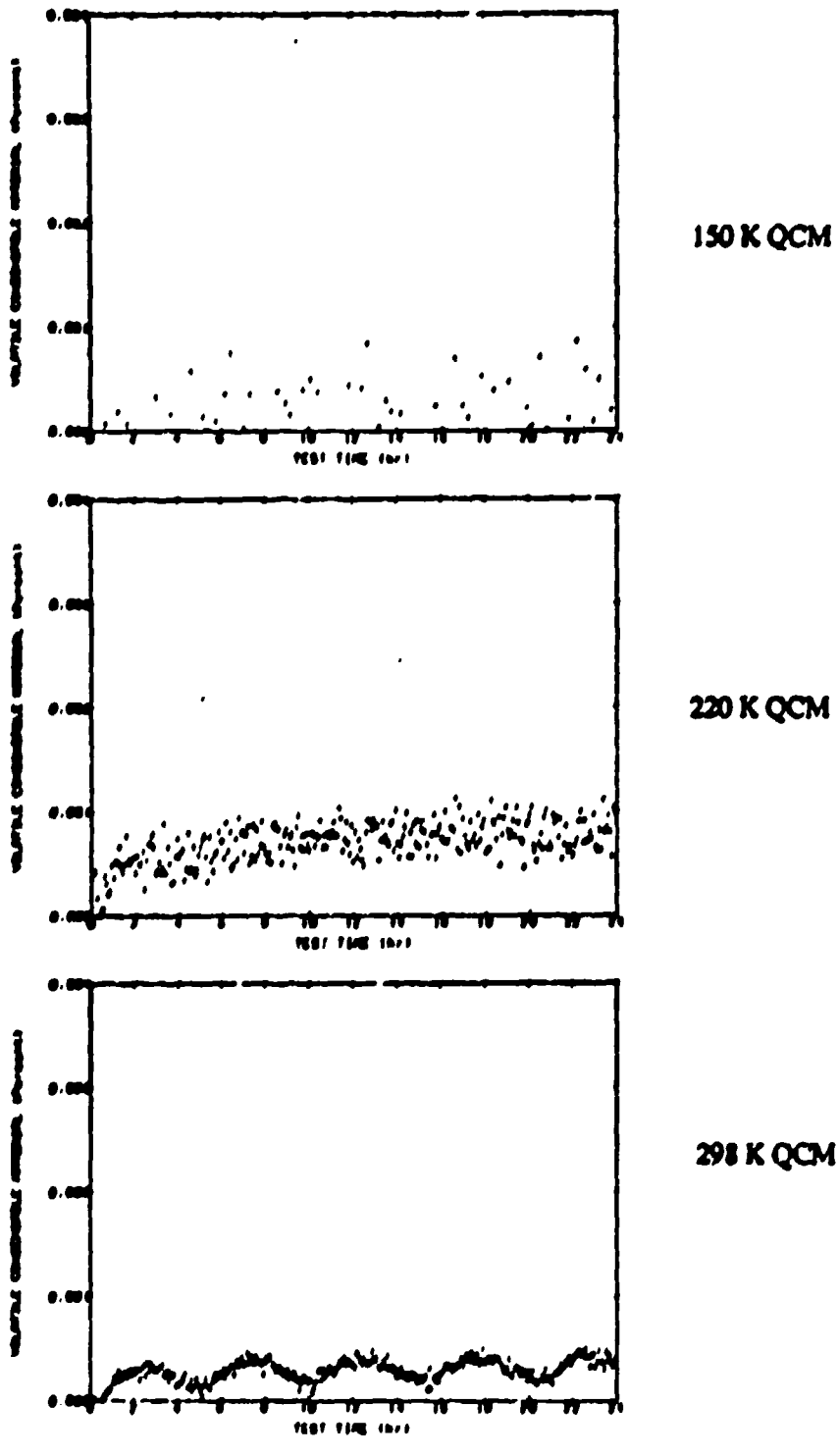


Fig. A-47 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an FEP Teflon Sample at 75°C.

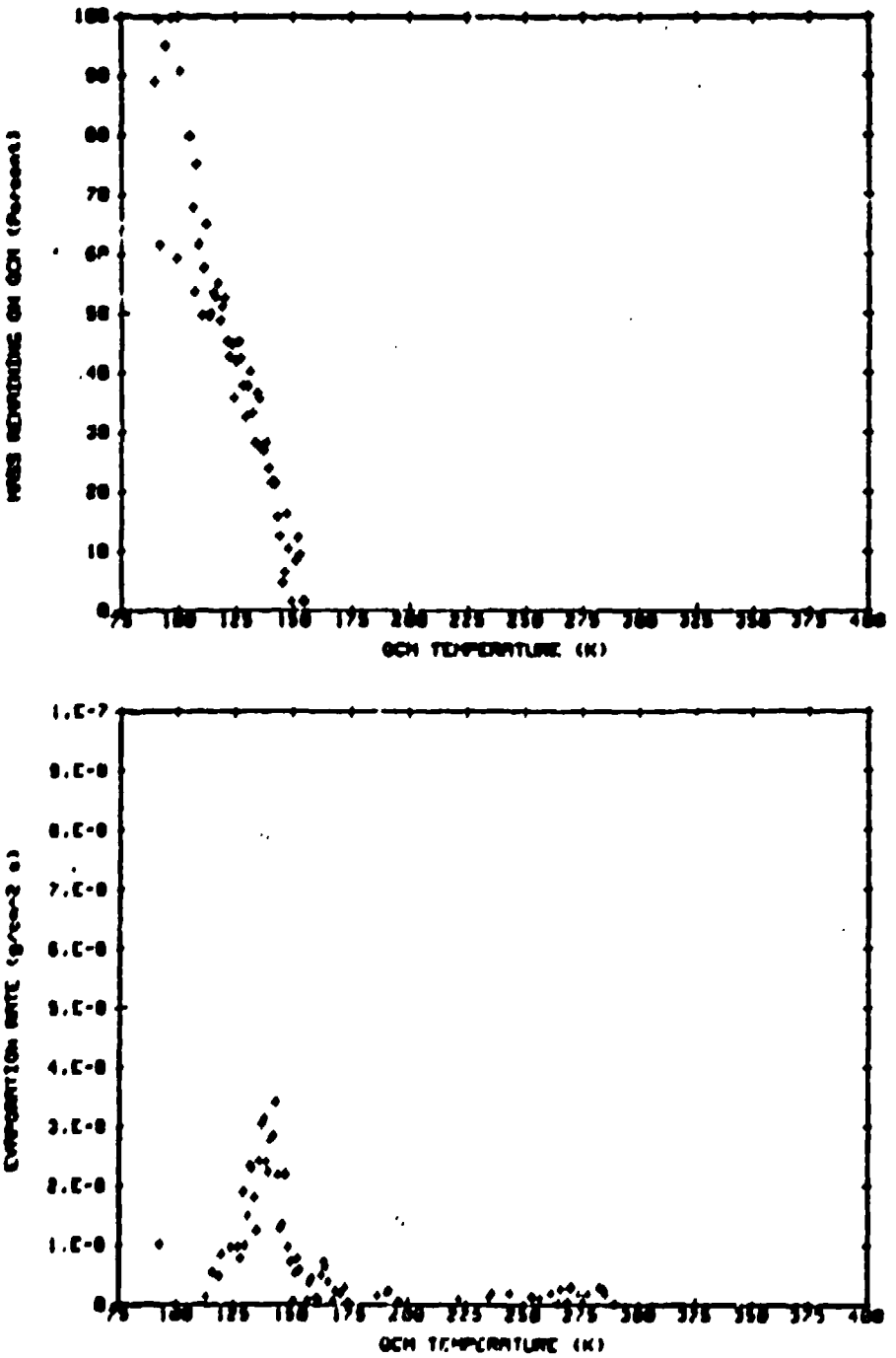


Fig. A-43 QTOA Data for Outgassing Products Collected on the 90 K QCM from an FEP Teflon Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-14

GC/MS Data for FEP Teflon at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

NO CONTAMINANT SPECIES FOUND IN THIS SAMPLE AT THIS TEMPERATURE

Table A-15

GC/MS Data for FEP Teflon at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
83	52.98	artifact
98	2.07	aliphatic hydrocarbons
103	1.93	aliphatic hydrocarbons
121	4.40	aliphatic hydrocarbons
148	1.02	aliphatic hydrocarbons
184	3.54	aliphatic hydrocarbon artifact
245	2.10	
405	7.22	aliphatic hydrocarbon artifact
416	3.05	artifact
455	2.90	artifact
465	1.84	artifact
841	16.94	artifact seen in blank run

NO CONTAMINANT SPECIES FOUND IN THE 125°C SAMPLE

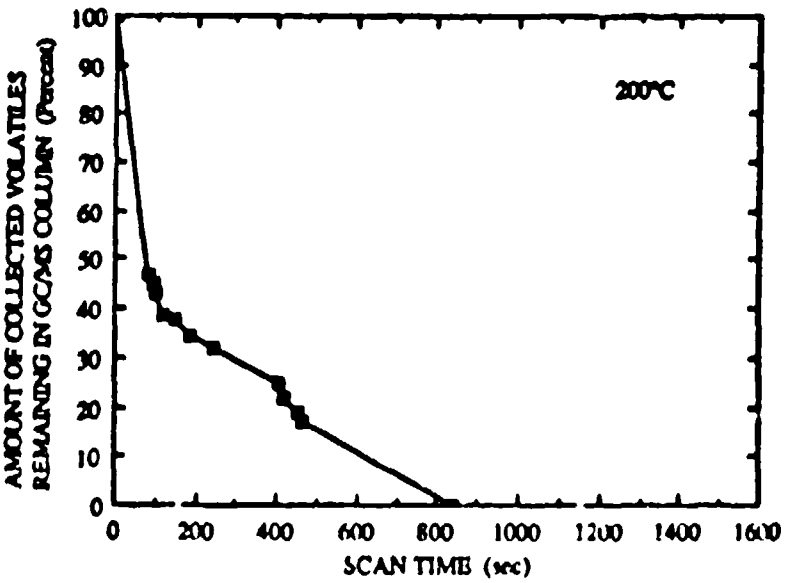


Fig. A-49 Amount of Collected Volatiles Remaining in GC/MS Column from 1½" Teflon at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Brayco 815Z oil

DATE TEST STARTED : August 20, 1986

GC/MS DATA FILES :

125°C Test : data not available
200°C Test : data not available

	Test Temperature (°C)		
	125	75	100
MATERIAL SAMPLE DATA :			
Area (cm^2)	8.3	15.07	13.75
Weight, pretest (g)	3.028824	2.695542	2.641292
Total mass loss (%)	no data	no data	0.03
ISOTHERMAL TEST DATA :			
Test duration (h)	119	119	119
QCM/Temperature Data File	G0820	G0828A	G0806
Mass Spectrometer Data File	no data	no data	no data
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0825	G0902	G0911
Mass Spectrometer Data File	no data	no data	no data

COMMENTS :

- material is a low-volatility, perfluorinated polyether oil, produced by Bray Oil Co.
- LMSC EPS# 34-464-0001266
- samples supplied by Burmah-Castrol Inc., Bray Products Division
- sample holders were stainless steel cups 0.9 inch I.D. by 0.1 inch deep
- sample configuration (125°C test): 2 SS cups full of oil
- sample configuration (75°C test): 3 SS cups 1/3 full of oil
- sample configuration (100°C test): 3 SS cups 1/3 full of oil
- no final sample weights available for 125°C and 75°C tests (Note 3, Sec. A.1.4)
- QCM shutters were apertured during Isothermal Tests and full open during QTA tests
- GC/MS data not available for this material (Note 5, Sec. A.1.4)
- mass spectrometer not in operation during this material test (Note 6, Sec. A.1.4)

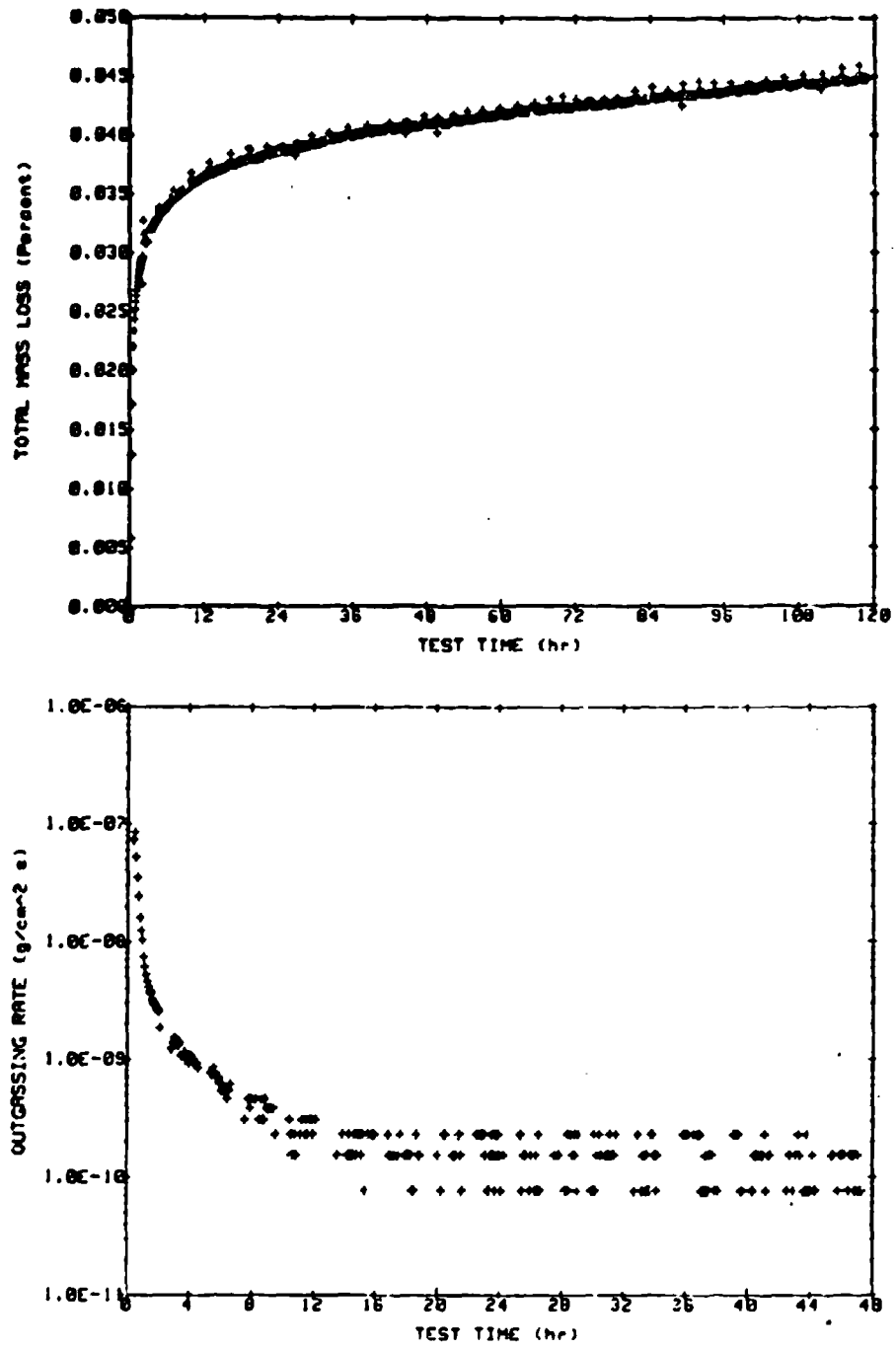


Fig. A-50 Total Mass Loss and Outgassing Rate as Functions of Time for a Brayco 815Z Sample at 125°C.

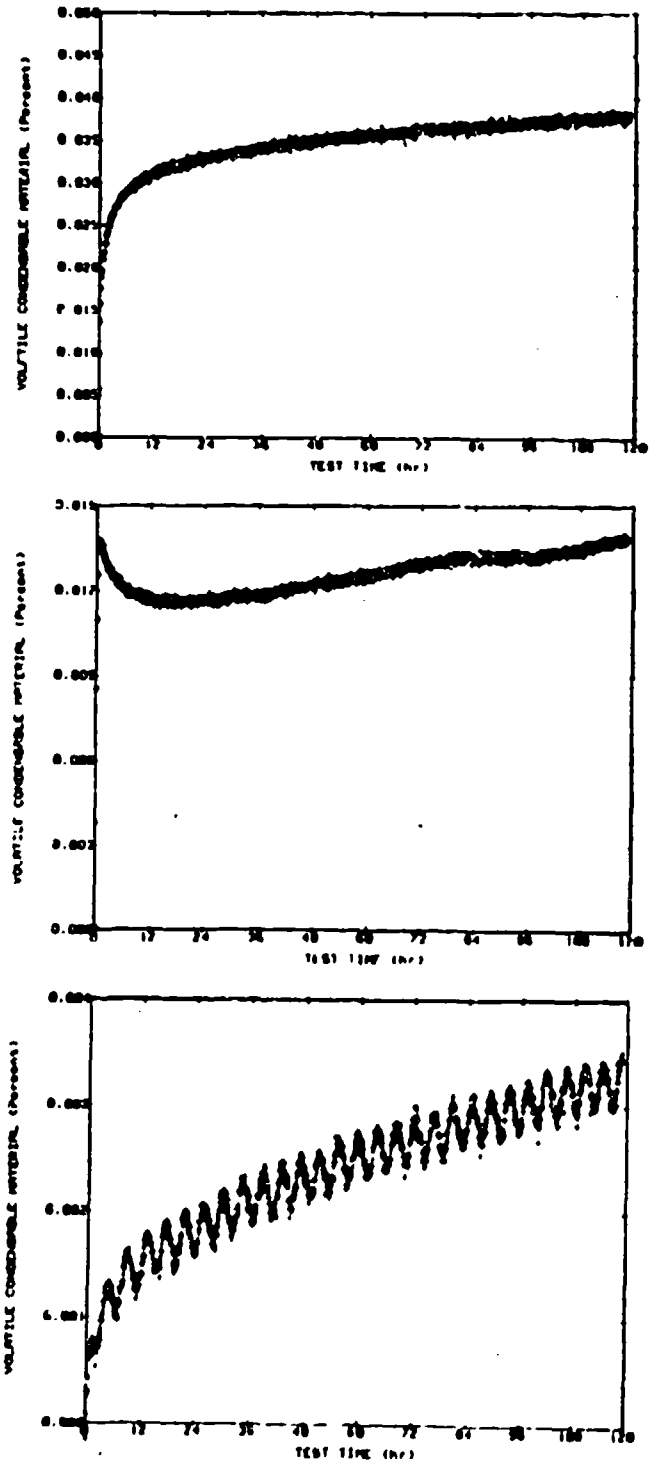


Fig. A-51 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Brayco 815Z Sample at 125°C.

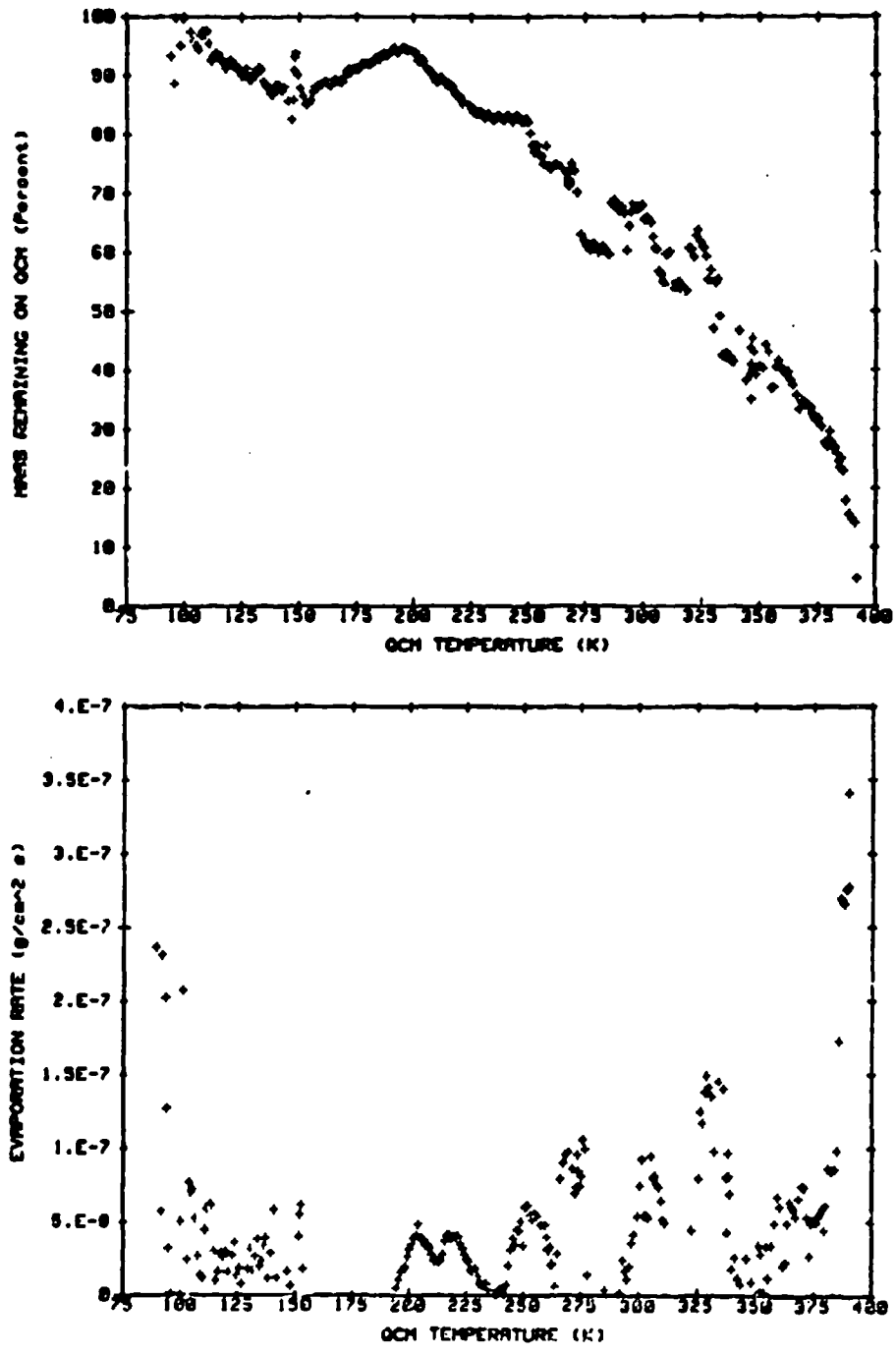


Fig. A-52 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Brayco 815Z Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

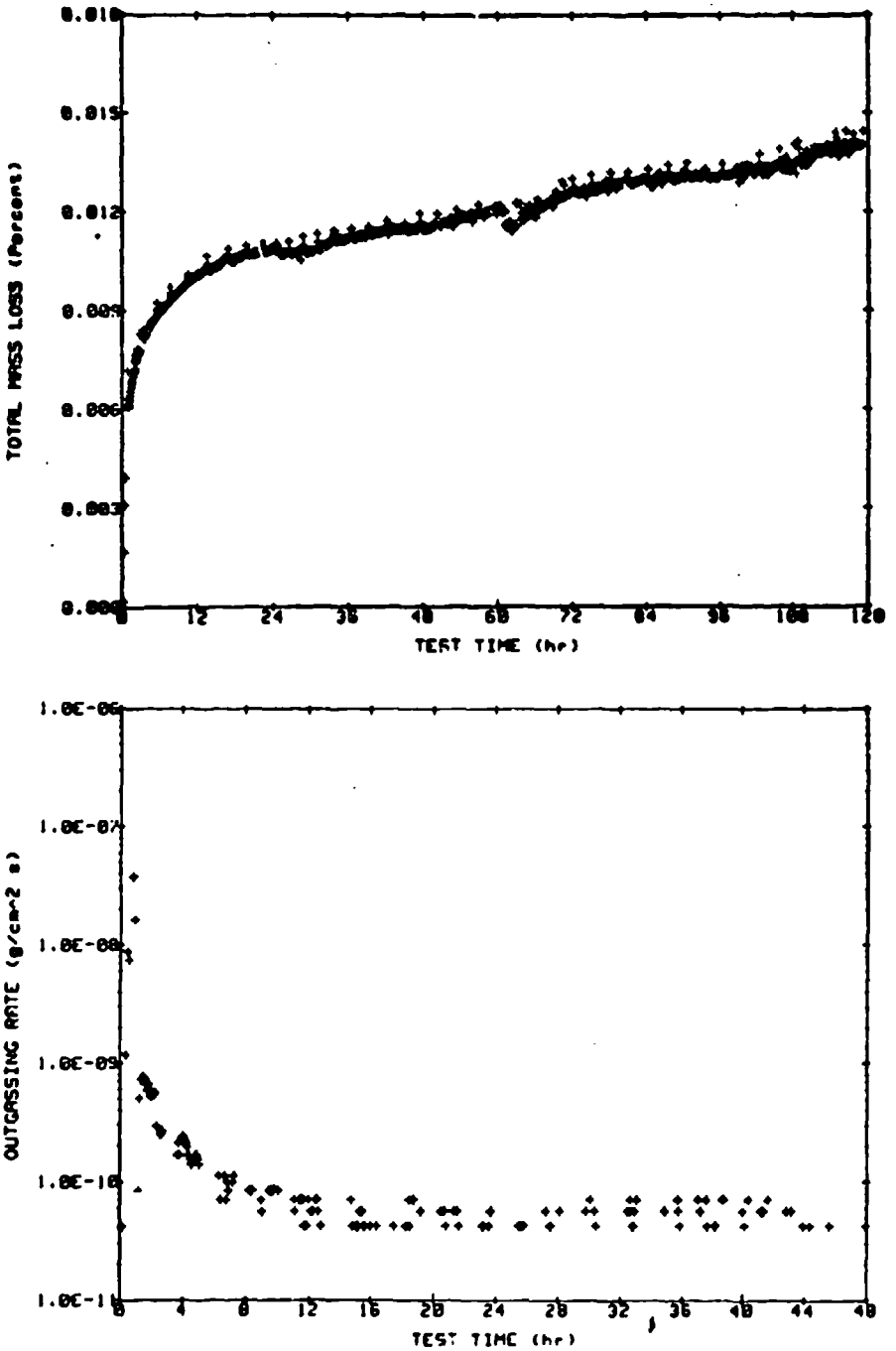


Fig. A-53 Total Mass Loss and Outgassing Rate as Functions of Time for a Brayco 815Z Sample at 75°C.

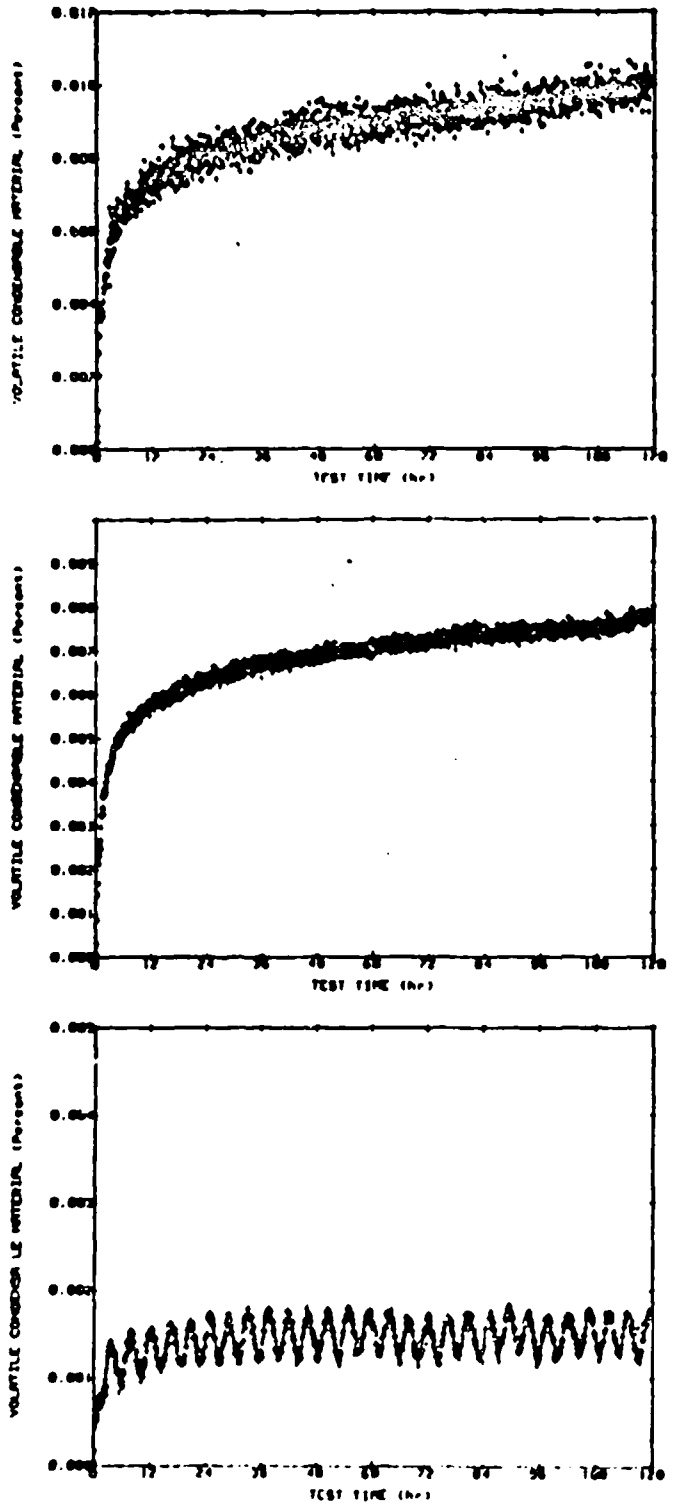


Fig. A-54 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Brayco 815Z Sample at 75°C.

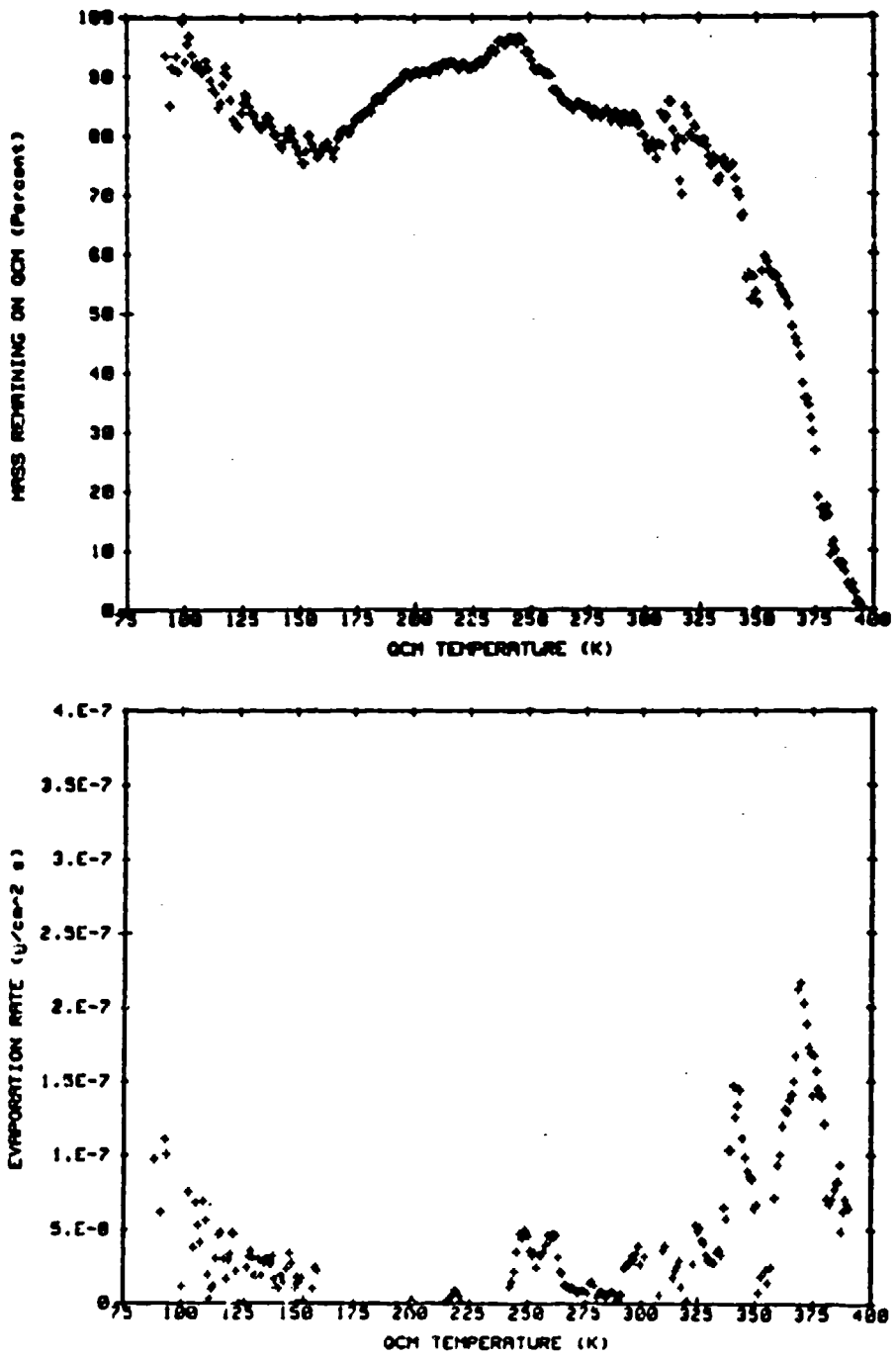


Fig. A-55 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Brayco 815Z Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

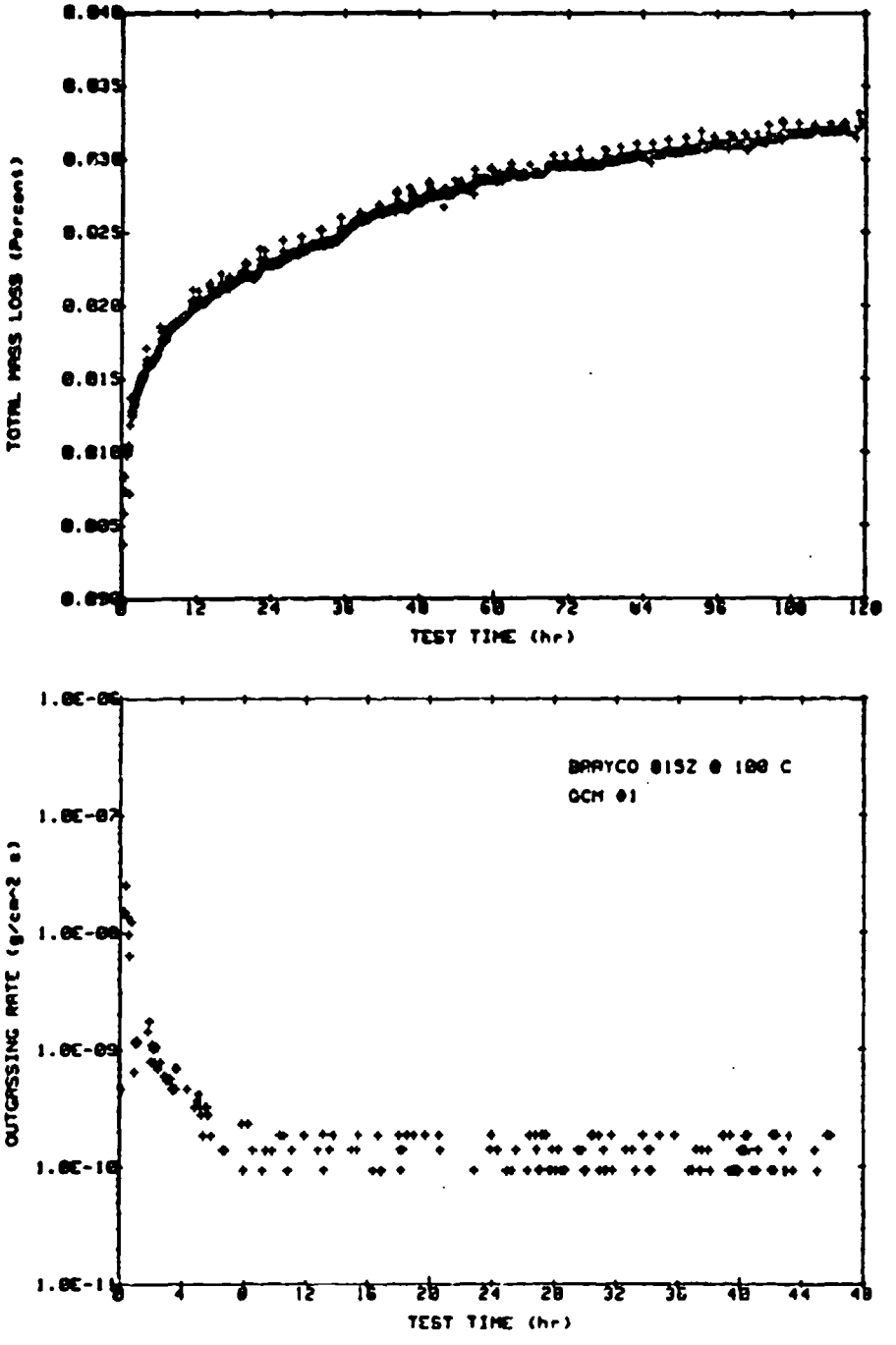


Fig. A-56 Total Mass Loss and Outgassing Rate as Functions of Time for a Brayco 815Z Sample at 100°C.

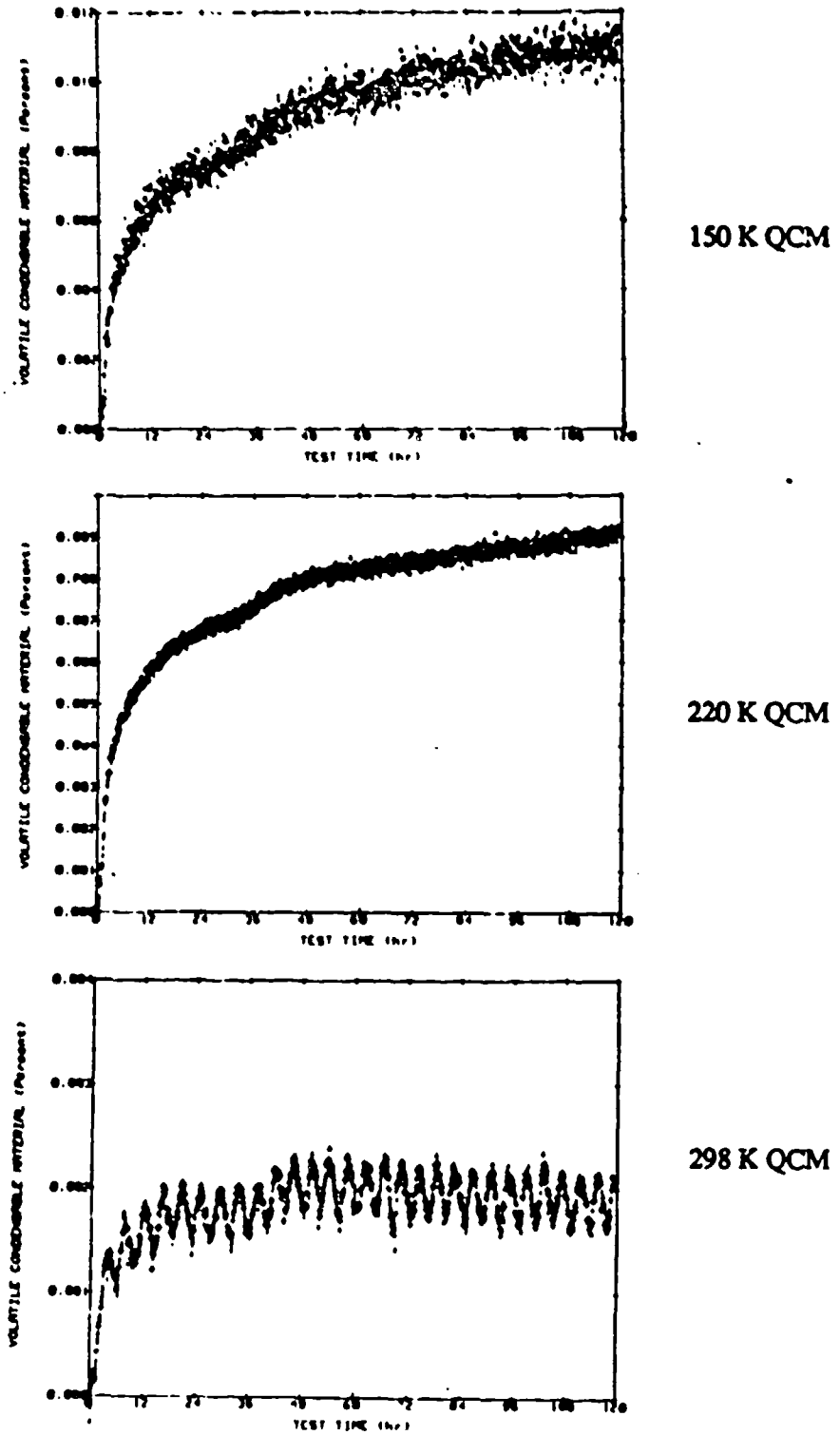


Fig. A-57 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Brayco 815Z Sample at 100°C.

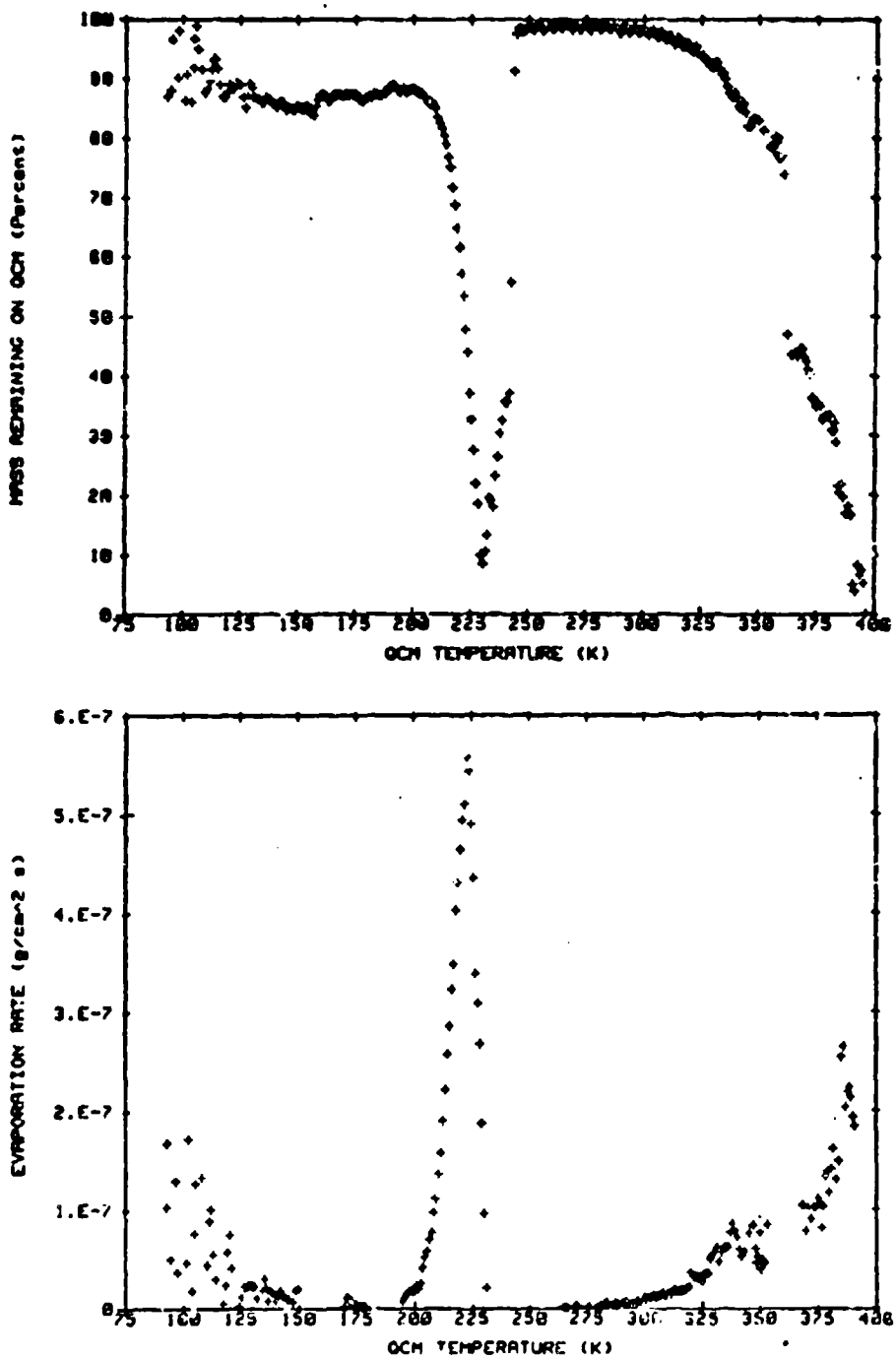


Fig. A-58 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Brayco 815Z Sample at 100°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-16

GC/MS Data for Brayco 813Z at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

Table A-17

GC/MS Data for Brayco 815Z at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 125°C

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 200°C

Fig. A-59 Amount of Collected Volatiles Remaining in GC/MS Column from Brayco 815Z at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Braycote 600 grease

DATE TEST STARTED : July 25, 1986

GC/MS DATA FILES :

125°C Test : data not available
200°C Test : data not available

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Area (cm^2)	7.18	7.18	7.18
Weight, pretest (g)	3.95355	3.689283	3.74549
Total mass loss (%)	no data	0.26	0.04
ISOTHERMAL TEST DATA :			
Test duration (h)	120	120	120
QCM/Temperature Data File	G0811	G0728	G0804
Mass Spectrometer Data File	no data	no data	no data
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0816Q	G0802Q	G0809Q
Mass Spectrometer Data File	no data	no data	no data

COMMENTS :

- material is a low-volatility, perfluorinated polyether grease produced by Bray Oil Co.
- LMSC EPS# 34-465-0000677
- samples supplied by Burmah-Castrol Inc., Bray Products Division
- sample holders were aluminum cups 0.6 inch I.D. by 0.2 inch high
- sample configuration (125°C test): 4 Al cups half-full of grease
- sample configuration (75°C test): 4 Al cups half-full of grease
- sample configuration (25°C test): 4 Al cups half-full of grease
- Al cups are arranged inside effusion cell not directly below the orifice
- no final sample weights available for 125°C test (Note 3, Sec. A.1.4)
- shutters were apertured during Isothermal Tests and full open during QTA Tests
- no QTA performed on 298 K QCM after 25°C Isothermal Test (Note 8, Sec. A.1.4)
- GC/MS data not available for this material (Note 5, Sec. A.1.4)
- mass spectrometer not in operation during this material test (Note 6, Sec. A.1.4)

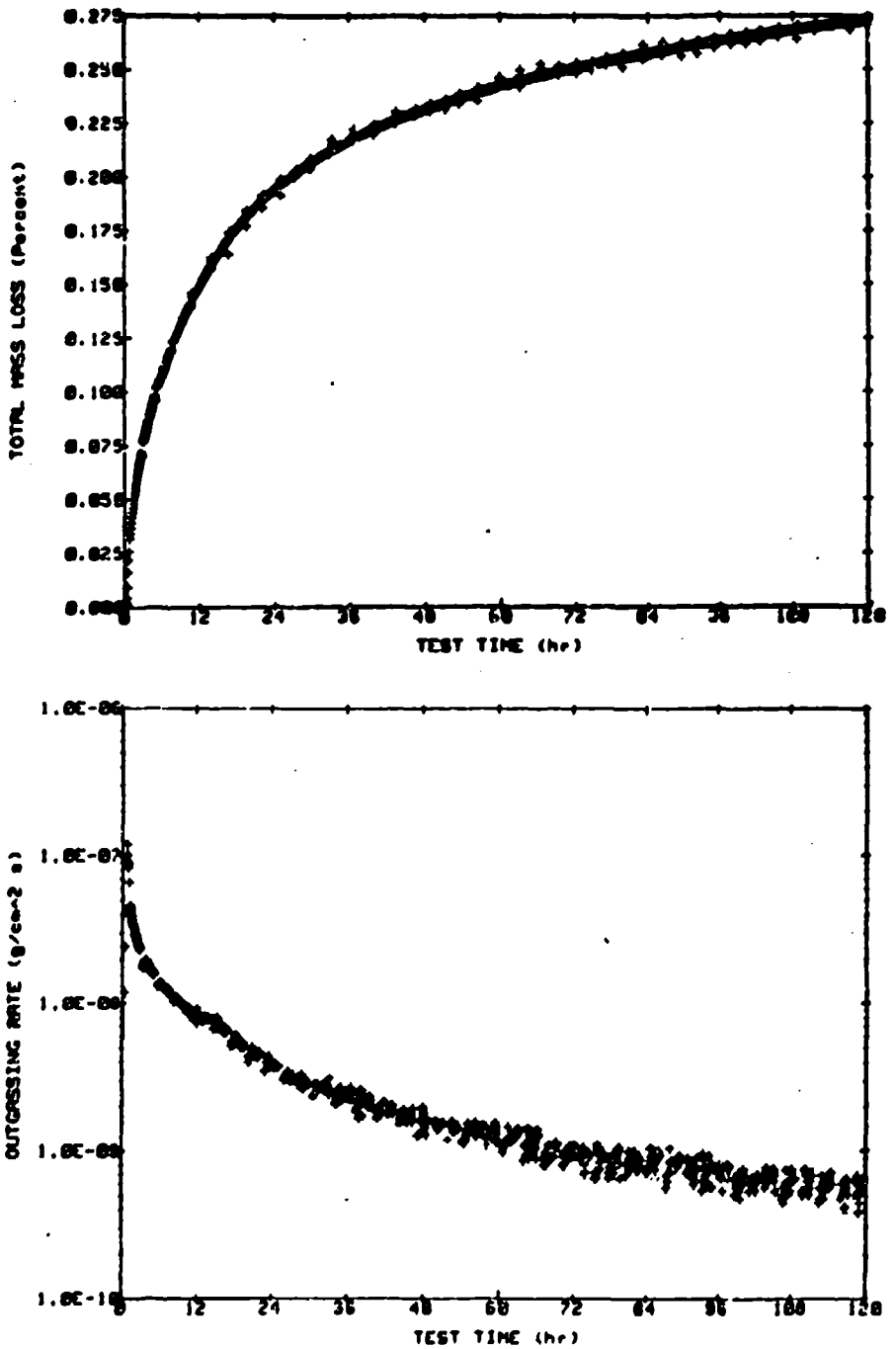


Fig. A-60 Total Mass Loss and Outgassing Rate as Functions of Time for a Braycote 600 Sample at 125°C.

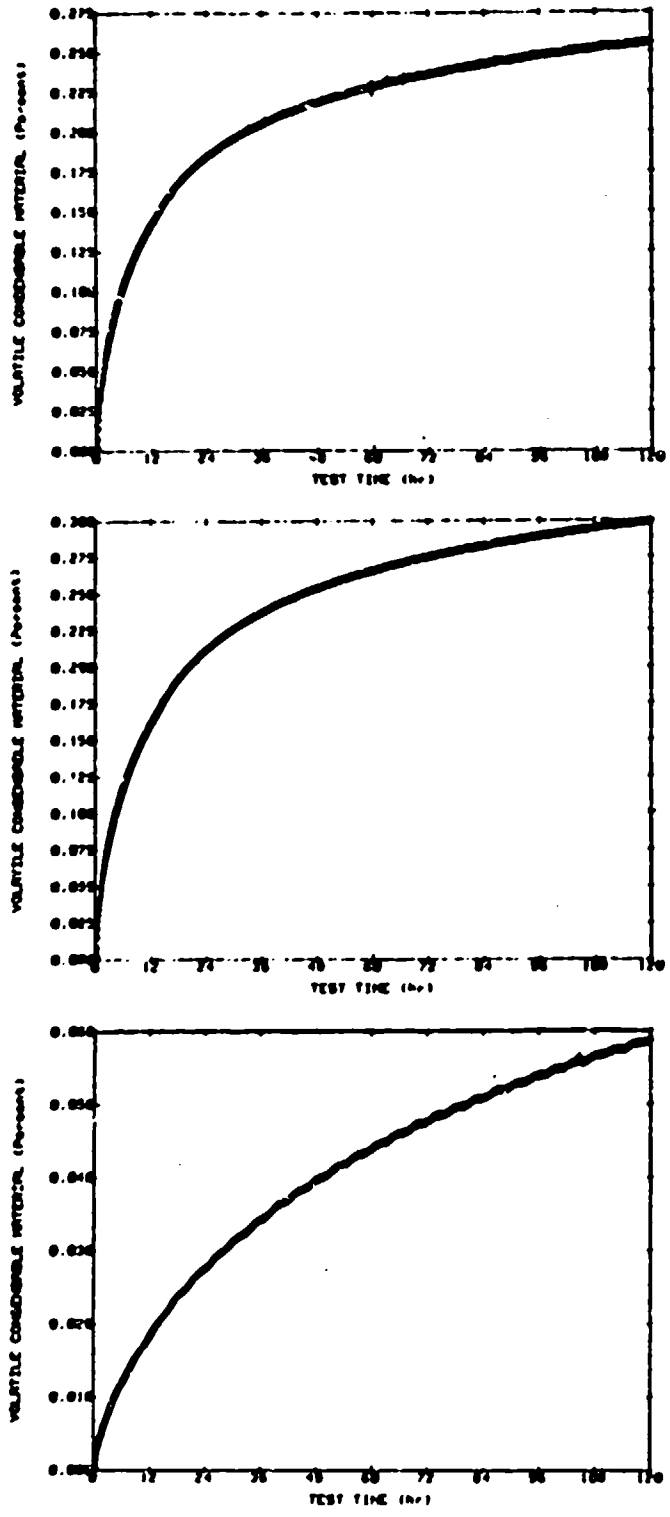


Fig. A-61 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Braycote 600 Sample at 125°C.

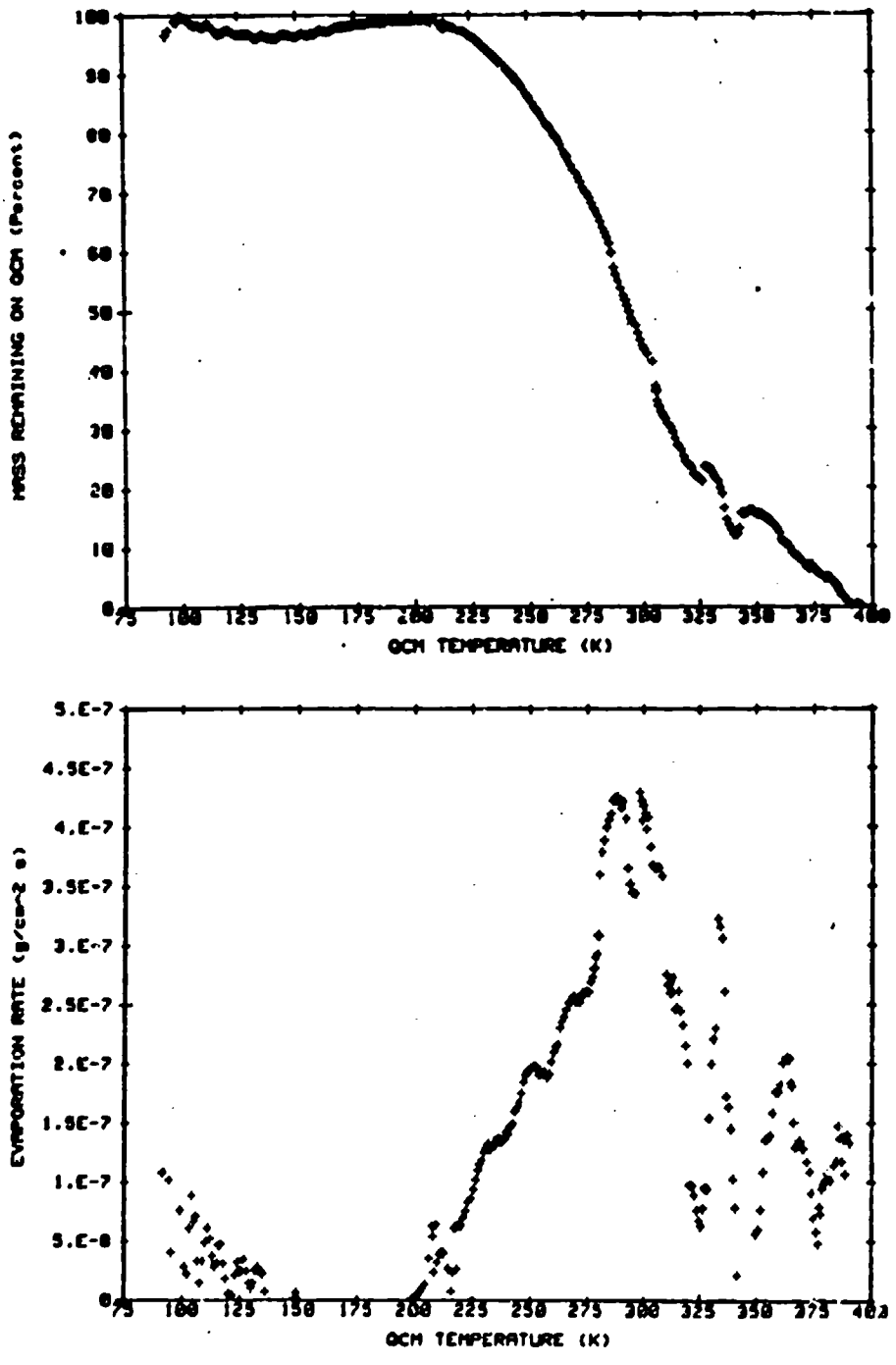


Fig. A-62 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Braycote 600 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

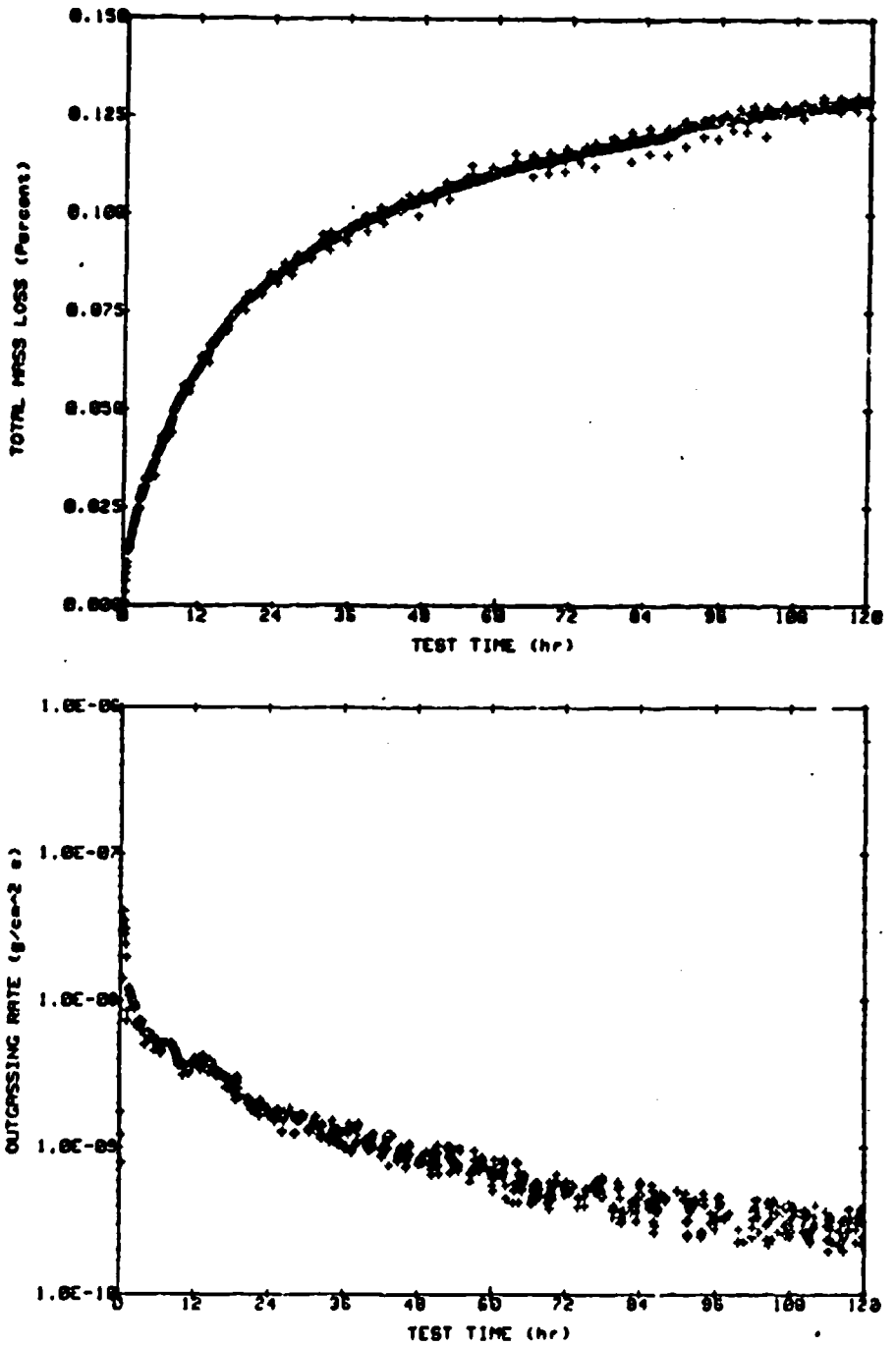


Fig. A-63 Total Mass Loss and Outgassing Rate as Functions of Time for a Braycote 600 Sample at 75°C.

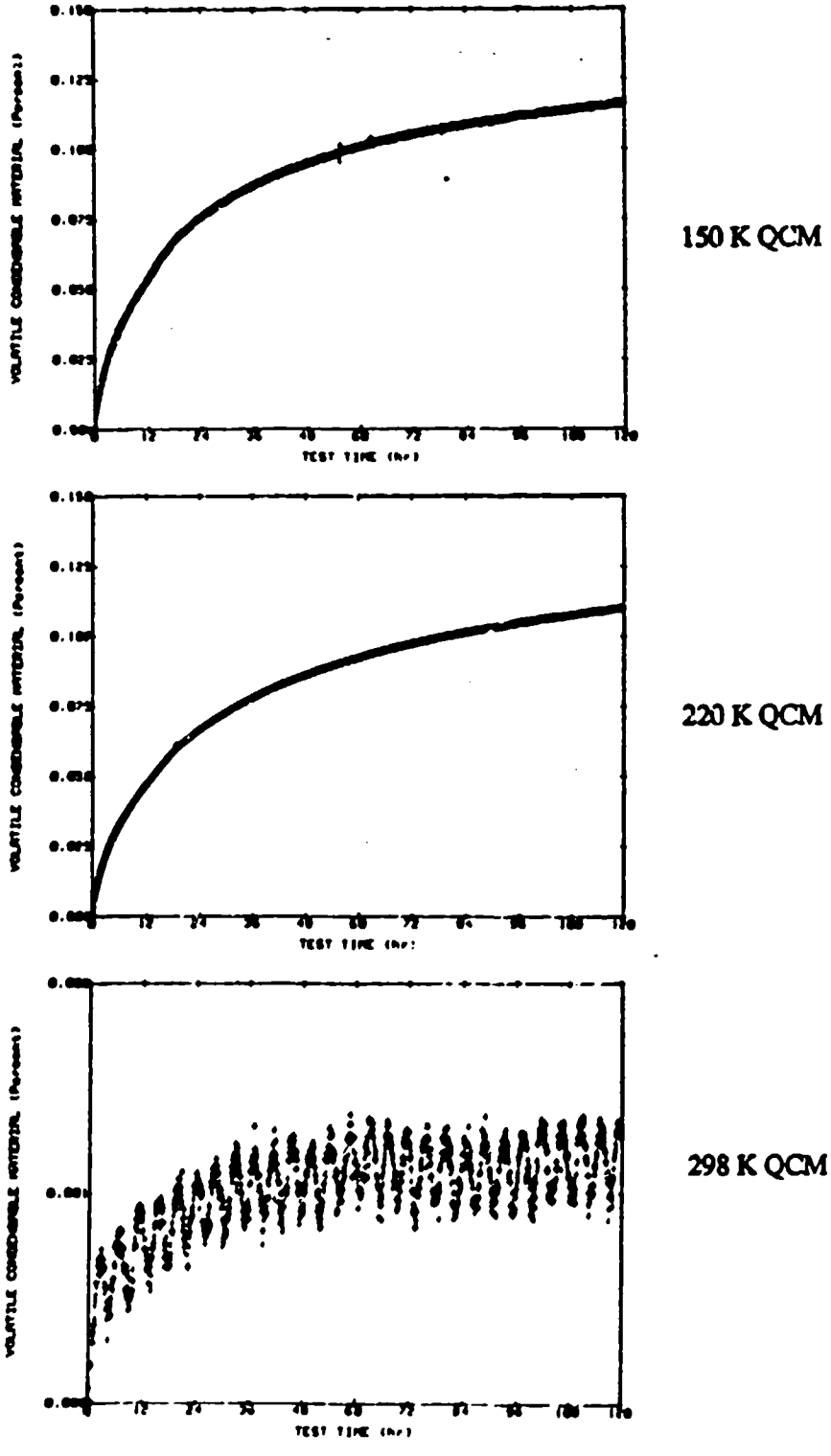


Fig. A-64 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Braycote 600 Sample at 75°C.

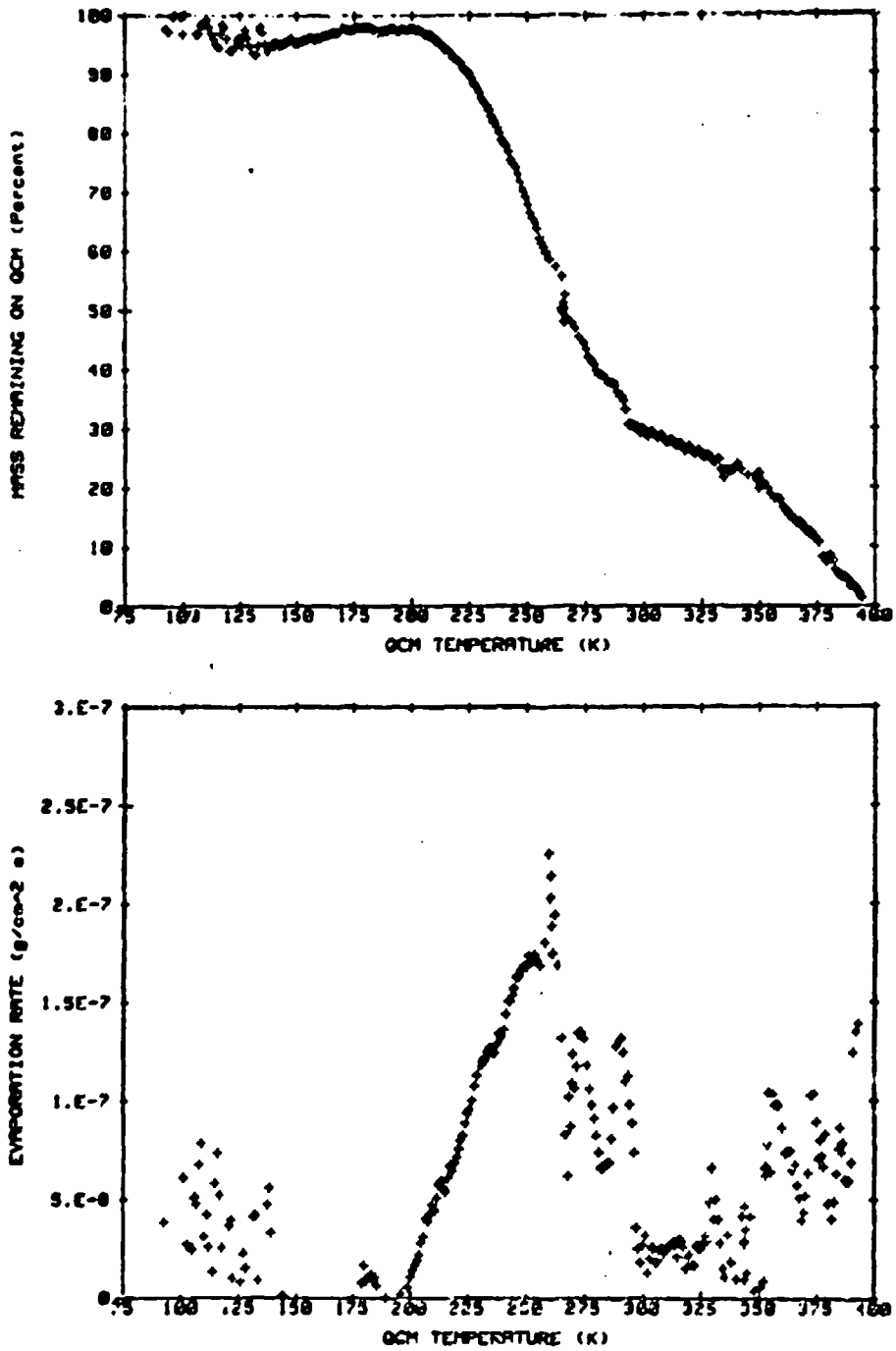


Fig. A-65 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Braycote 600 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

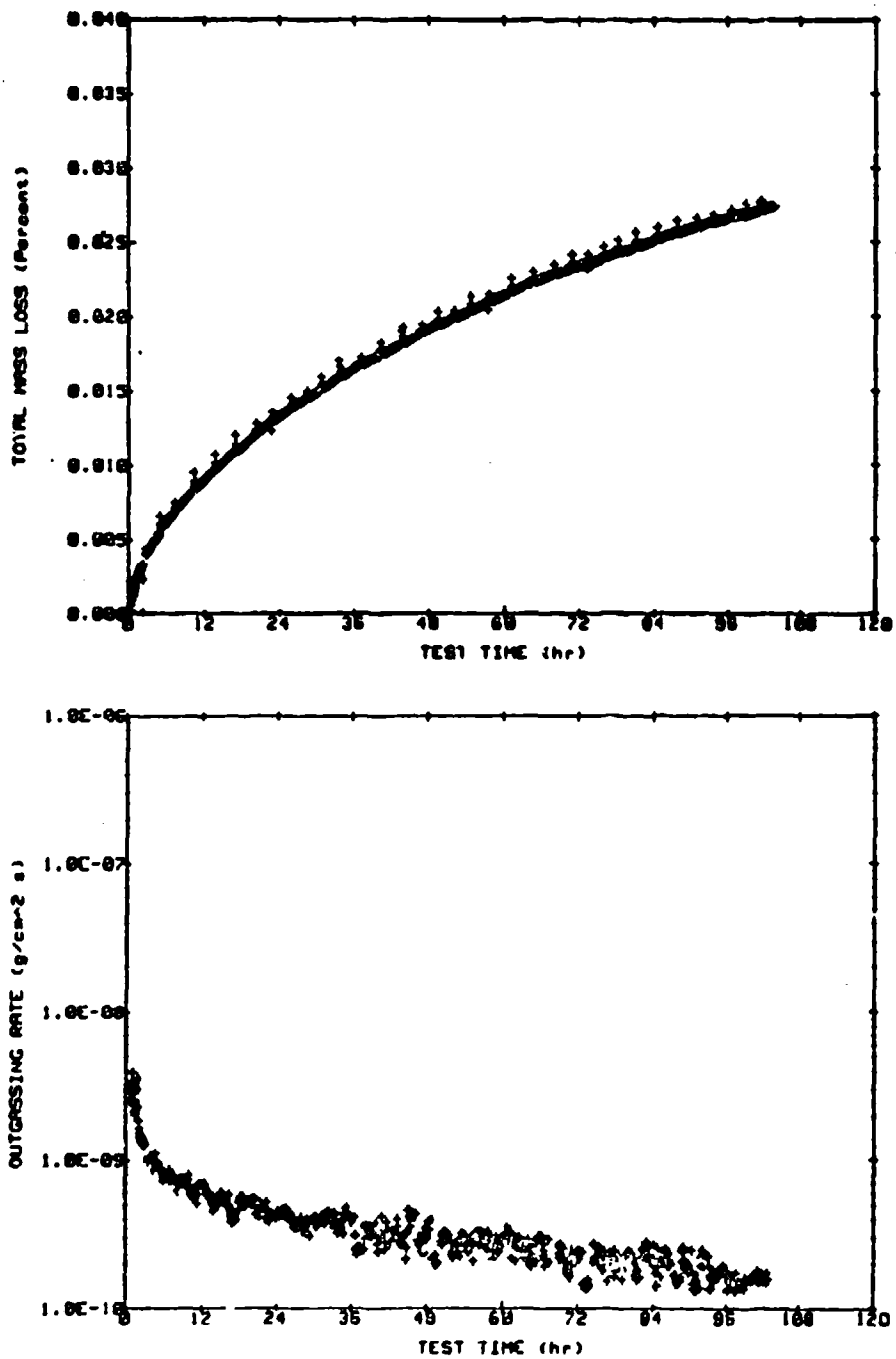


Fig. A-66 Total Mass Loss and Outgassing Rate as Functions of Time for a Braycote 600 Sample at 25°C.

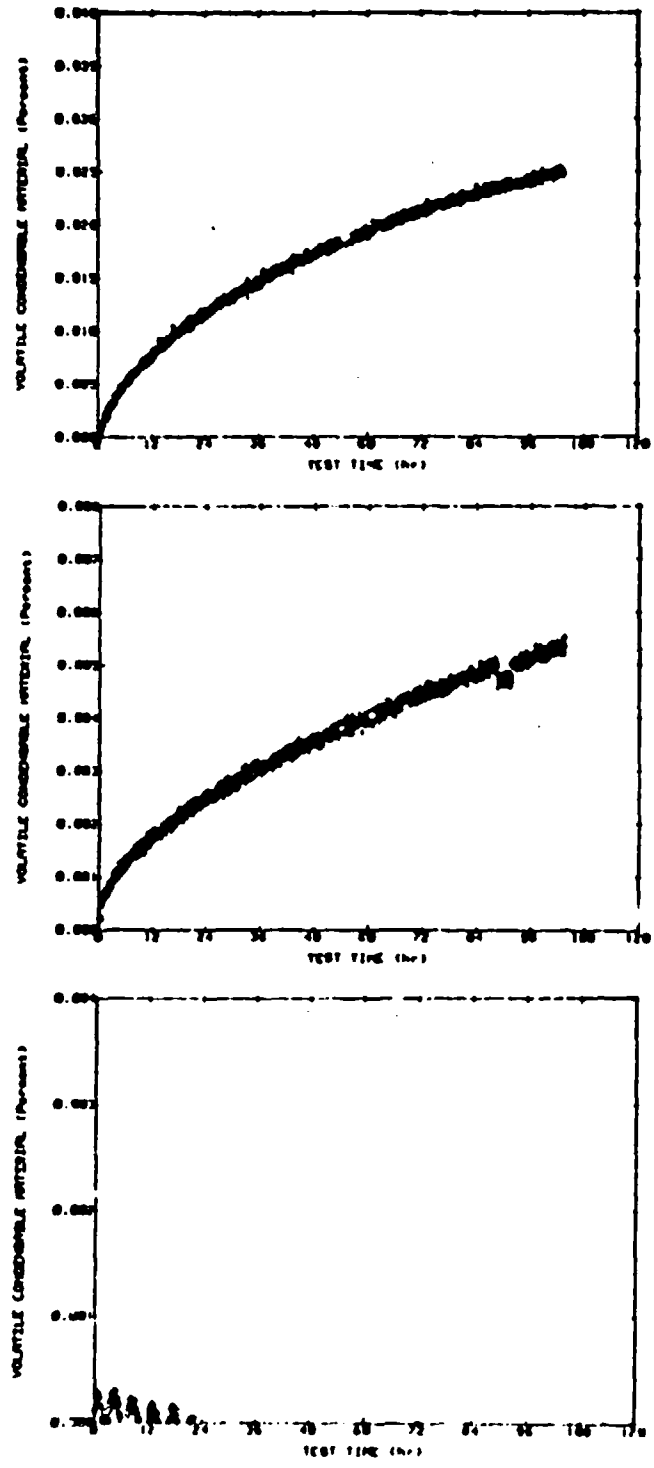


Fig. A-67 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Braycote 600 Sample at 25°C.

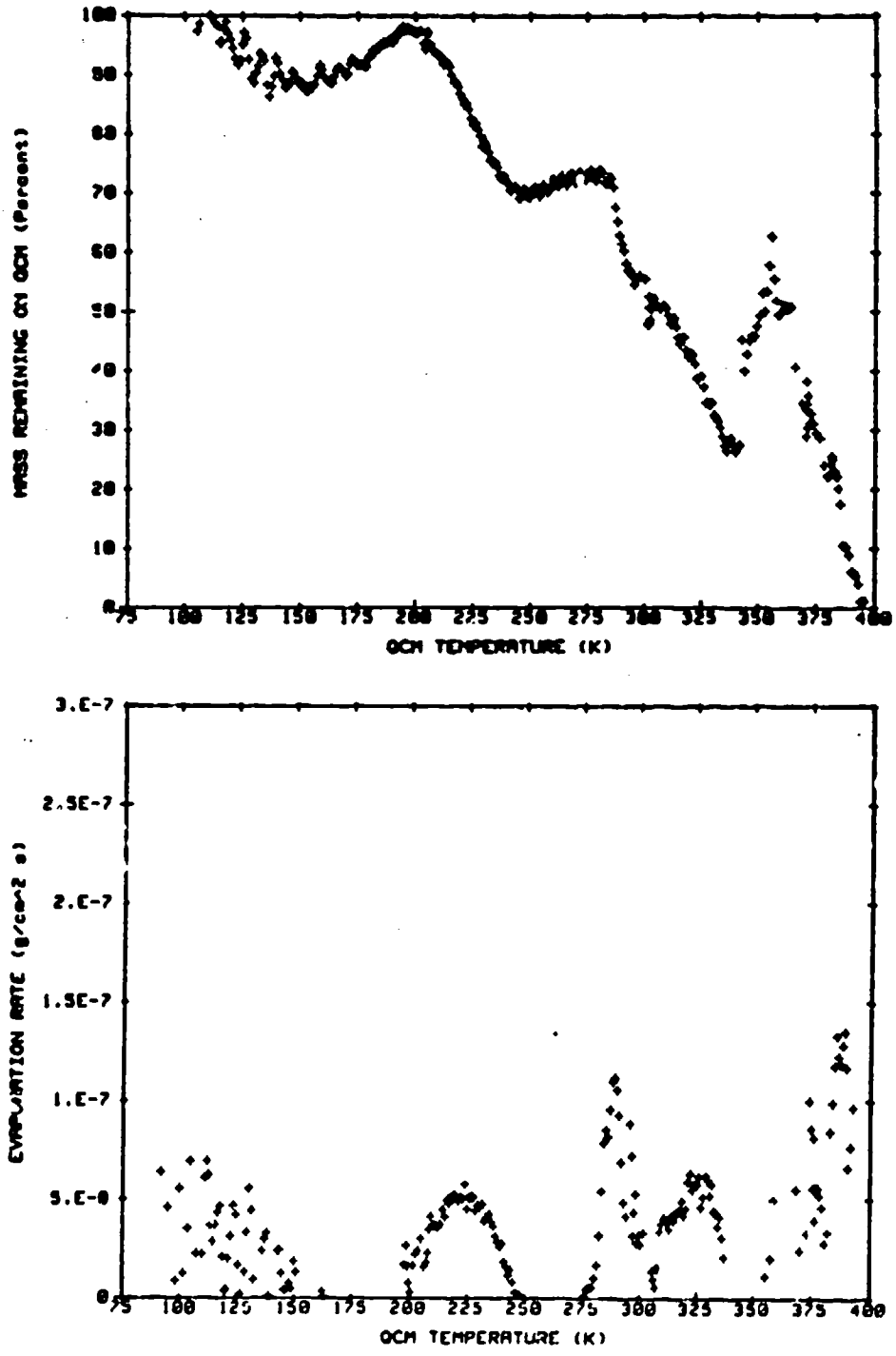


Fig. A-68 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Braycote 600 Sample at 25°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-18

GC/MS Data for Braycote 600 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

Table A-19

GC/MS Data for Braycote 600 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 125°C

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 200°C

Fig. A-69 Amount of Collected Volatiles Remaining in GC/MS Column from Braycote 600 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Krytox 143AD

DATE TEST STARTED : February 20, 1987

GC/MS DATA FILES :

125°C Test : JG23MAY88E
200°C Test : JG23MAY88C

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Area (cm^2)	10.09	10.09	10.09
Weight, pretest (g)	4.0	4.0	4.0
Total mass loss (%)	no data	no data	no data
ISOTHERMAL TEST DATA :			
Test duration (h)	63	45	96
QCM/Temperature Data File	G0220	G0225	G0305
Mass Spectrometer Data File	no data	no data	no data
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0223Q	G0227Q	G0309Q
Mass Spectrometer Data File	no data	no data	no data

COMMENTS :

- material is a perfluoroalkylpolyether oil produced by E.I. DuPont DeNemours Co.
- LMSC EPS# 34-402-0000000
- samples supplied by E.I. du Pont de Nemours, Chemicals and Pigments Department
- sample holders were stainless steel cups 0.9 inch I.D. by 0.1inch deep
- sample configuration (125°C test): 2 SS cups full of oil
- sample configuration (75°C test): 2 SS cups full of oil
- sample configuration (25°C test): 2 SS cups full of oil
- initial sample weights are estimatedto ± 10% (Note 1, Sec. A.1.4)
  final sample weights are unknown
- QCM shutters were apertured during Isothermal Tests and full open during QTA tests
- no QTA performed on 298 K QCM after 25°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer not in operation during this material test (Note 6, Sec. A.1.4)

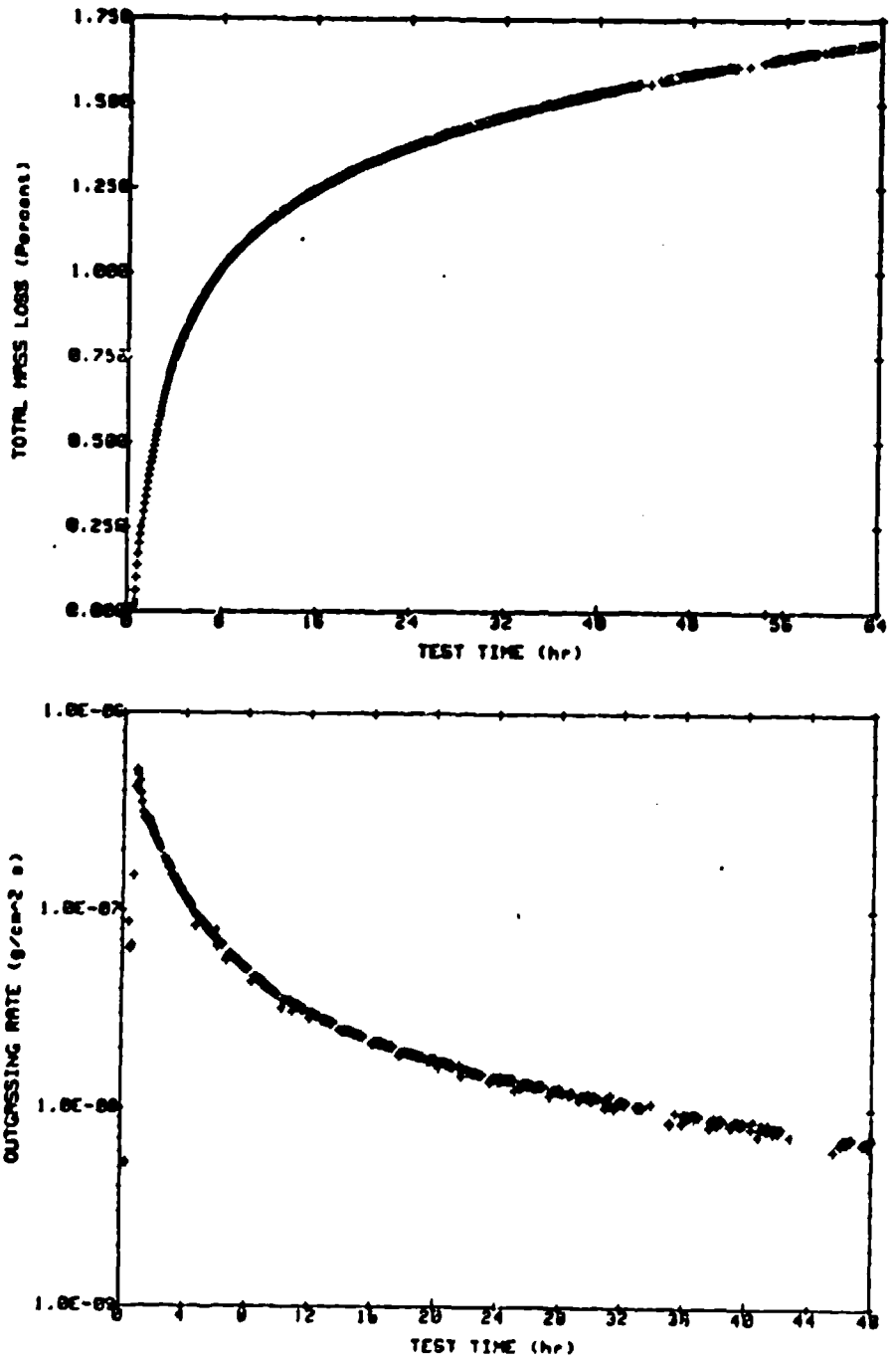


Fig. A-70 Total Mass Loss and Outgassing Rate as Functions of Time for a Krytox 143 AD Sample at 125°C.

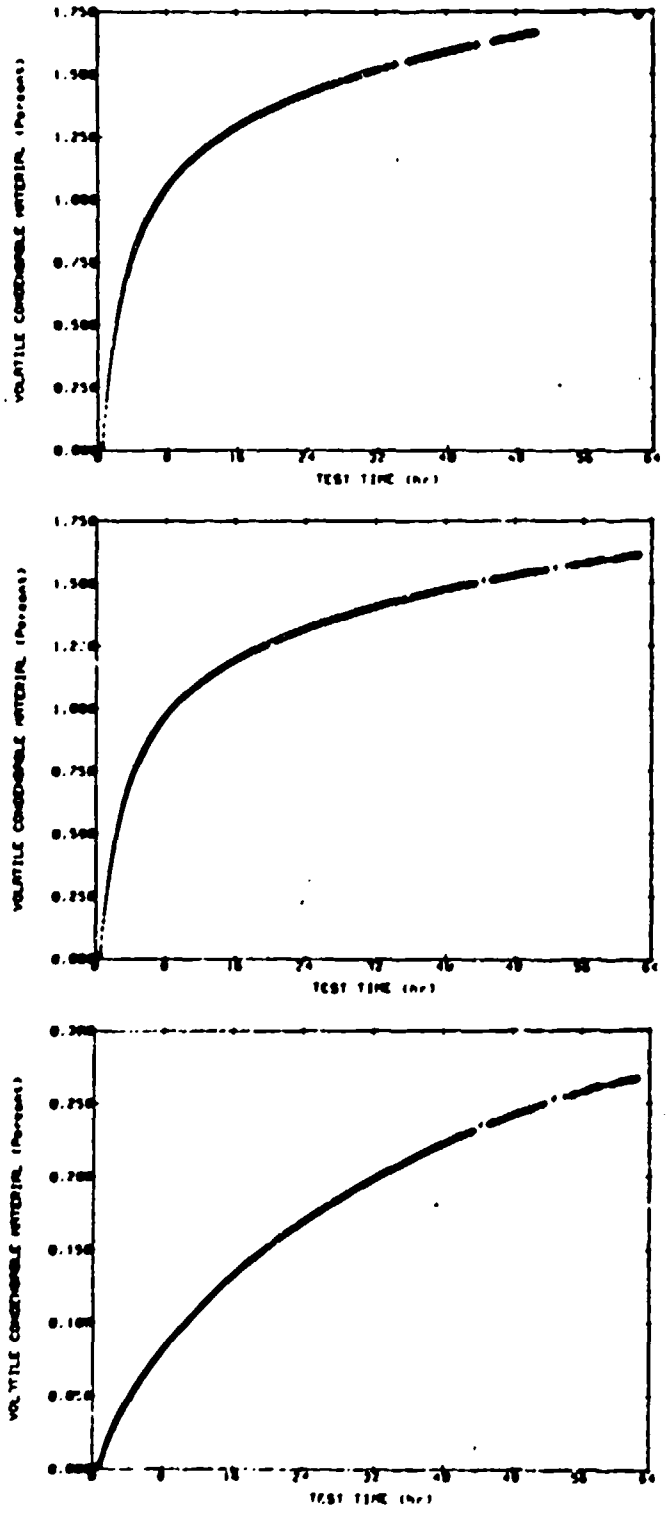


Fig. A-71 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Krytox 143 AD Sample at 125°C.

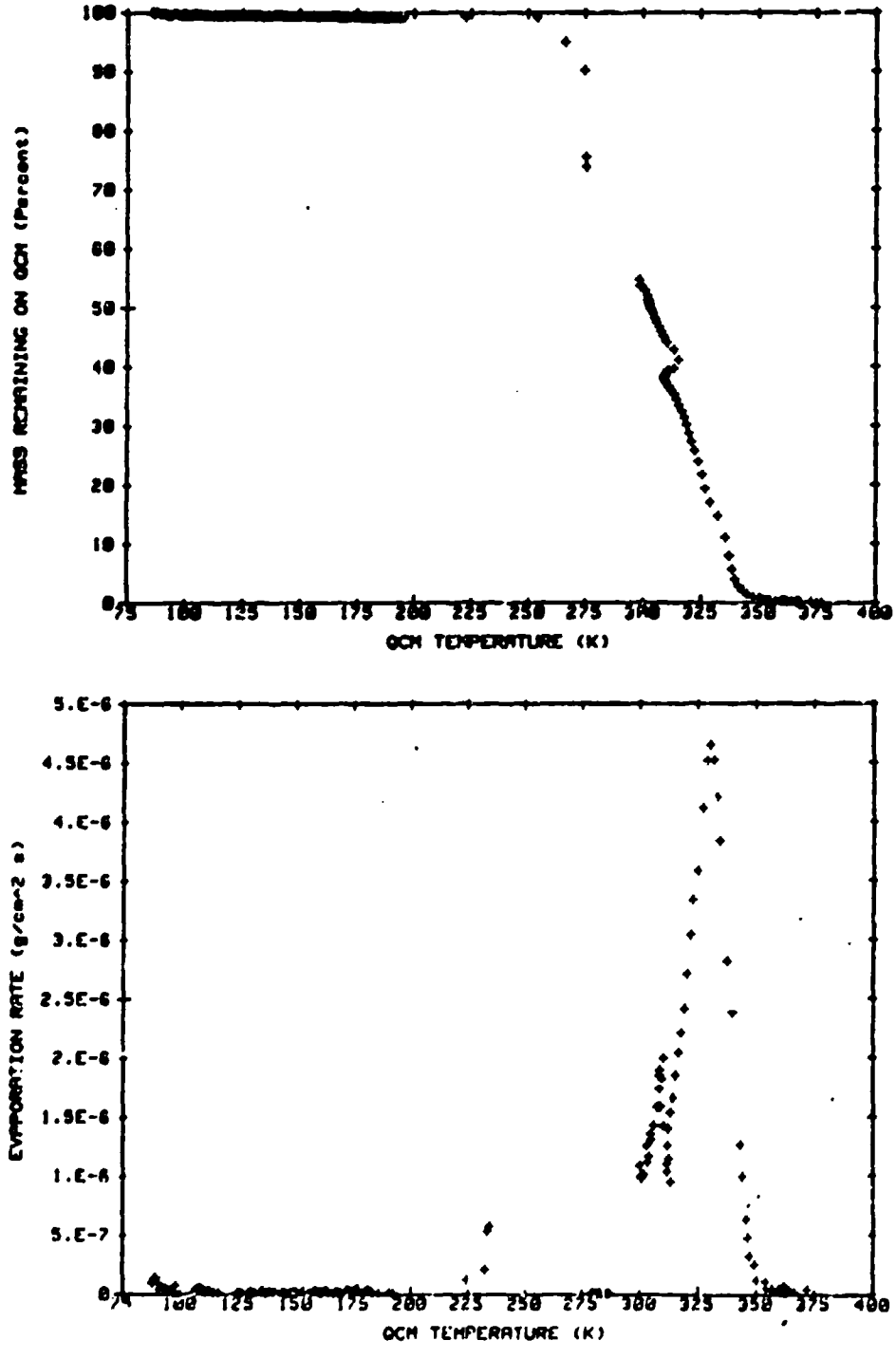


Fig. A-72 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Krytox 143 AD Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

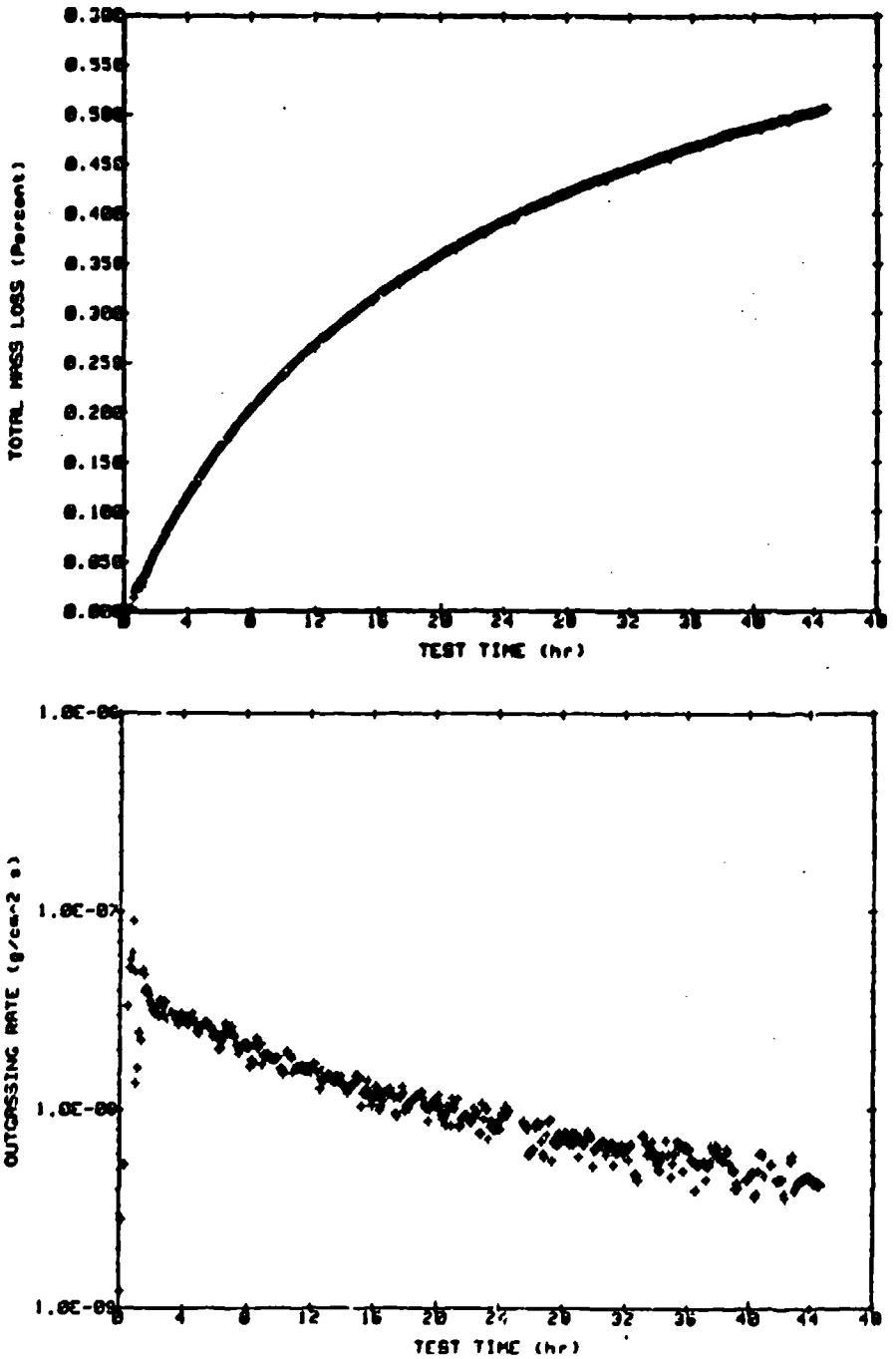
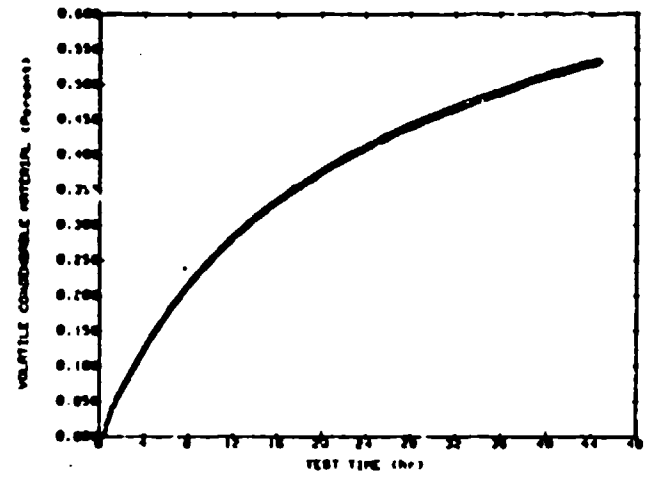
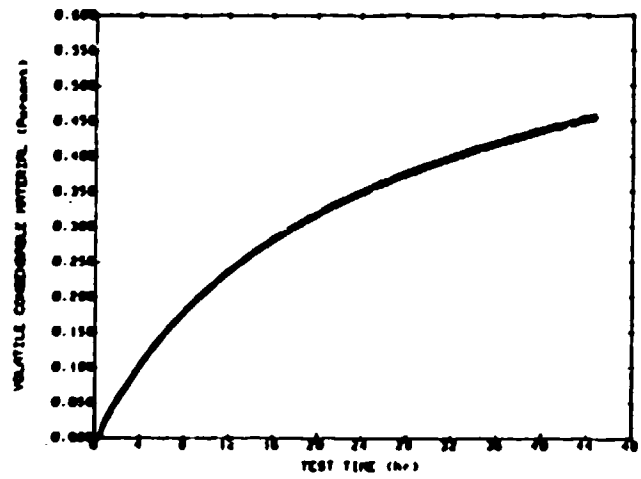


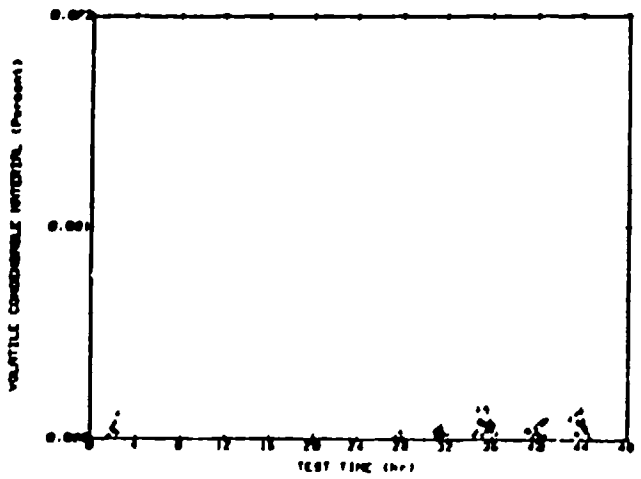
Fig. A-73 Total Mass Loss and Outgassing Rate as Functions of Time for a Krytox 143 AD Sample at 75°C.



150 K QCM



220 K QCM



298 K QCM

Fig. A-74 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Krytox 143 AD Sample at 75°C.

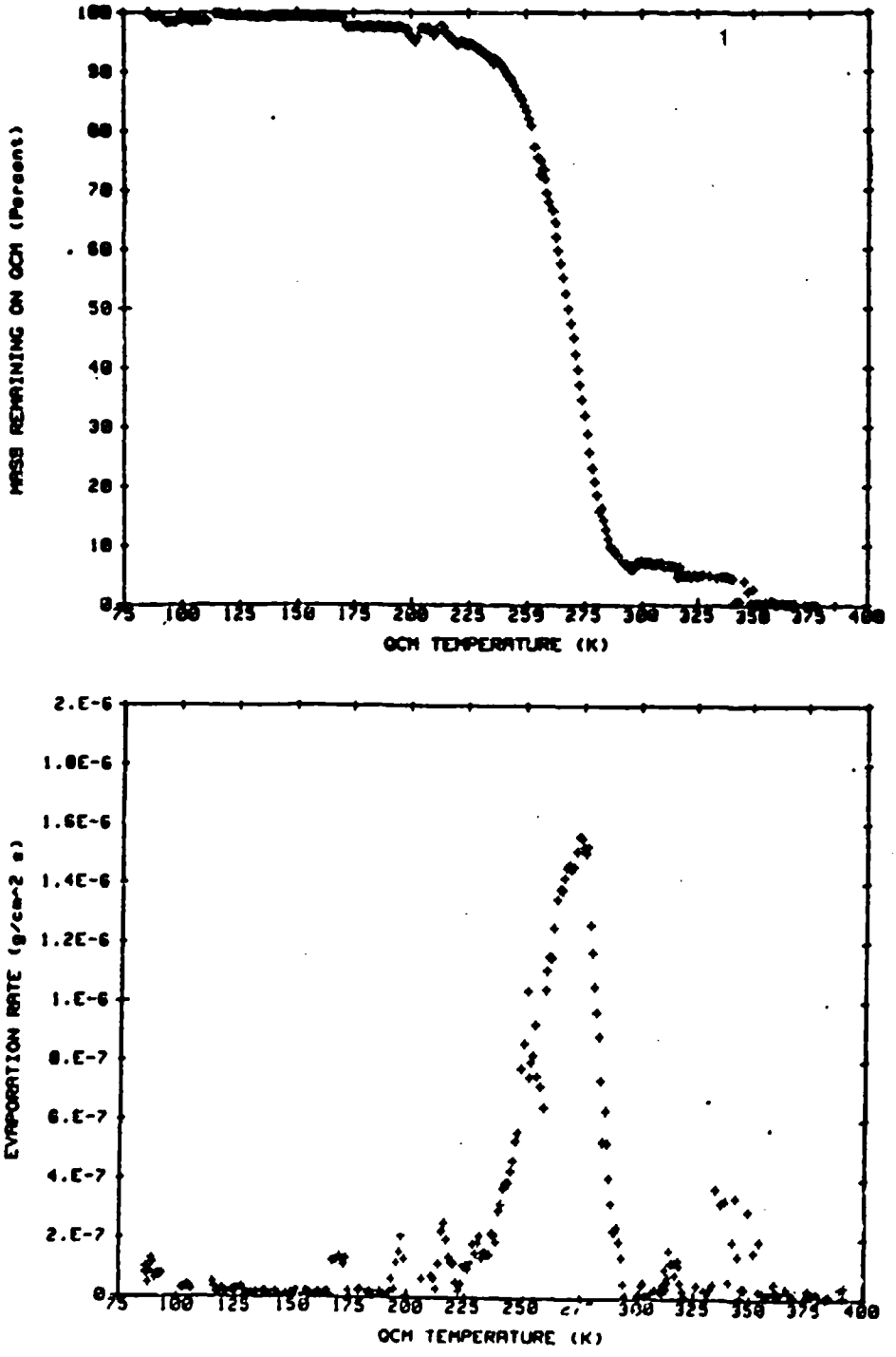


Fig. A-75 QTGA. Data for Outgassing Products Collected on the 90 K QCM from a Krytox 143 AD Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Function of Temperature.

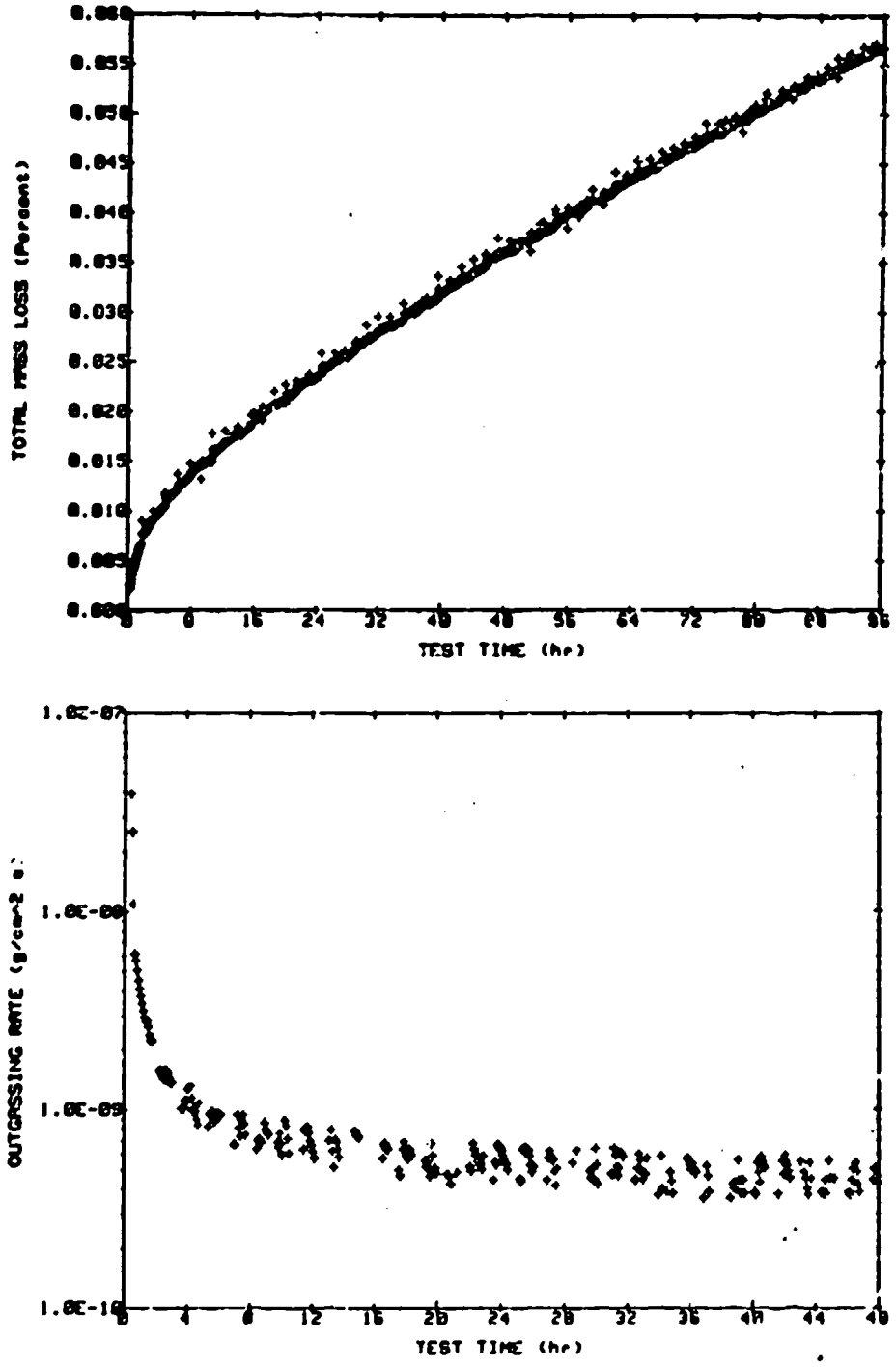


Fig. A-76 Total Mass Loss and Outgassing Rate as Functions of Time for a Krytox 143 AD Sample at 25°C.

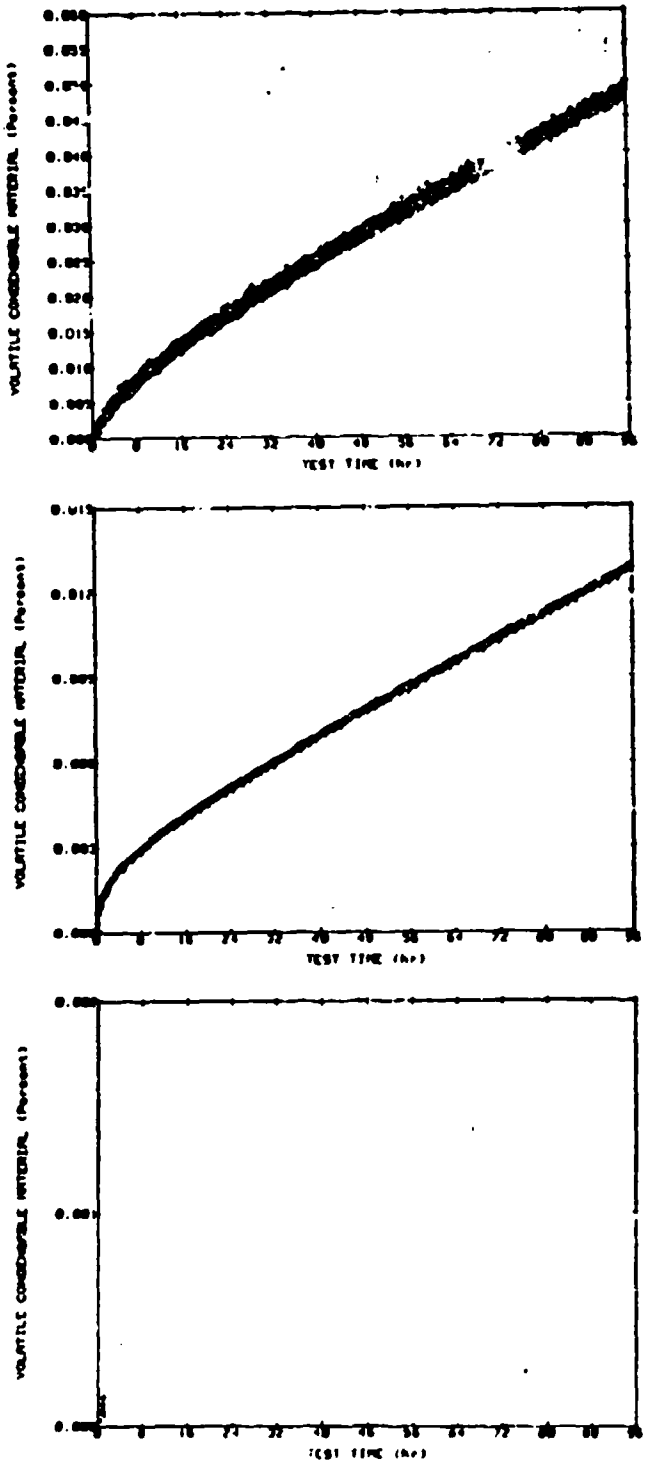


Fig. A-77 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Krytox 143 AD Sample at 25°C.

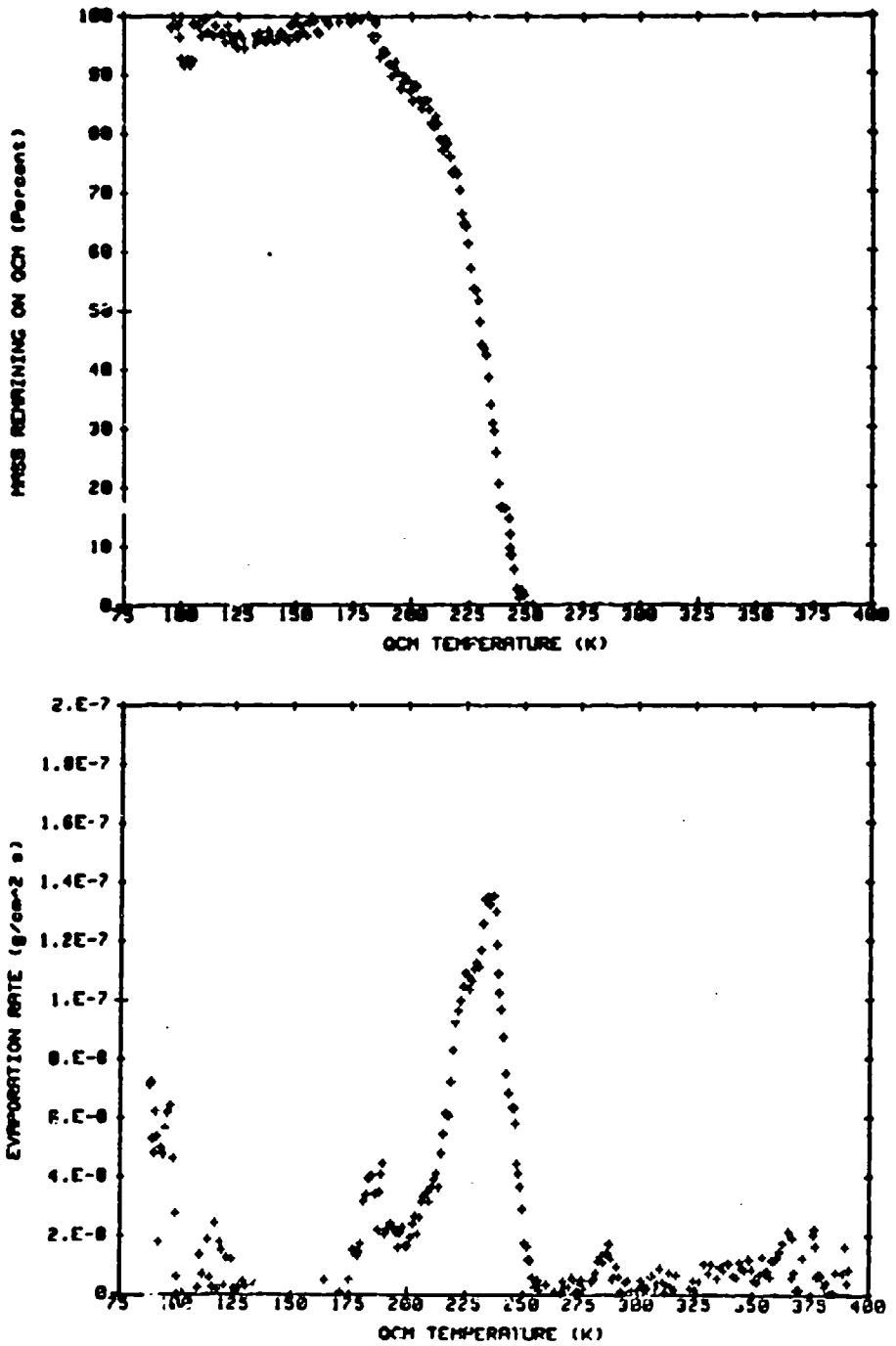


Fig. A-78 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Krytox 143 AD Sample at 25°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-20

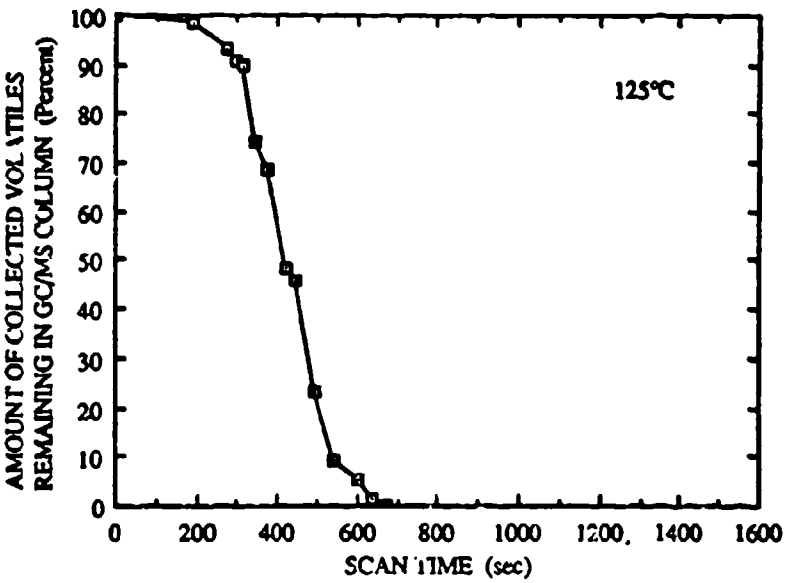
GC/MS Data for Krytox 143 AD at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
192	1.39	unknown fluorocarbon
271	5.52	unknown fluorocarbon
300	2.10	unknown fluorocarbon
314	1.33	unknown fluorocarbon
344	1.46	unknown fluorocarbon
373	3.86	unknown fluorocarbon
423	20.44	unknown fluorocarbon
449	2.34	unknown fluorocarbon
492	22.62	unknown fluorocarbon
542	14.04	unknown fluorocarbon
600	3.93	unknown fluorocarbon
639	3.51	artifact
673	1.66	unknown fluorocarbon

Table A-2[1]

GC/MS Data for Krytox 143 AD at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
265	0.69	unknown fluorocarbon
342	2.44	unknown fluorocarbon
369	0.62	unknown fluorocarbon
380	0.47	unknown fluorocarbon
415	5.33	unknown fluorocarbon
440	1.06	unknown fluorocarbon
502	8.21	unknown fluorocarbon
524	1.51	unknown fluorocarbon
569	8.37	unknown fluorocarbon
588	0.70	unknown fluorocarbon
621	5.19	unknown fluorocarbon
640	1.59	unknown fluorocarbon
640	0.36	artifact seen in blank run
654	0.78	artifact seen in blank run
686	6.90	artifact seen in blank run
697	0.42	unknown fluorocarbon
738	9.40	unknown fluorocarbon
753	1.51	artifact seen in blank run
766	1.21	unknown fluorocarbon
797	12.33	artifact seen in blank run
843	8.32	unknown fluorocarbon
882	6.34	unknown fluorocarbon
917	4.36	unknown fluorocarbon
946	3.76	unknown fluorocarbon
974	2.72	unknown fluorocarbon
995	2.67	unknown fluorocarbon
1017	1.79	unknown fluorocarbon
1030	0.78	unknown fluorocarbon
1045	0.18	unknown fluorocarbon



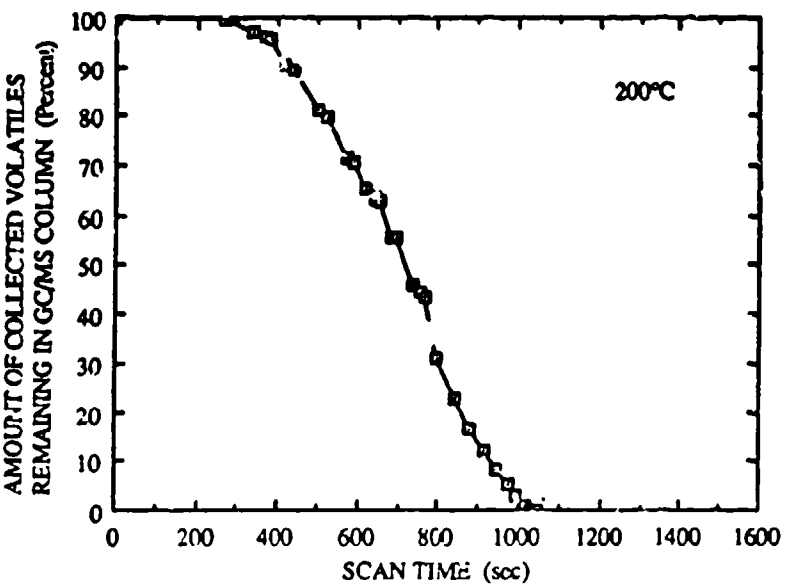


Fig. A-79 Amount of Collected Volatiles Remaining in GC/MS Column from Krytox 143AD at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : VacKote MLD 73-91 oil

DATE TEST STARTED : August 17, 1987

GC/MS DATA FILES :

125°C Test : KN11AUG87E
200°C Test : KN11AUG87C

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Area (cm^2)	15.14	15.14	15.14
Weight, pretest (g)	3.34692	3.26316	3.10824
Total mass loss (%)	no data	0.40	no data
ISOTHERMAL TEST DATA :			
Test duration (h)	26	24	24
QCM/Temperature Data File	G0817	G0827	G0830
Mass Spectrometer Data File	"	"	"
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0818Q	G0828Q	G0831Q
Mass Spectrometer Data File	"	"	"

COMMENTS :

- material is a parafinic hydrocarbon oil produced by Ball Aerospace, Systems Division
- samples supplied by Lt. P.M. Falco, USAF/AFWAL/MLBT
- sample holders were stainless steel cups 0.9 inch I.D. by 0.1 inch deep
- sample configuration (125°C test): 3 SS cups full of oil
- sample configuration (75°C test): 3 SS cups full of oil
- sample configuration (25°C test): 3 SS cups full of oil
- no final sample weights available for 125°C and 25°C tests (Note 3, Sec. A.1.4)
- interlock chamber evacuated with mechanical pump (Note 10, Sec. A.1.4)
- only first 5 hours of mass spectrometer data stored for 25°C Isothermal Test
- no QTA performed on 220 K and 298 K QCMs after 25°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 400

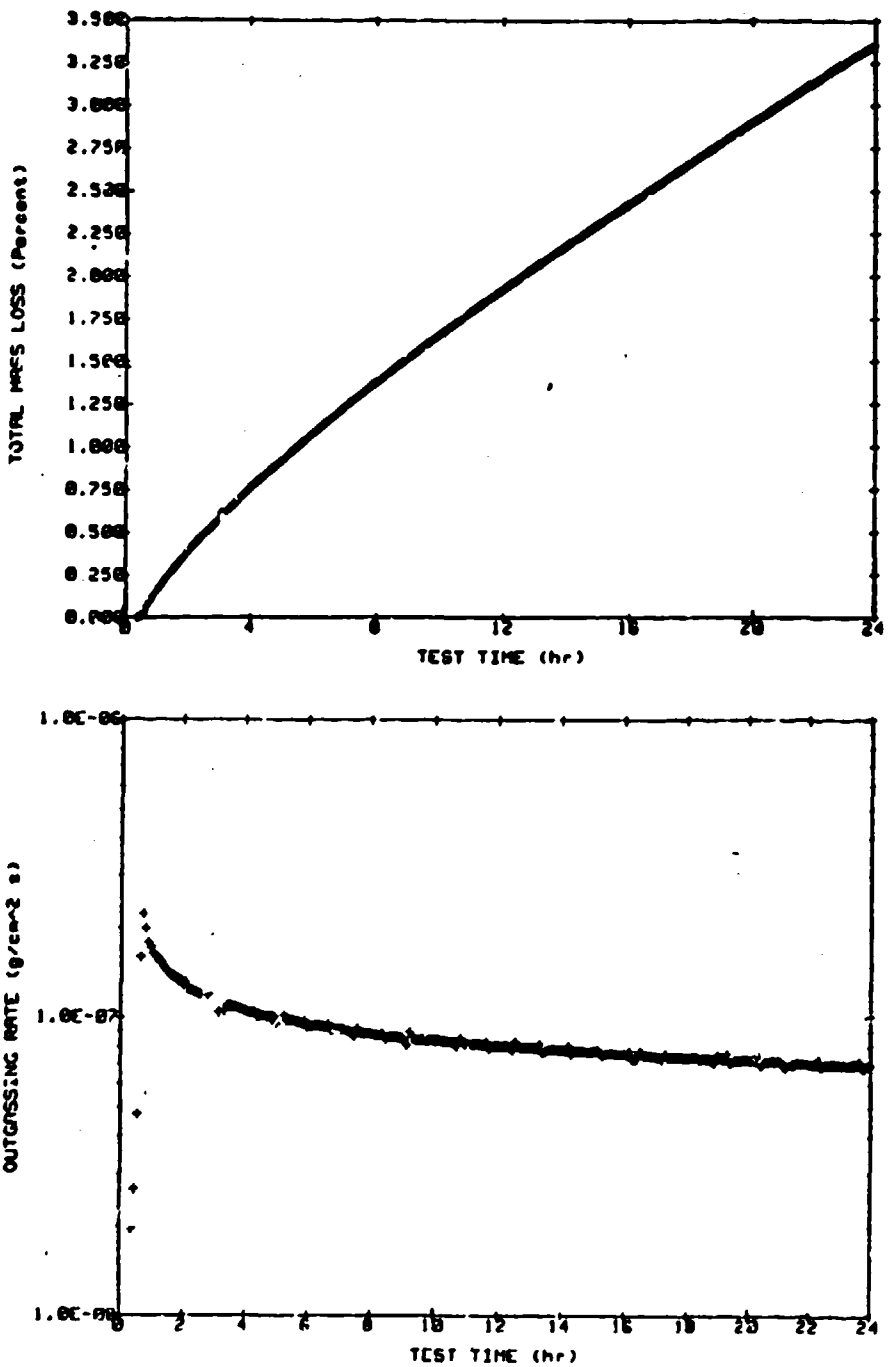
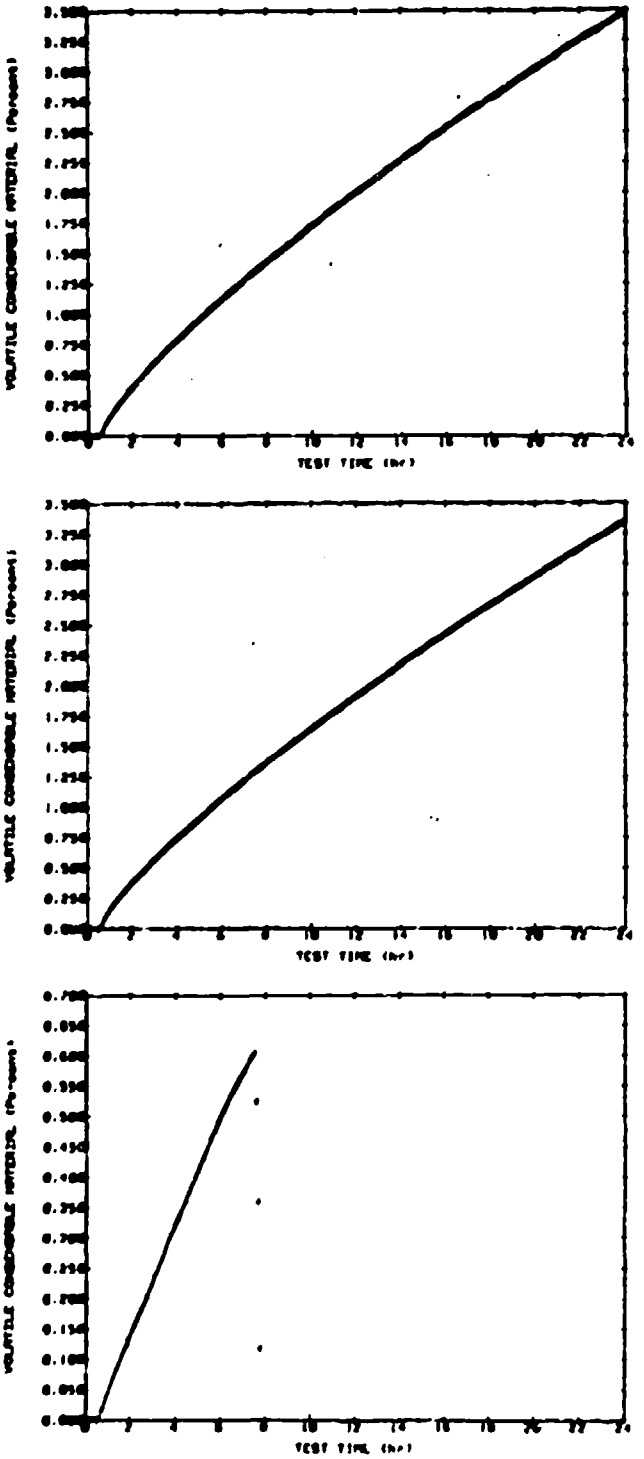


Fig. A-80 Total Mass Loss and Outgassing Rate as Functions of Time for a VacKote MLD 73-91 Sample at 125°C.



150 K QCM

220 K QCM

298 K QCM

Fig. A-81 Volatile Condenseble Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a VacKote MLD 73-91 Sample at 125°C.

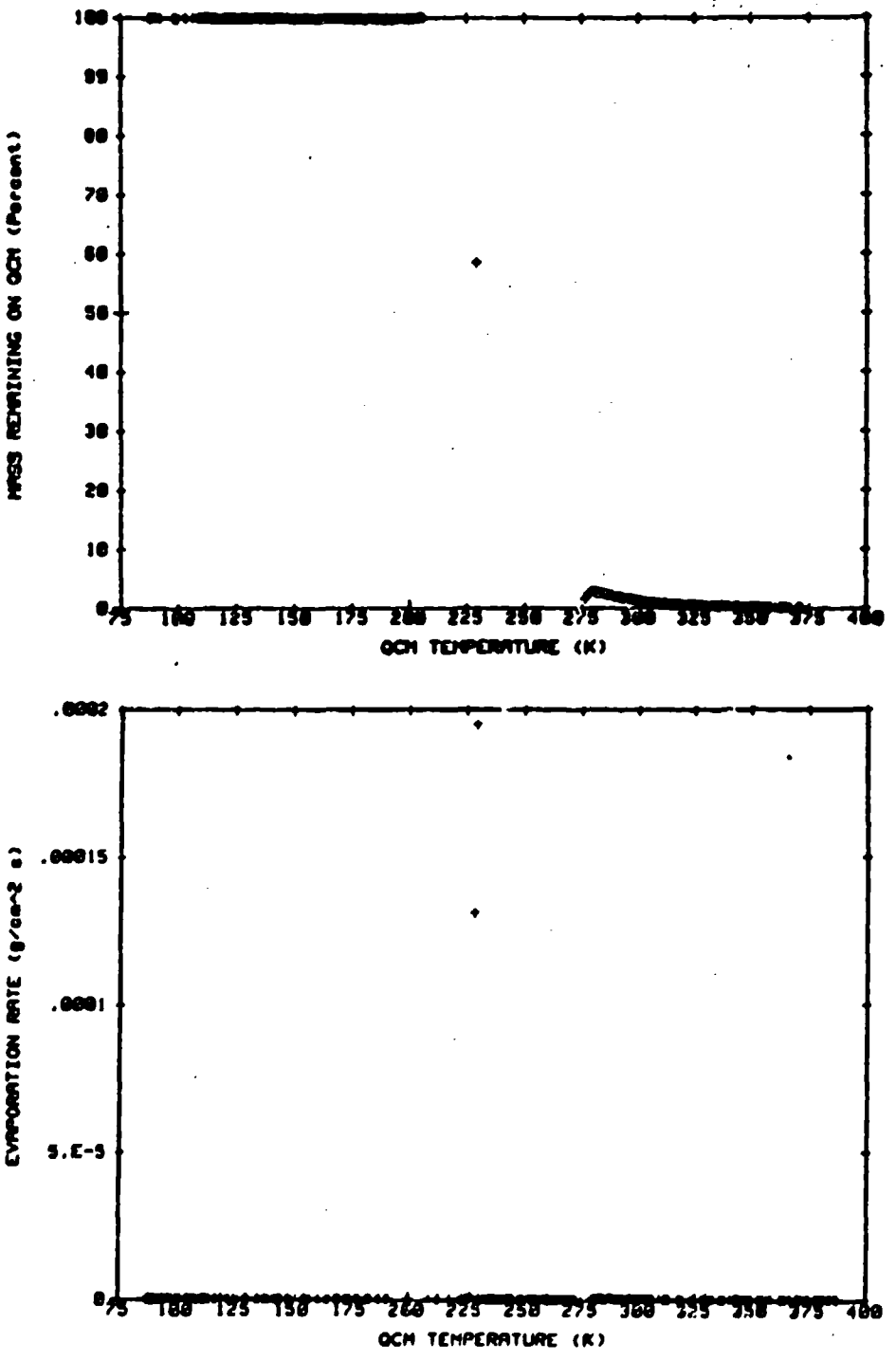


Fig. A-82 QTGA Data for Outgassing Products Collected on the 90 K QCM from a VacKote MLD 73-91 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

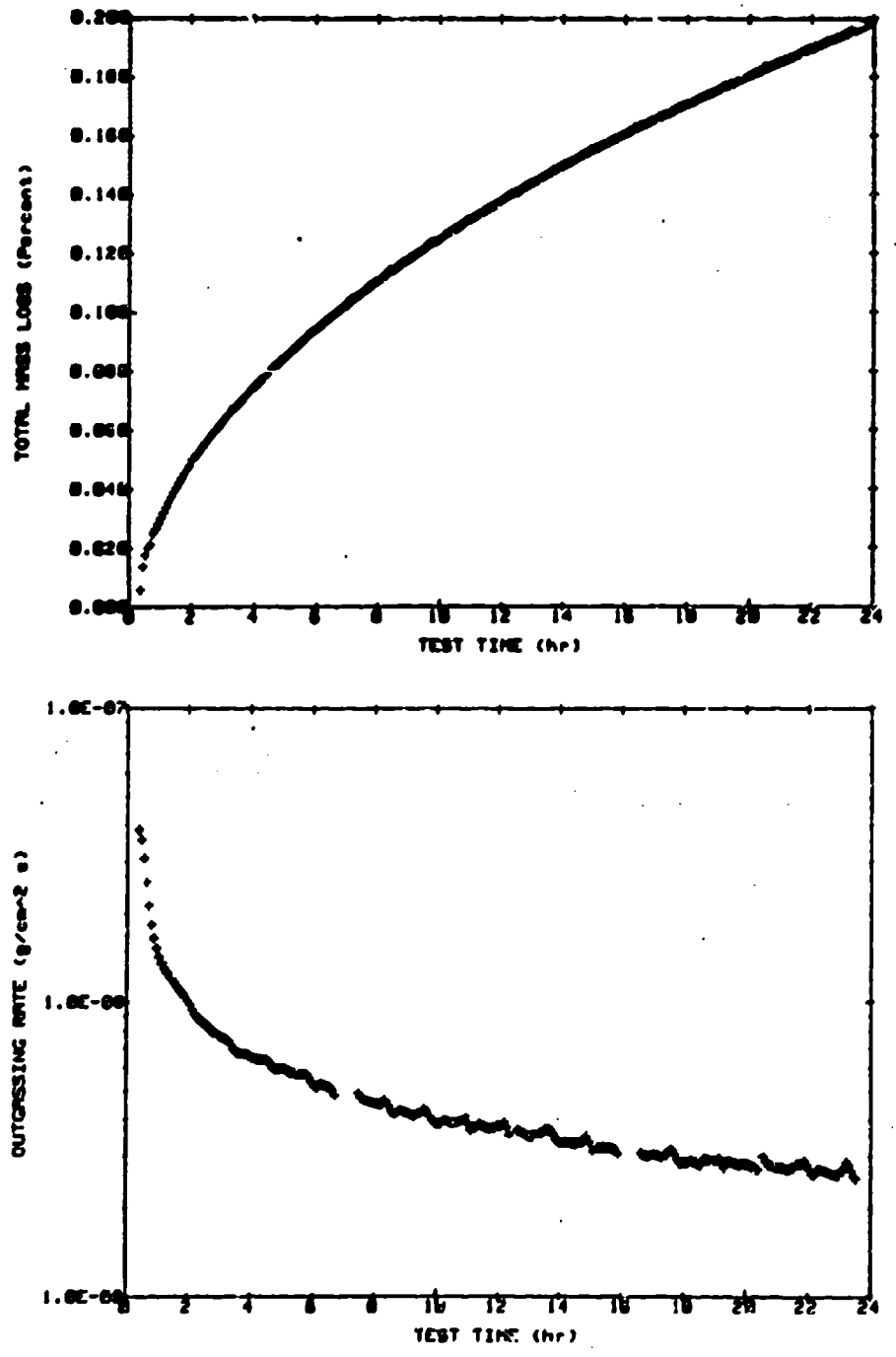
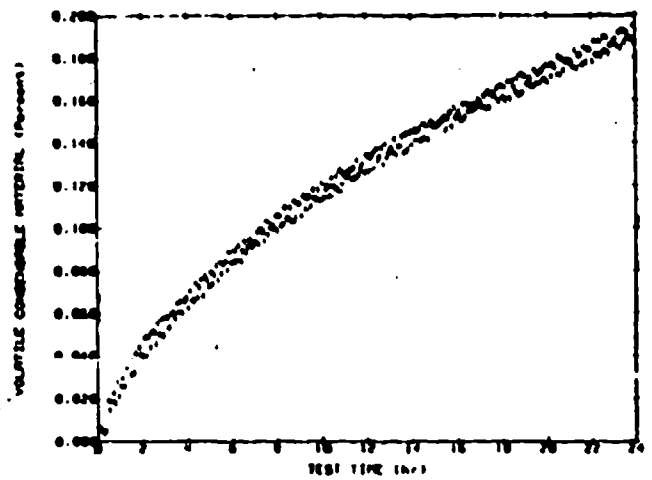
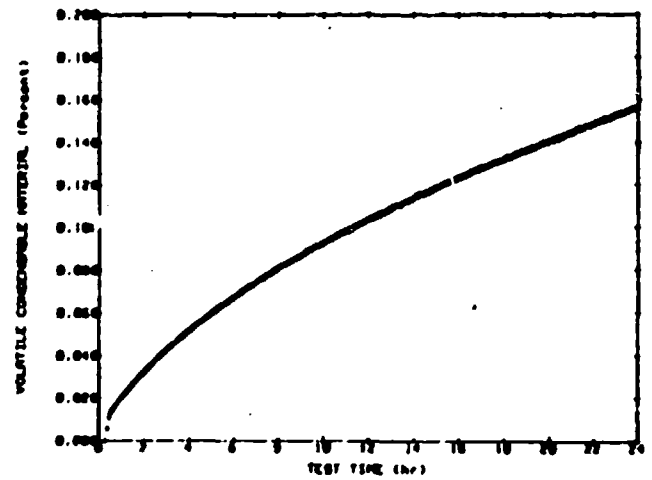


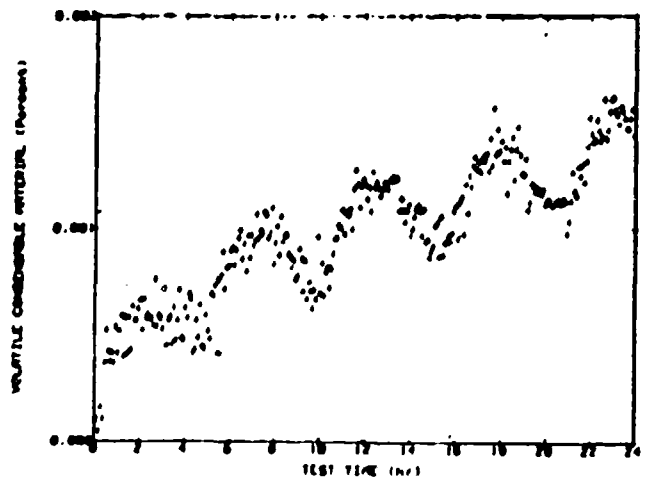
Fig. A-83 Total Mass Loss and Outgassing Rate as Functions of Time for a VacKote MLD 73-91 Sample at 75°C.



150 K QCM



220 K QCM



298 K QCM

Fig. A-84 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a VacKote MLD 73-91 Sample at 75°C.

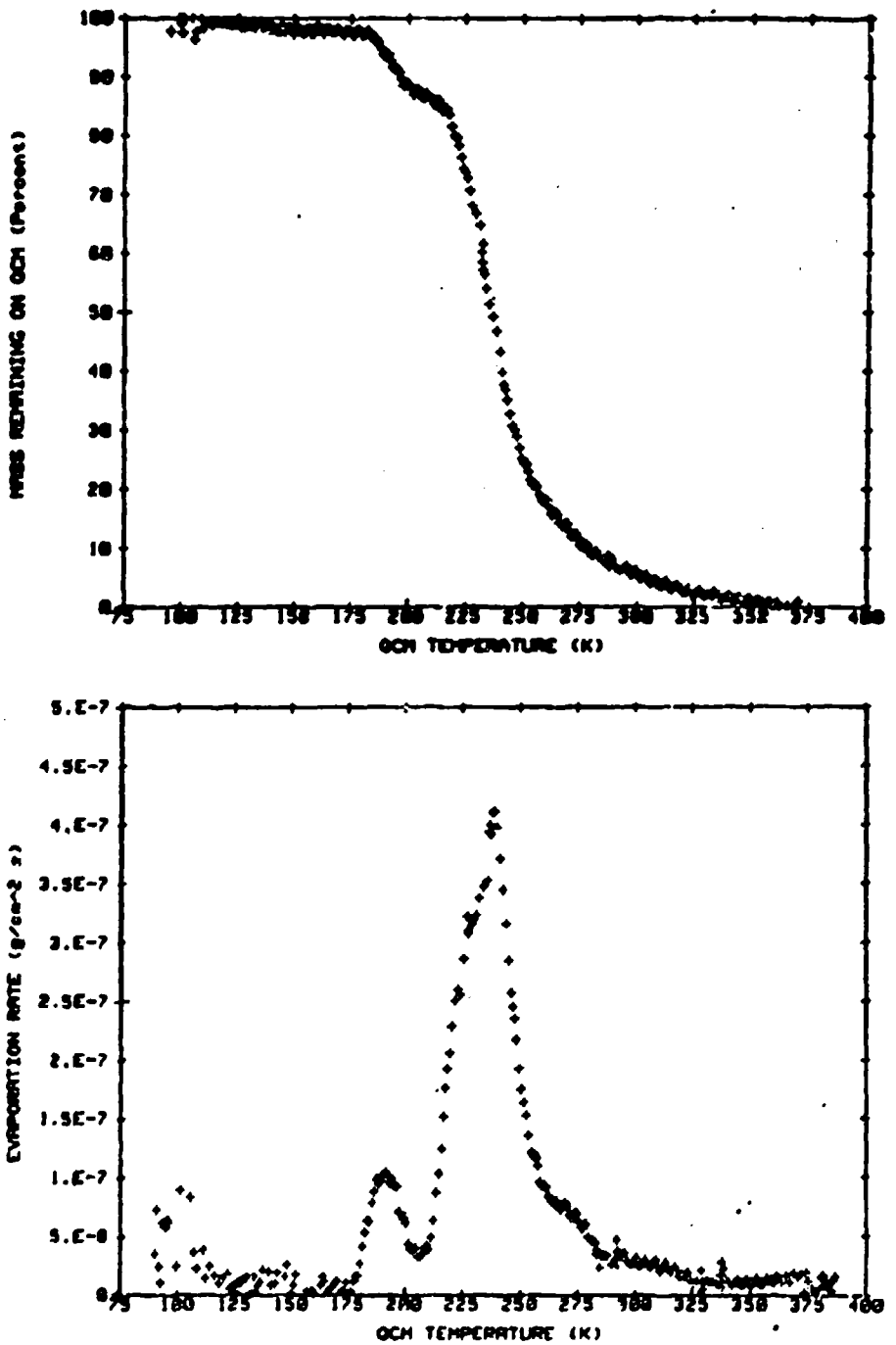


Fig. A-85 QTGA Data for Outgassing Products Collected on the 90 K QCM from a VacKote MLD 73-91 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

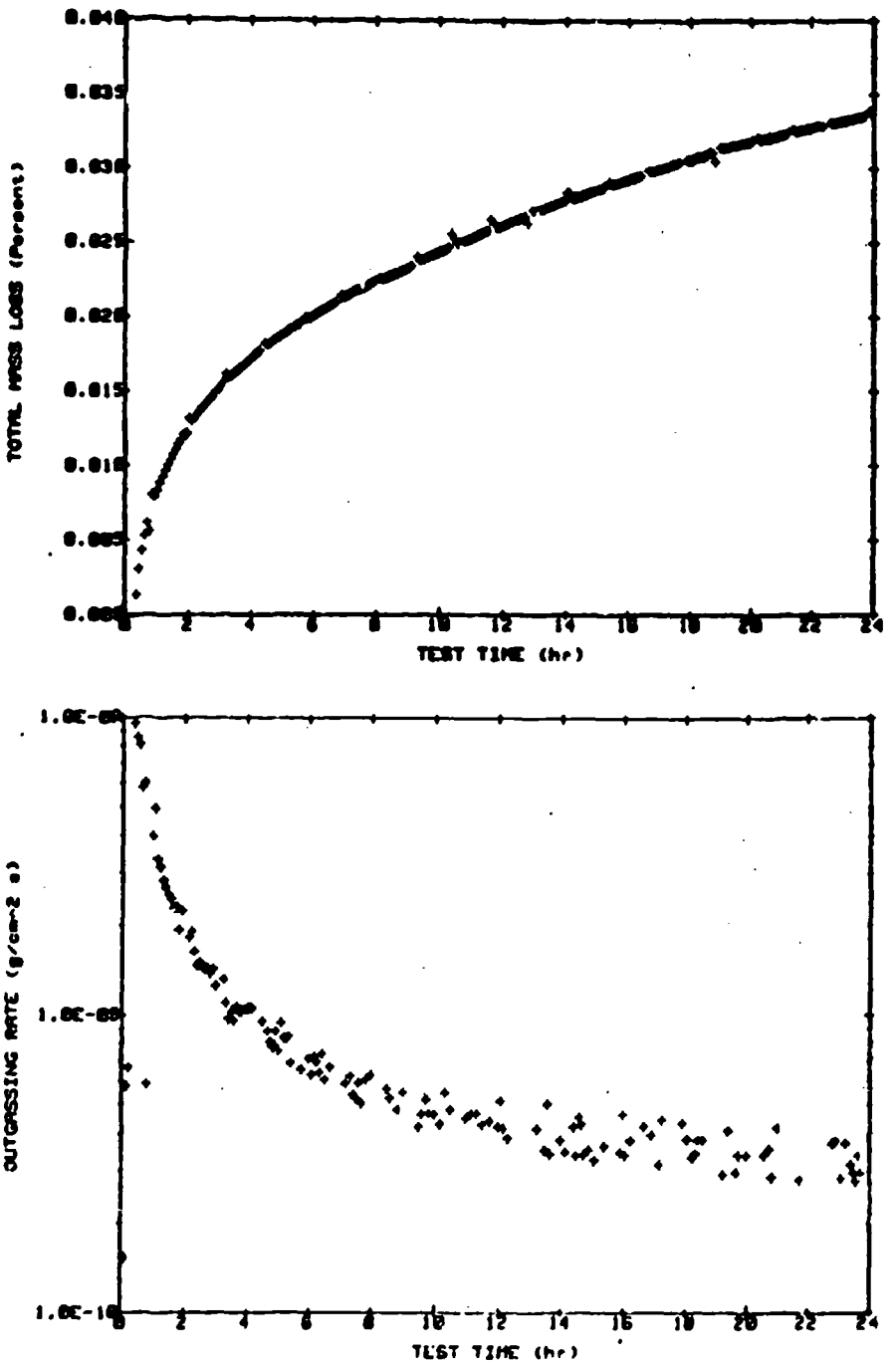


Fig. A-86 Total Mass Loss and Outgassing Rate as Functions of Time for a VacKote MLD 73-91 Simple at 25°C.

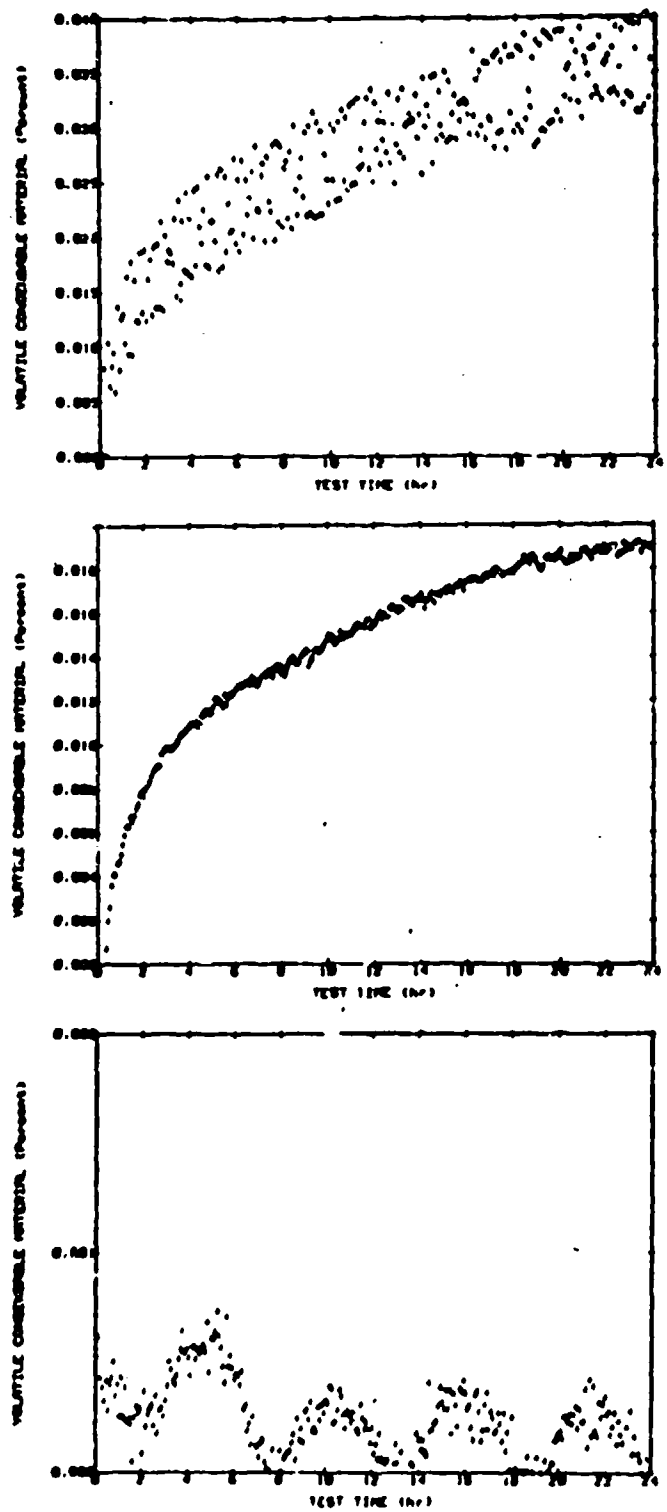
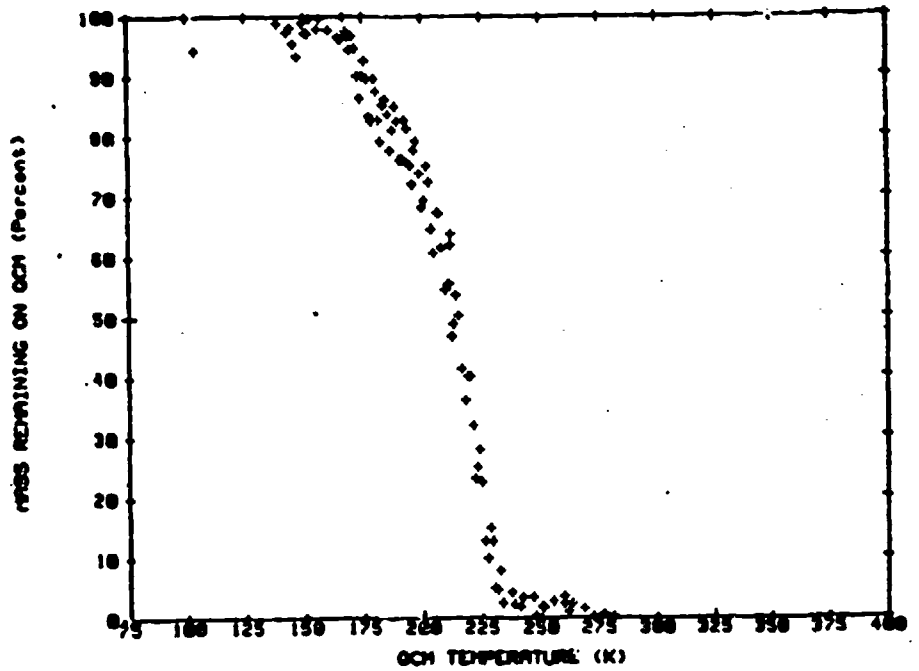


Fig. A-87 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a VacKote MLD 73-91 Sample at 25°C.



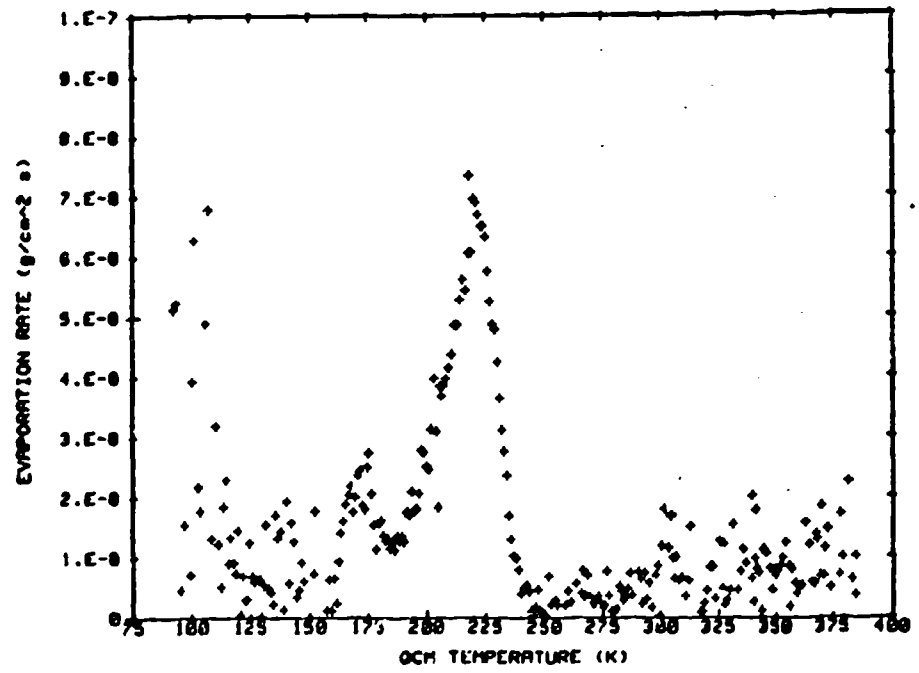


Fig. A-88 QTGA Data for Outgassing Products Collected on the 90 K QCM from a VacKote MLD 73-91 Sample at 25°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-22

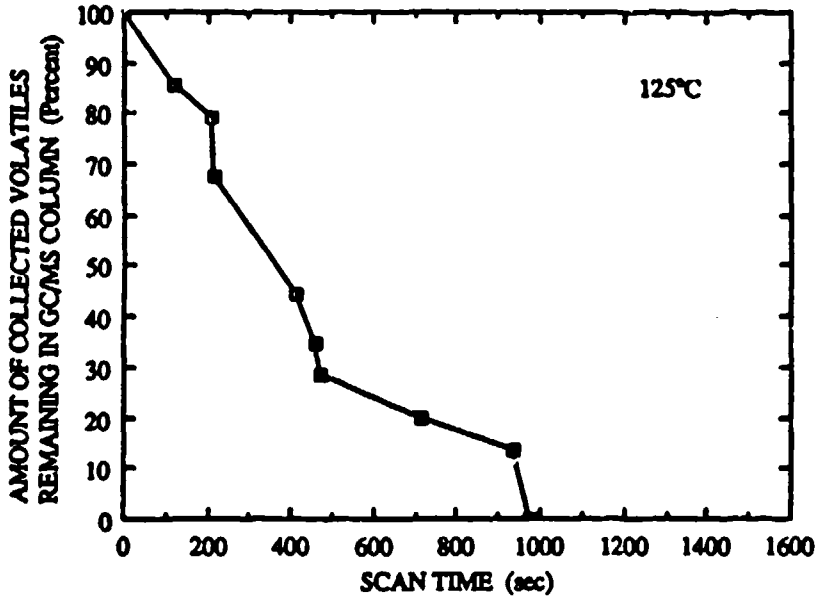
GC/MS Data for VacKote MLD 73-91 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
120	14.65	freon TF
206	6.12	heptane
213	11.55	3, 3-dimethyl-2-butanone
409	23.36	artifact seen in blank run
457	9.62	artifact seen in blank run
467	6.25	
716	8.41	C_8H_{15} cyclic amine ?
931	6.62	
973	13.43	

Table A-23

GC/MS Data for VacKote MLD 73-91 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
205	0.87	heptane
212	1.35	3, 3 dimethyl butanone
408	0.96	artifact seen in blank run
456	0.47	artifact seen in blank run
466	0.19	artifact seen in blank run
635	2.31	hydrocarbon
690	2.08	"
702	0.65	"
713	0.47	"
717	2.84	"
724	0.91	"
749	0.38	"
805	0.49	"
837	1.18	"
858	0.70	"
879	0.54	"
883	0.76	"
931	0.65	"
973	1.09	"
1019	2.80	"
1053	1.06	"
1062	4.31	"
1109	1.21	"
1128	3.44	"
1141	1.23	"
1161	0.90	"
1170	2.60	"
1172	0.93	"
1182	1.81	"
1187	2.05	"
1192	1.22	"
1239	2.79	"
1247	2.89	"
1284	5.18	"
1294	12.01	"
1326	2.33	"
1346	4.02	"
1386	1.89	"
1389	1.19	"
1392	1.10	"
1421	3.49	"
1451	2.16	"
1453	2.59	"
1549	13.88	"



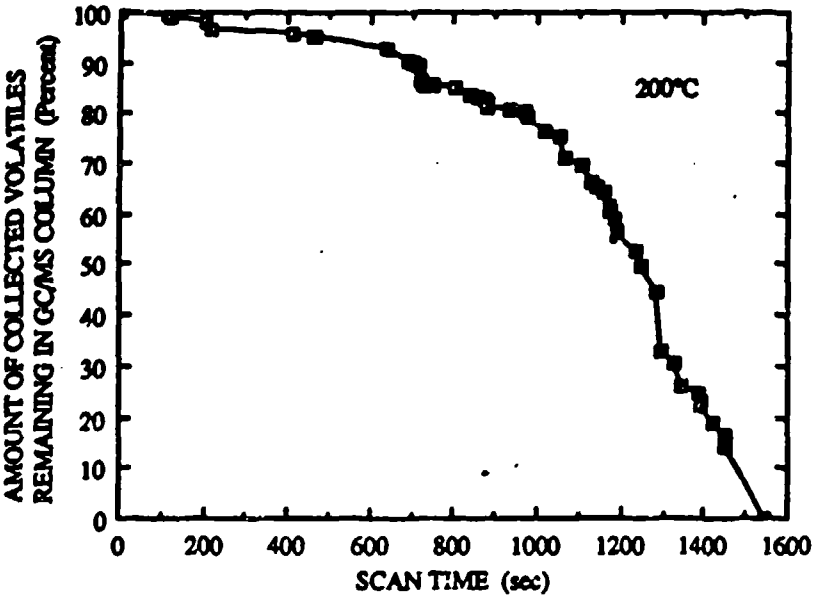


Fig. A-89 Amount of Collected Volatiles Remaining in GC/MS Column from VacKote MLD73-91 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : S/13G/LO-V10 paint

DATE TEST STARTED : March 25, 1988

GC/MS DATA FILES :

125°C Test: JG7APR88G
200°C Test: JG7APR88C

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	26.74	26.74
Weight, pretest (g)	1.46489	1.40055
Total mass loss (%)	1.00	0.45
ISOTHERMAL TEST DATA :		
Test duration (h)	24	24
QCM/Temperature Data File	G0325	G0327
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0326Q	G0328Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a low-outgassing, white, thermal control paint with SWS Silicone Corp. V10 silicone binder and zinc oxide pigment
- material is produced by Illinois Institute of Technology Research Institute
- LMSC EPS# 37-489-0000000
- samples supplied by Cliff Cerbus, University of Dayton Research Institute
- sample substrates were aluminum discs 0.945 inch diameter by 0.043 inch thick
- sample configuration (125°C test): 5 Al discs sprayed on one side
- sample configuration (75°C test): 5 Al discs sprayed on one side
- initial sample weights and substrate weights measured at University of Dayton
- final sample weights measured at LMSC
- mass spectrometer scanning m/e = 10 to 500

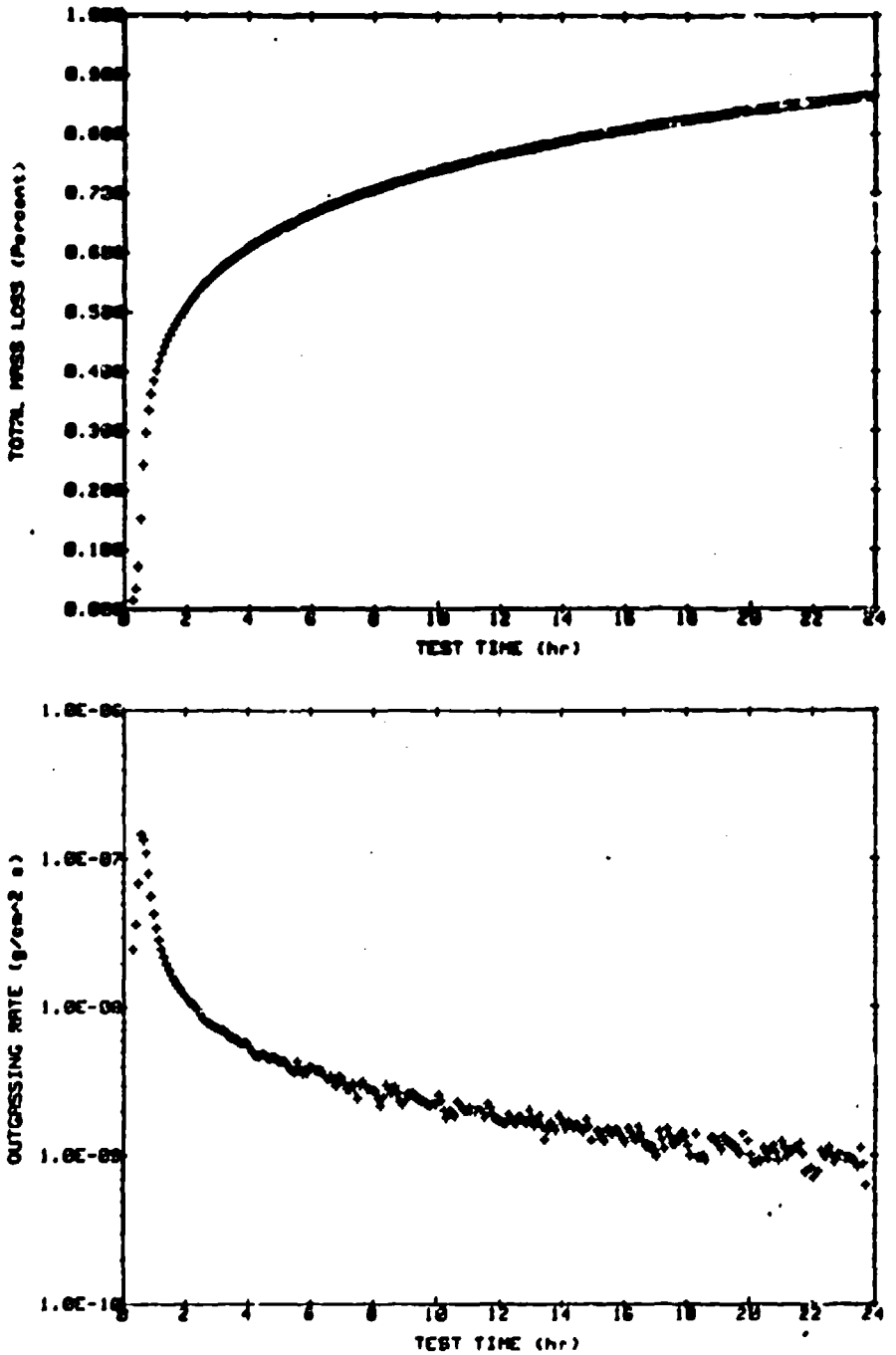


Fig. A-90 Total Mass Loss and Outgassing Rate as Functions of Time for an S/13G/LO-V10 Sample at 125°C.

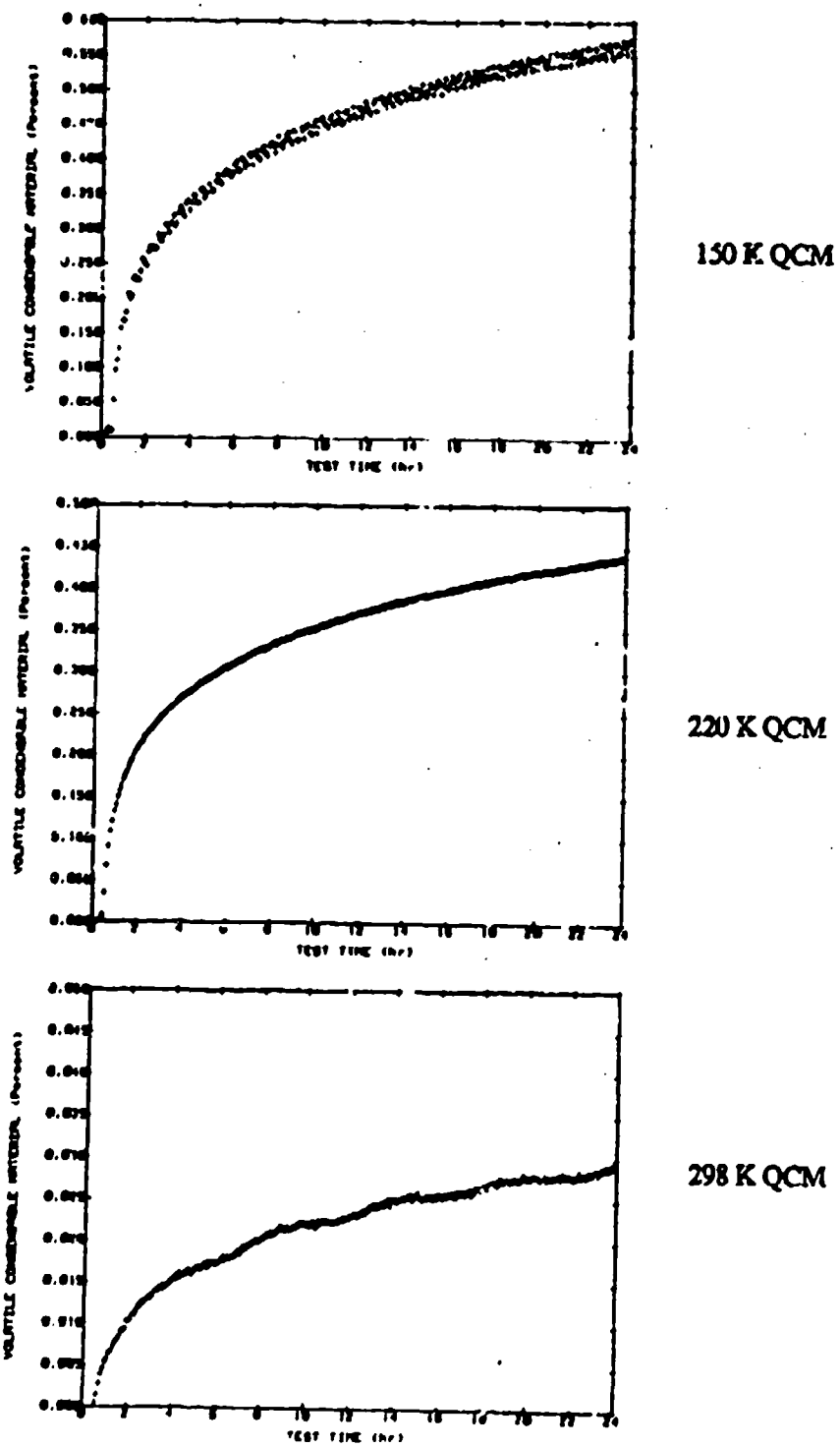


Fig. A-91 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an S/13G/LO-V10 Sample at 125°C.

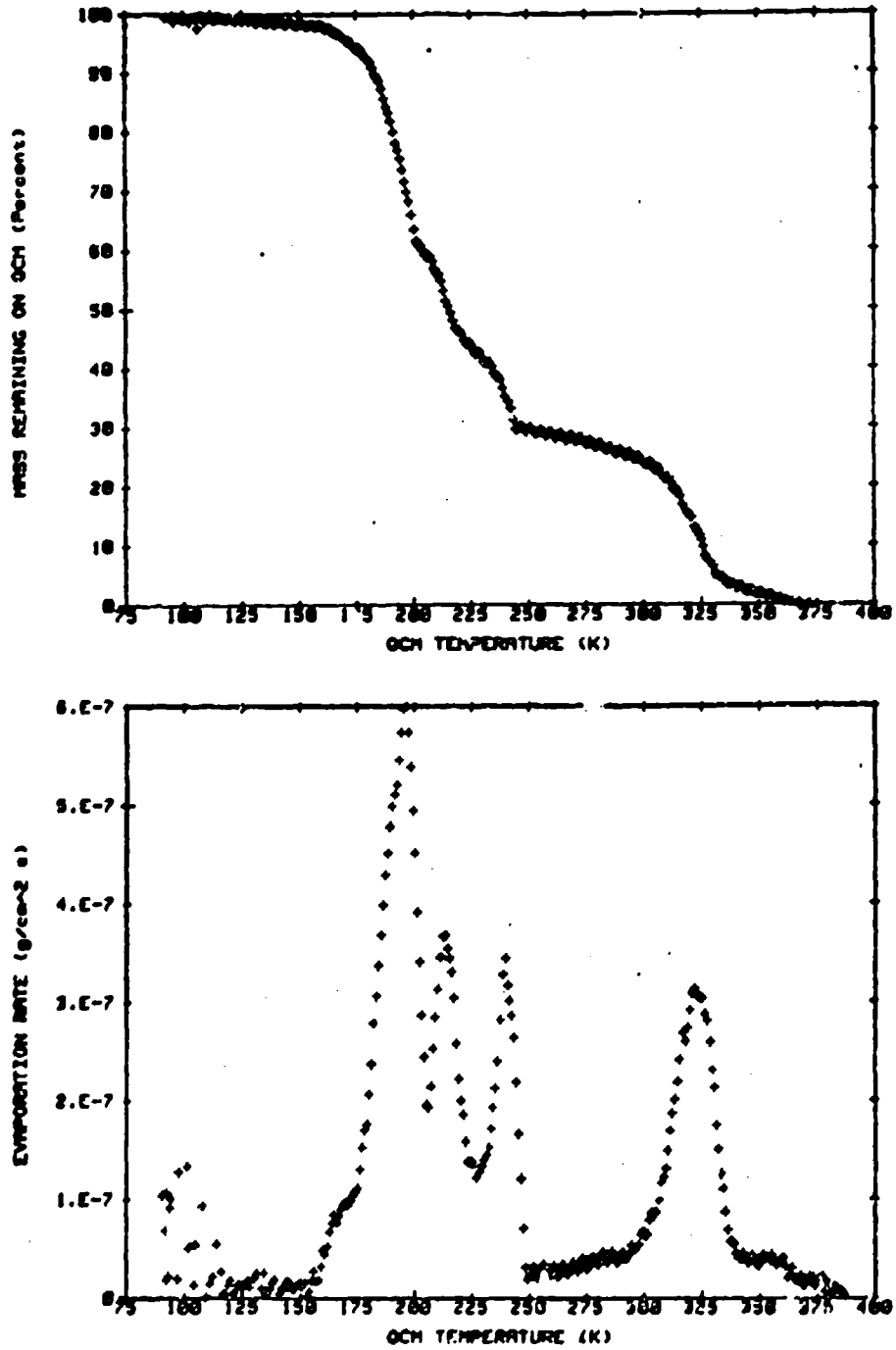


Fig. A-92 QTGA Data for Outgassing Products Collected on the 90 K QCM from an S/13G/LO-V10 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

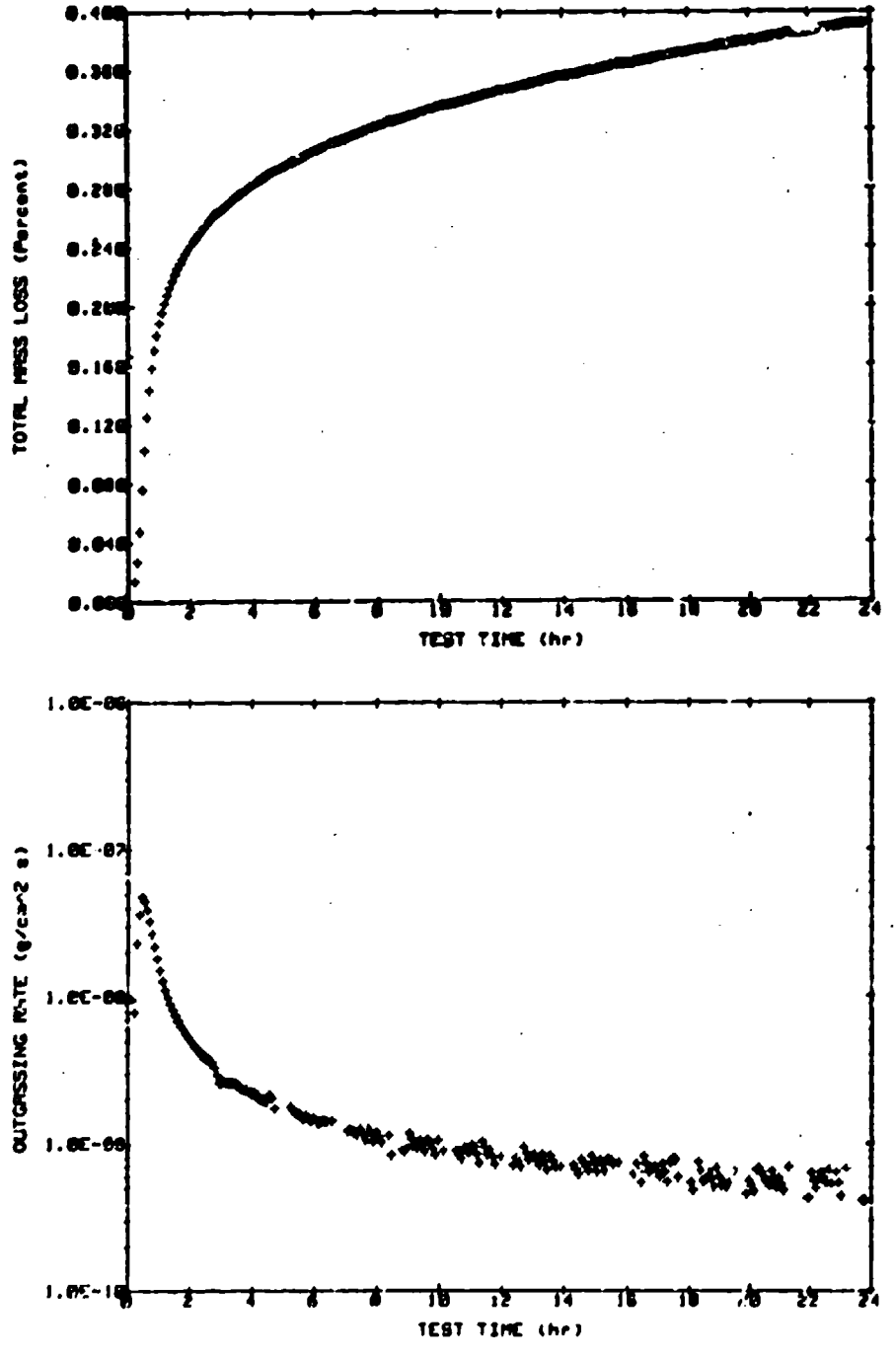


Fig. A-93 Total Mass Loss and Outgassing Rate as Functions of Time for an S/13G/LO-V10 Sample at 75°C.

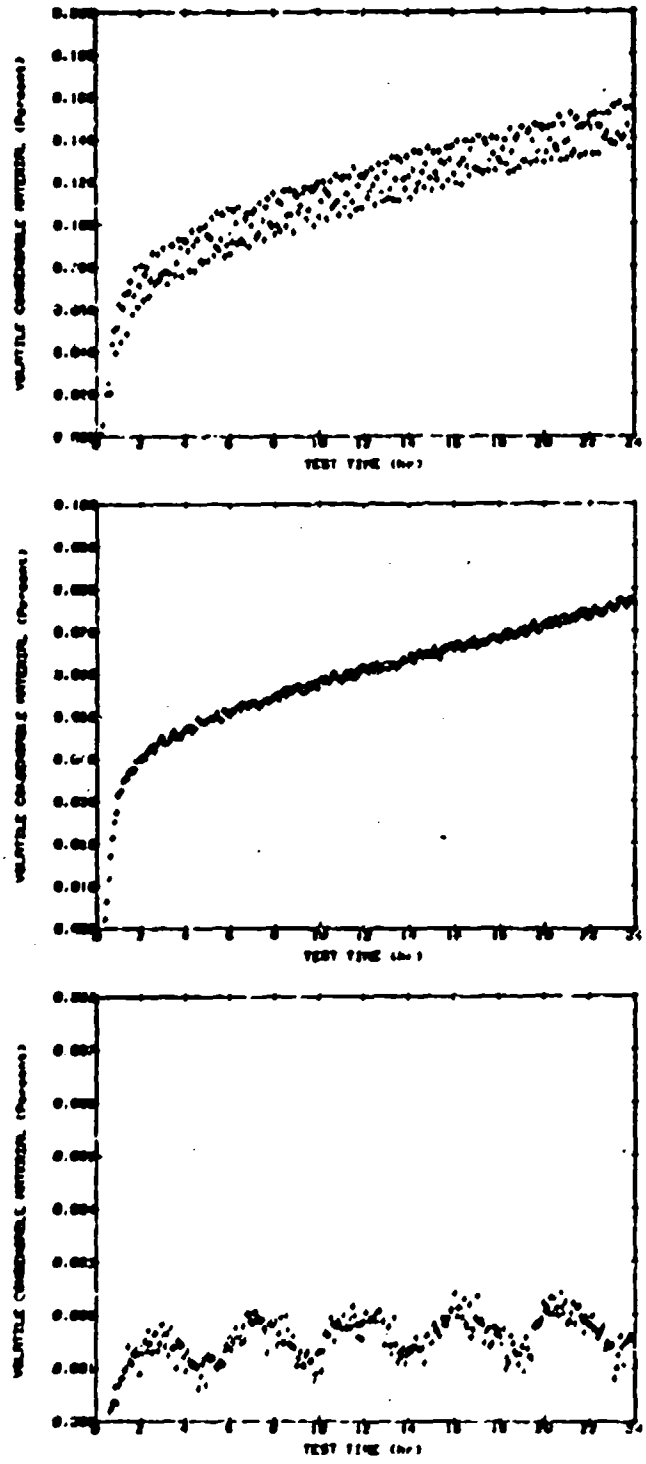
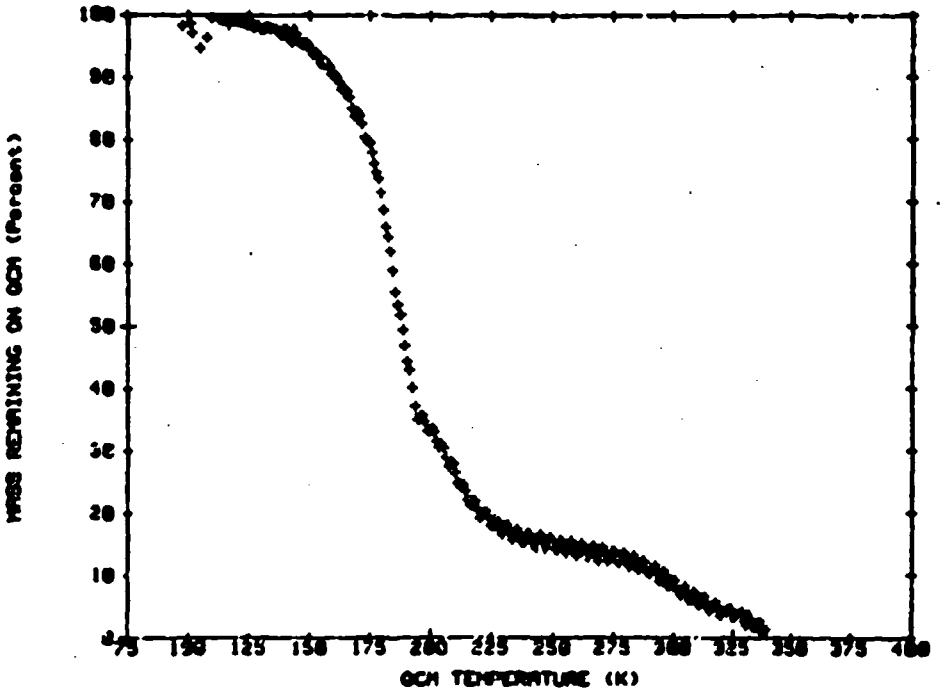


Fig. A-94 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an S/13G/LO-V10 Sample at 75°C.



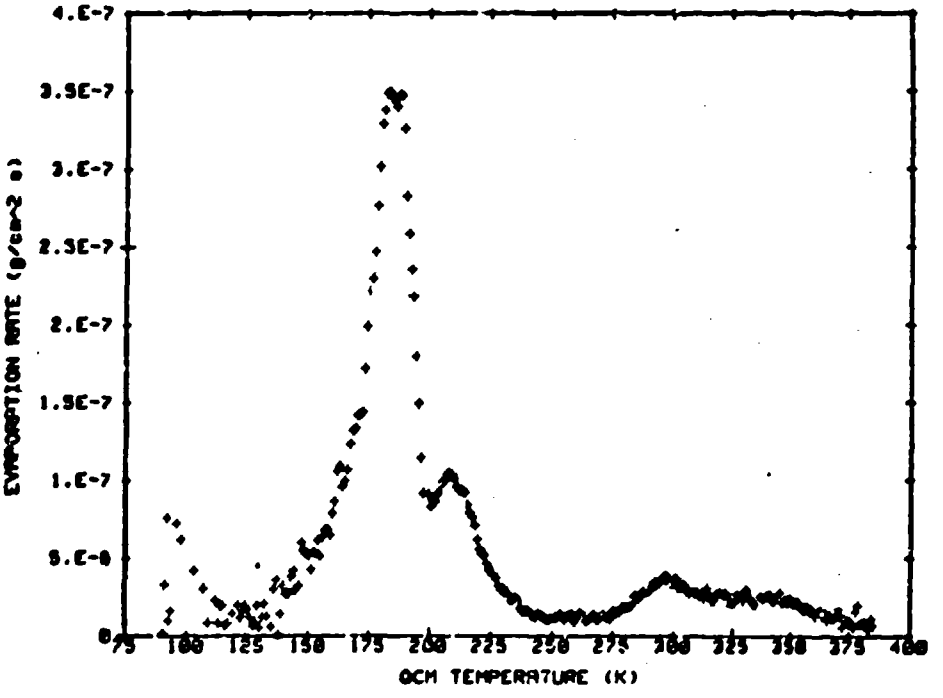


Fig. A-95 QTGA Data for Outgassing Products Collected on the 90 K QCM from an S/13G/LO-V10 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-24

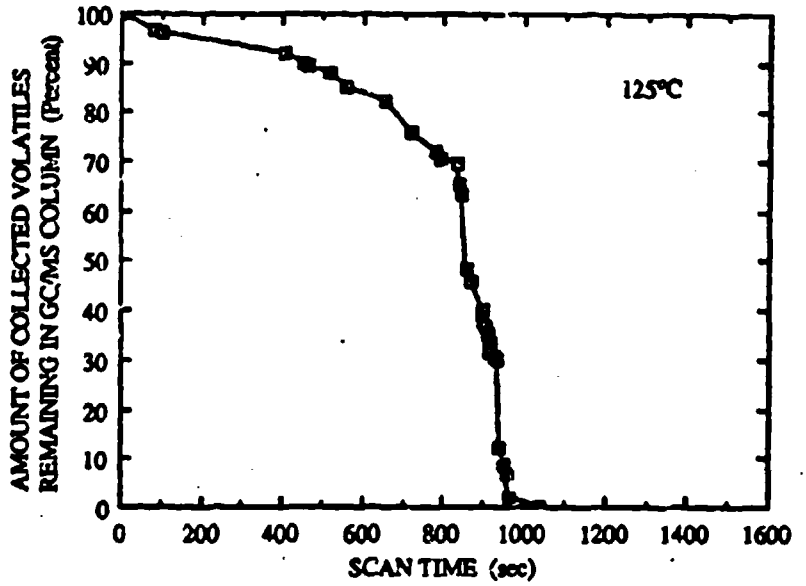
GC/MS Data for S/13G/LO-V10 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
83	3.52	CO_2 artifact
104	0.56	
405	4.05	artifact
455	1.89	artifact
465	0.83	
515	1.21	nonanal ?
558	3.06	artifact seen in #2 blank run, 4-7-88
654	2.82	aliphatic hydrocarbon
719	6.14	aliphatic hydrocarbon
781	3.70	aliphatic hydrocarbon
794	1.59	
832	1.22	
840	4.36	aliphatic hydrocarbon
843	1.89	
855	14.86	dodecanoic acid
869	2.49	
896	5.88	aliphatic hydrocarbon
900	2.44	
902	0.96	
911	1.25	
915	1.79	
918	1.96	
925	1.28	
933	0.45	
942	17.69	unspecified ester
949	3.50	dodecane
955	2.00	
961	4.59	tetradecanoic acid
1040	2.03	unspecified ester

Table A-25

GC/MS Data for S/13G/LO-V10 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
83	1.95	CO_2 artifact
90	0.96	butane
96	0.85	ethanol
104	0.79	2-propanol
117	0.29	silicone compound
172	0.71	1-butanol
292	1.57	hexamethyl cyclotrisiloxane
405	0.13	artifact
433	0.11	artifact
592	12.46	octanoic acid
654	0.20	
719	13.23	dec noic acid
781	0.27	
848	48.54	dodecanoic acid
855	1.59	
869	0.26	
896	0.81	
900	0.45	
911	0.14	
915	0.27	
918	0.29	
925	0.20	
942	3.84	ester ?
949	0.96	
955	0.66	
962	1.39	tetradecanoic acid
1042	2.32	ester ?
1048	0.26	
1059	0.88	
1093	0.21	
1132	1.20	ester ?
1138	0.79	
1150	0.21	
1190	0.24	
1227	0.50	
1241	0.28	
1249	0.20	



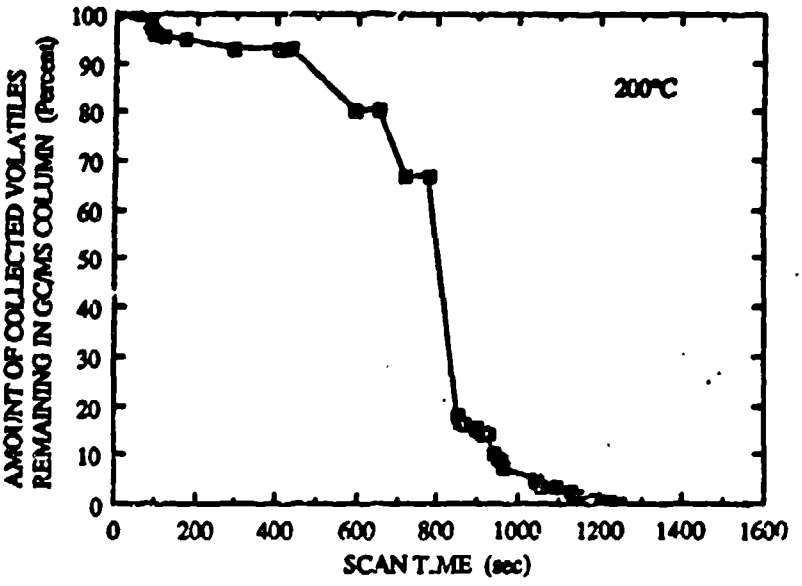


Fig. A-96 Amount of Collected Volatiles Remaining in GC/MS Column from S/13G/LO-V10 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Chemglaze Z306 paint

DATE TEST STARTED : March 19, 1988

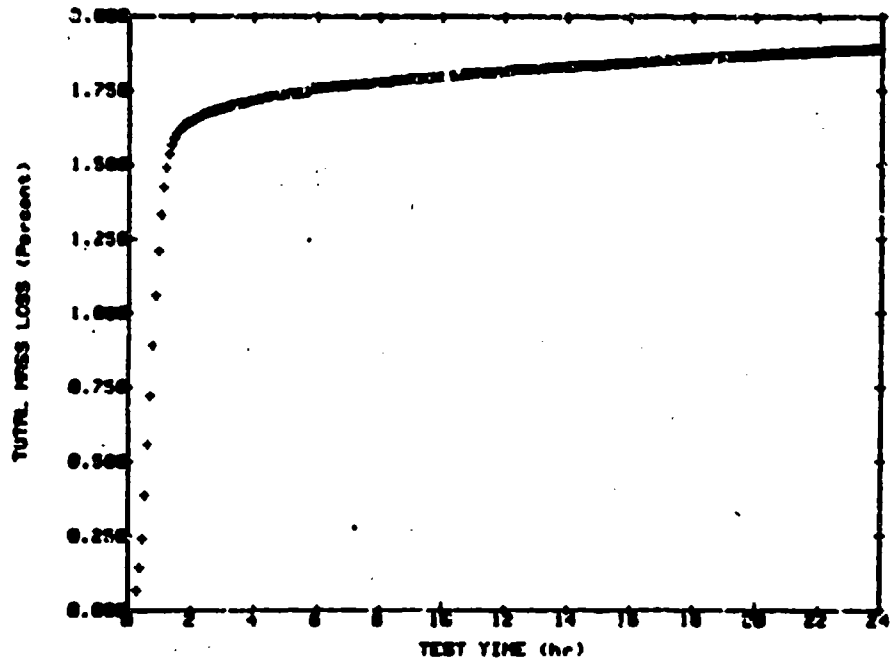
GC/MS DATA FILES :

125°C Test : JG7APR88E
200°C Test : JG7APR88D

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	39.15	39.15
Weight , pretest (g)	0.59144	0.60470
Total mass loss (%)	2.52	2.40
ISOTHERMAL TEST DATA :		
Test duration (h)	24	24
QCM/Temperature Data File	G0319	G0323
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0320Q	G0324Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a one-component, flat-black coating with carbon black pigment and polyurethane binder produced by Lord Corp.
- LMSC EPS# 37-494-0100134
- samples supplied by B.C. Petrie, LMSC Materials & Processes Engineering (O/62-92)
- sample substrates were aluminum discs 1.0 inch diameter by 0.13 inch thick
- sample configuration (125°C test): 5 Al discs sprayed on one side
- sample configuration (75°C test): 5 Al discs sprayed on one side
- mass spectrometer scanning m/e = 10 to 500
- mass spectrometer recalibrated between 125°C and 75°C Isothermal Tests



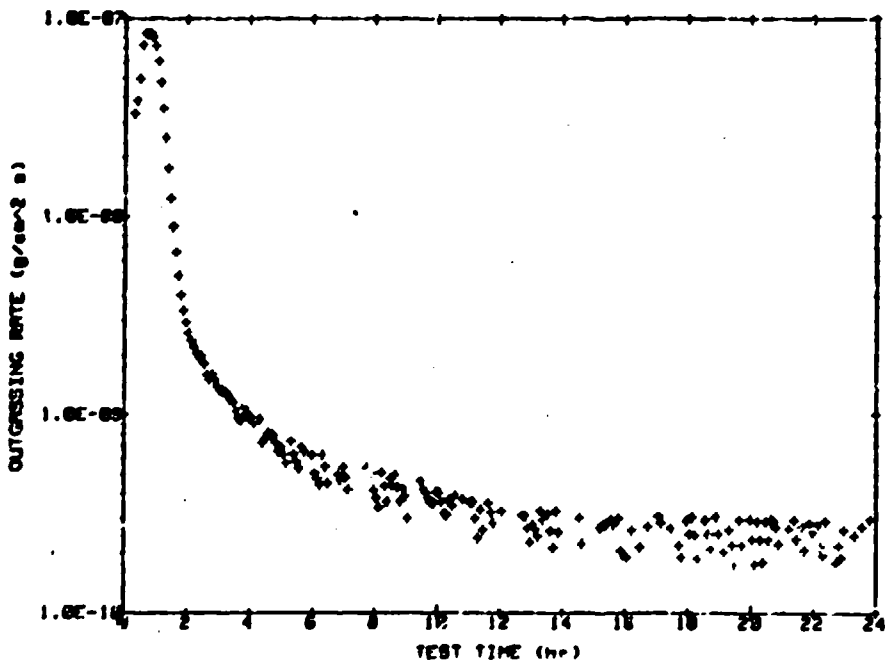


Fig. A-97 Total Mass Loss and Outgassing Rate as Functions of Time for a Chemglaze Z306 Sample at 125°C.

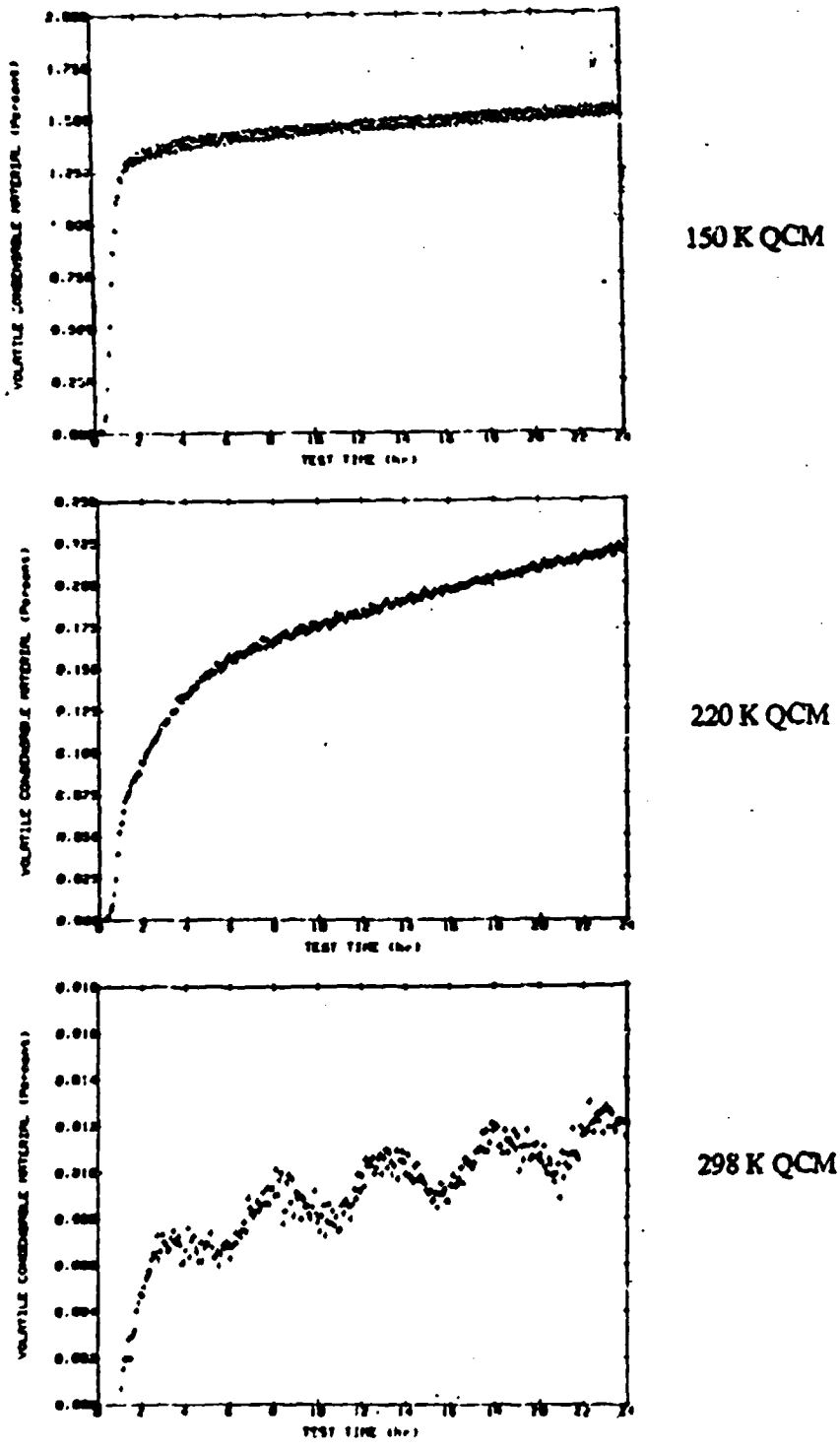


Fig. A-98 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Chemglaze Z306 Sample at 125°C.

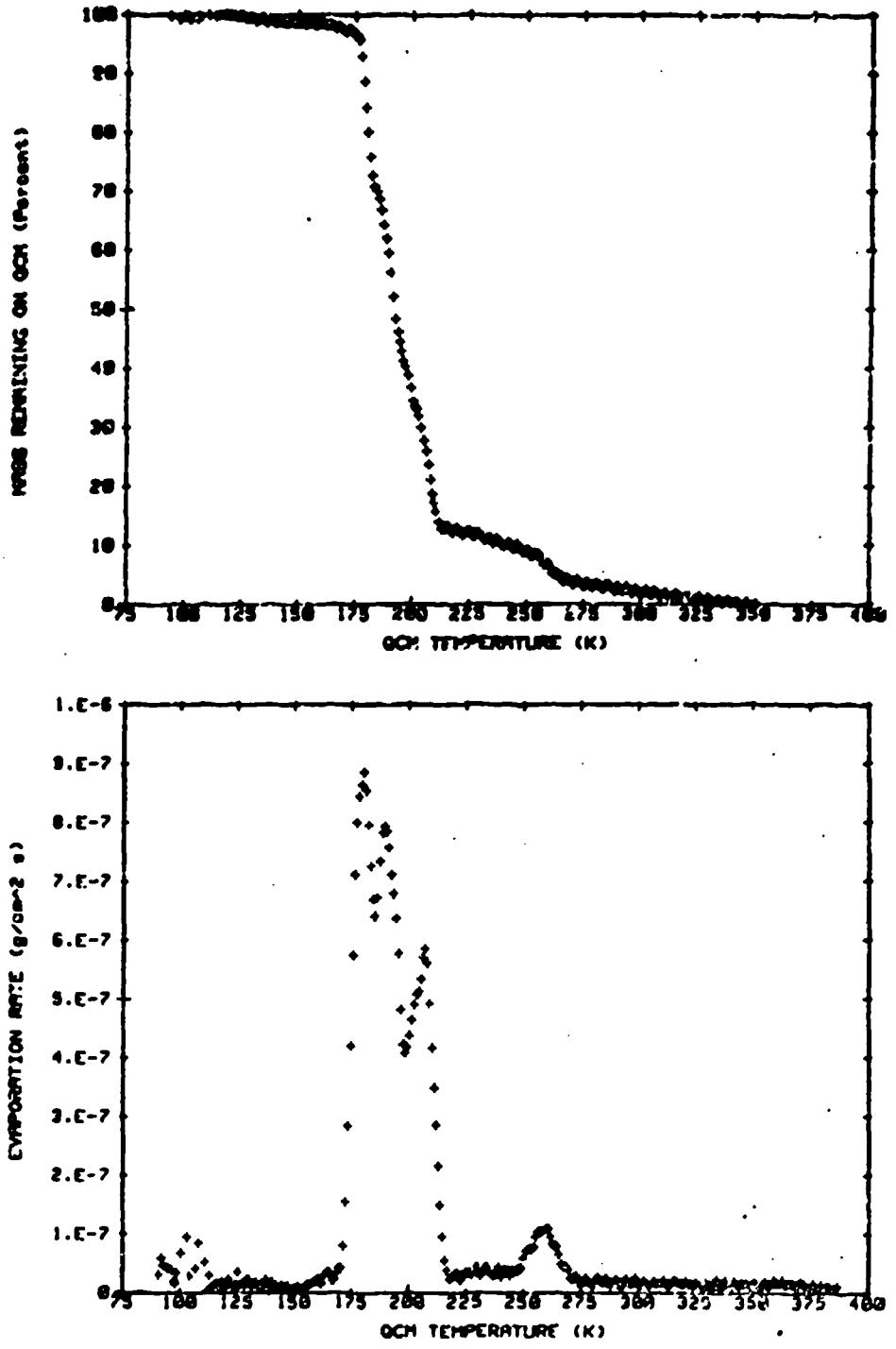


Fig. A-99 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Chemglaze Z306 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

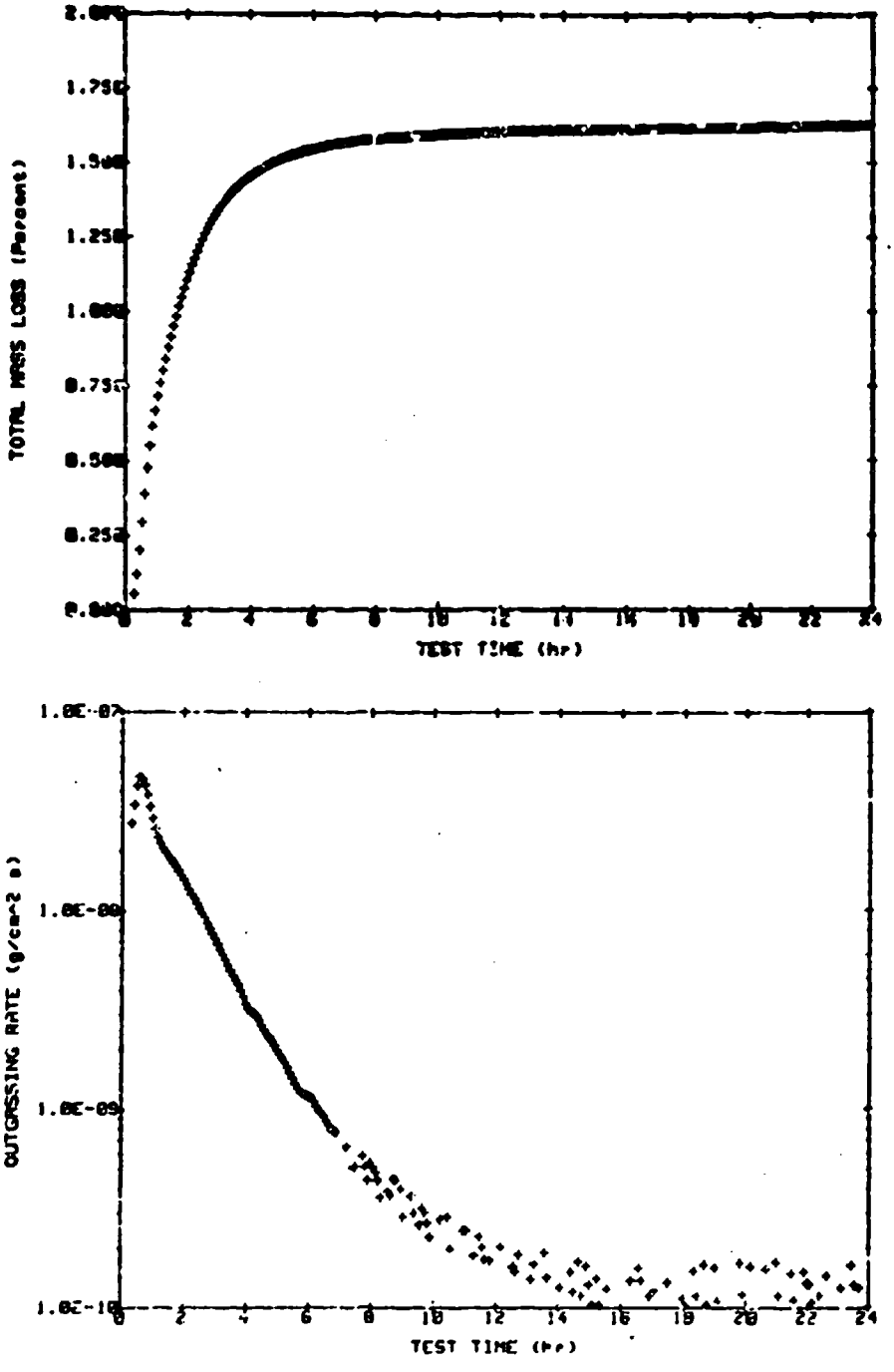


Fig. A-100 Total Mass Loss and Outgassing Rate as Functions of Time for a Chemglaze Z306 Sample at 75°C.

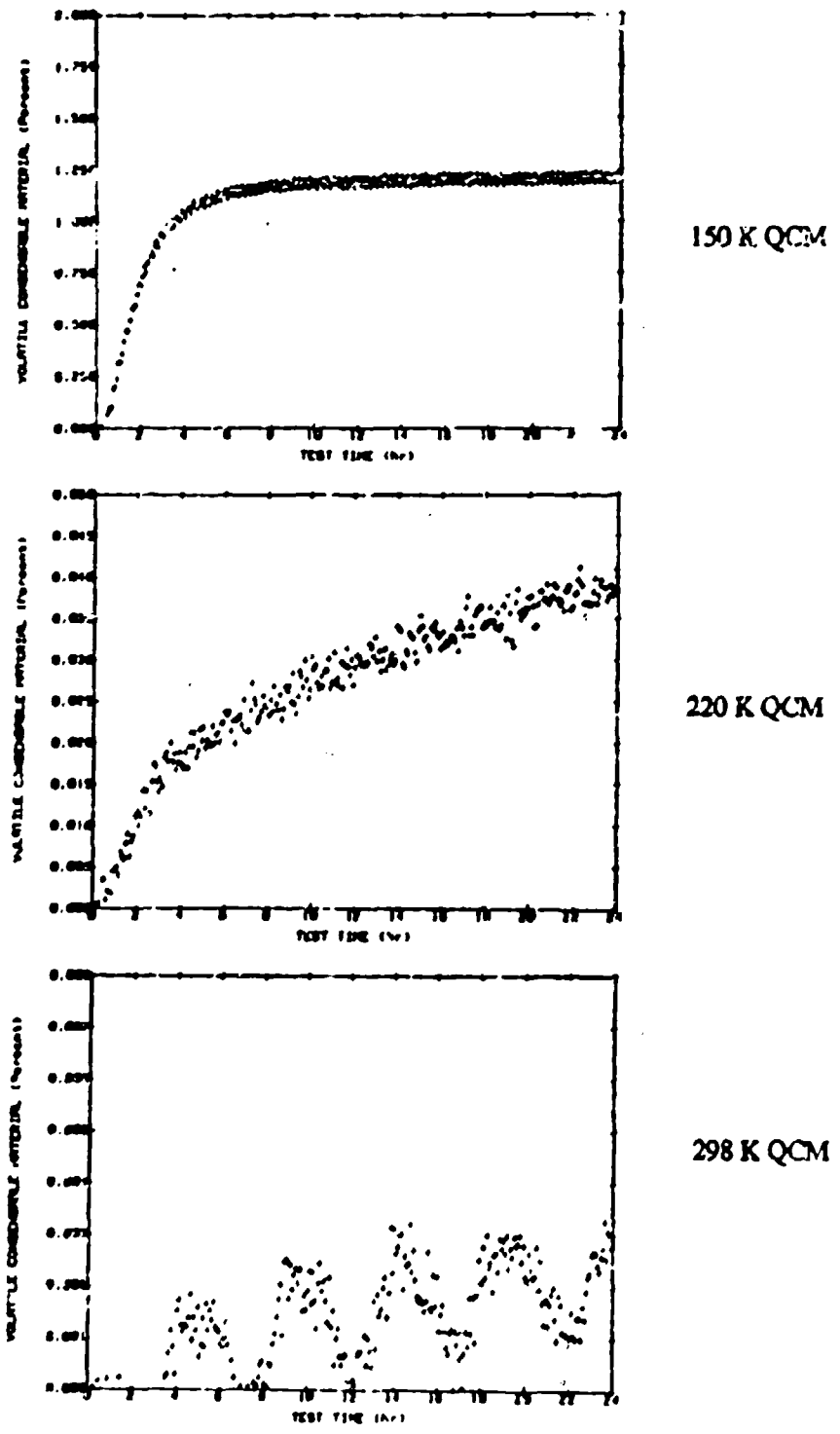


Fig. A-101 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a Chemglaze Z306 Sample at 75°C.

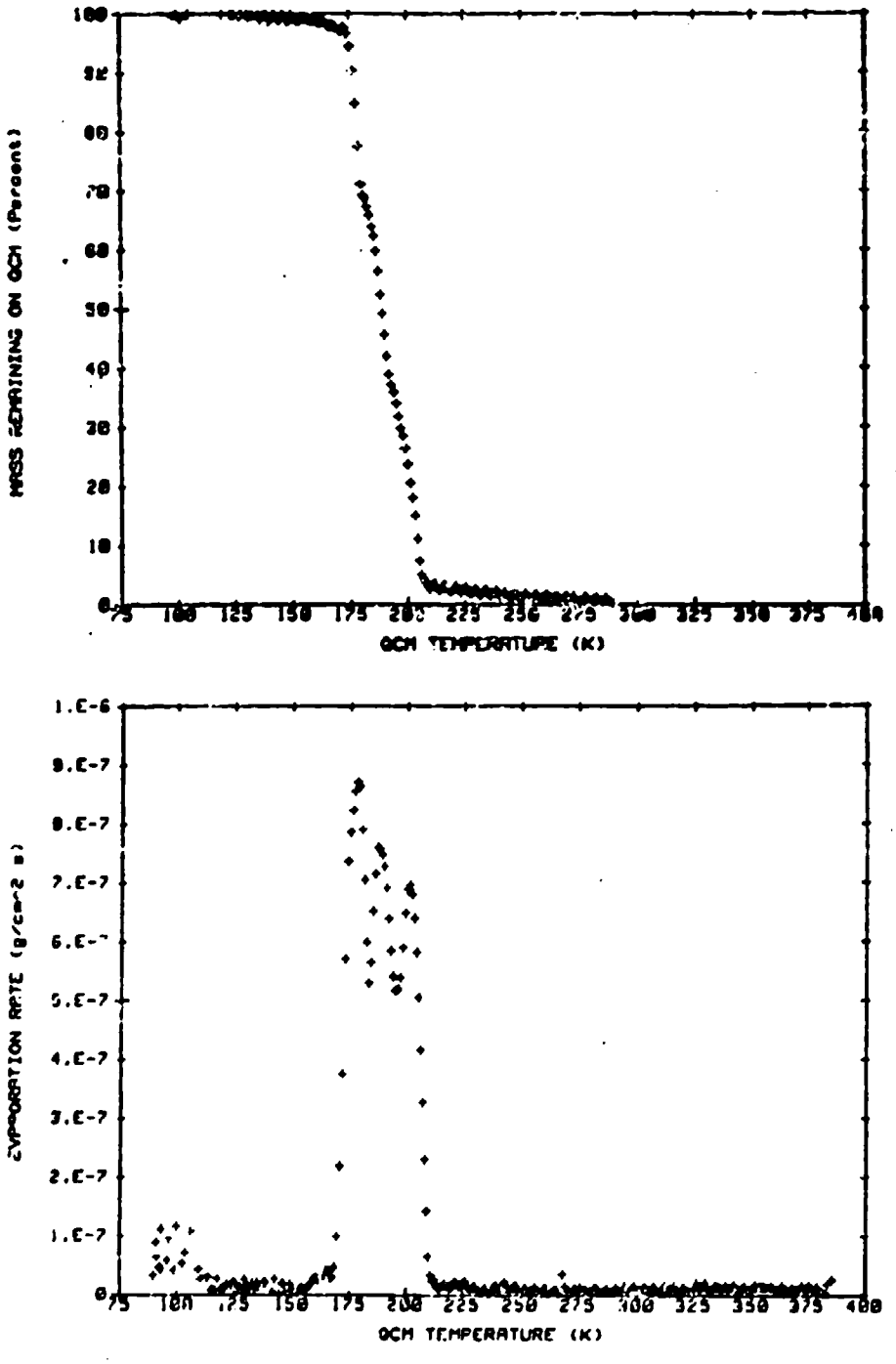


Fig. A-102 QTGA Data for Outgassing Products Collected on the 90 K QCM from a Chemglaze Z306 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-26

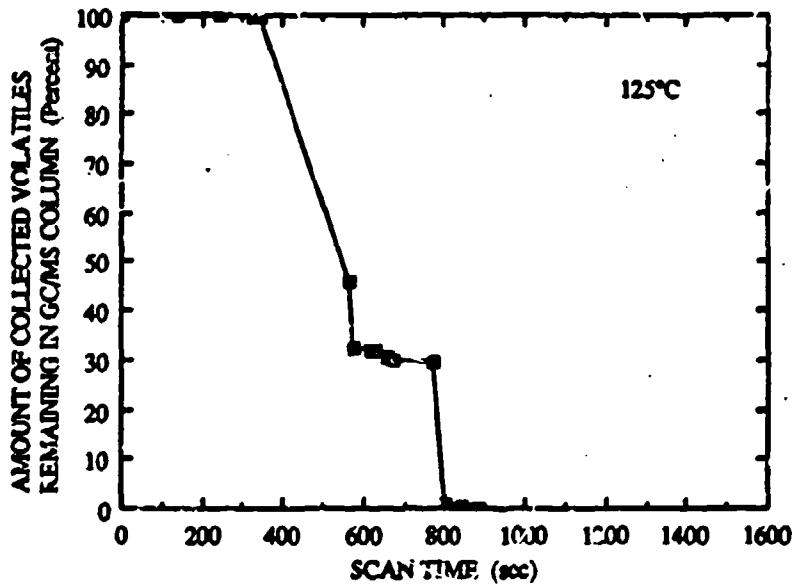
GC/MS Data for Chemglaze Z306 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
137	0.07	
244	0.05	
330	0.42	
344	0.07	
566	53.36	isomer of #574, ($C_7H_{16}O_3$) alcohol
574	13.75	1-(2-methoxypropoxy)-2-propanol
619	0.35	alcohol
629	0.18	
662	1.08	alcohol
671	0.67	alcohol
775	0.52	$C_{14}H_{18}O_2$ cyclic olefin ketone
801	28.40	butylated hydroxy toluene (B.H.T.)
842	0.73	
880	0.34	

Table A-27

GC/MS Data for Chemglaze Z306 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
83	2.95	CO_2 artifact
103	0.25	
129	0.98	2-methyl-1-pentene
138	1.00	4-methyl-2-pentene
150	0.21	
179	1.94	1-methoxy-2-propanol
224	0.21	4-methyl-2-pentanone
240	0.73	4-methyl-2-pentanol
245	0.11	
275	0.12	
297	0.06	
330	0.42	
344	0.40	
388	2.23	2-(2-methoxyethoxy) ethanol
433	0.18	
437	0.68	1-(2-methoxy-1-methyl ethoxy)-2-propanol
554	0.67	
566	40.08	isomer of #573, ($C_7H_{16}O_3$) alcohol
574	9.78	1-(2-methoxy propoxy)-2-propanol
619	0.22	alcohol
629	0.15	
662	0.72	alcohol
673	0.43	alcohol
697	6.39	toluene diisocyanate (T.D.I.)
725	0.31	
775	0.80	$C_{14}H_{18}O_2$ cyclicolefin ketone
800	23.50	butylated hydroxy toluene (B.H.T.)
843	0.23	
1273	4.24	triphenyl phosphate



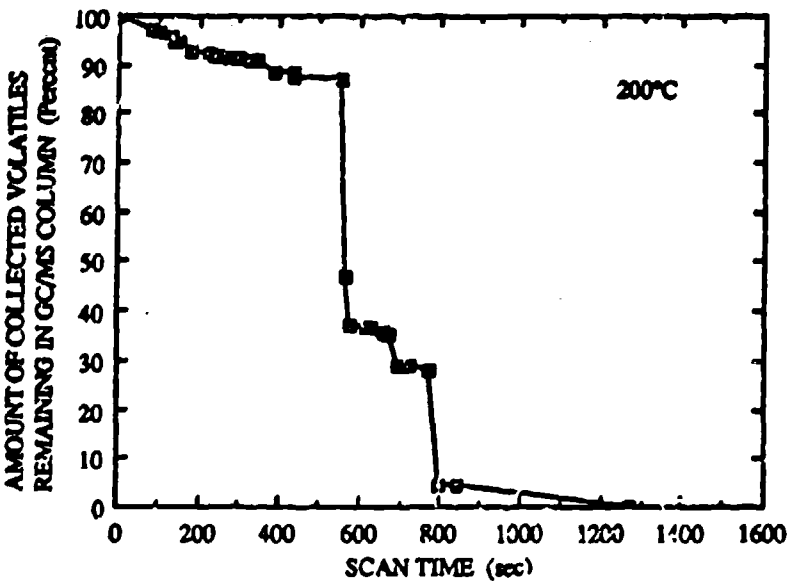


Fig. A-103 Amount of Collected Volatiles Remaining in GC/MS Column from Chemglaze Z306 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : DC Q9-6313 thermal control coating

DATE TEST STARTED : July 21, 1987

GC/MS DATA FILES :

125°C Test : data not available
200°C Test : data not available

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Area (cm^2)	17.88	18.53	18.31
Weight, pretest (g)	0.69	0.43	0.54
Total mass loss (%)	.39	.40	.19
ISOTHERMAL TEST DATA :			
Test duration (h)	121	113	120
QCM/Temperature Data File	G0721	G0729	G0807
Mass Spectrometer Data File	"	"	"
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0727Q	G0803Q	G0812Q
Mass Spectrometer Data File	"	"	"

COMMENTS :

- material is a thermal control coating with silver flakes and polysiloxane resin binder manufactured by D.A. Vance, LPARL Thermal Sciences Laboratory (O/92-40)
- the polysiloxane resin is produced by Dow Corning Corp.
- samples supplied by H.B. Gjerde, LMSC Materials & Processes Engineering (O/62-92)
- sample substrates were aluminum discs 1.0 inch diameter by 0.1inch thick
- sample configuration (125°C test): 3 Al discs sprayed on one side
- sample configuration (75°C test): 3 Al discs sprayed on one side
- sample configuration (25°C test): 3 Al discs sprayed on one side
- initial sample weights are ± 10% (Note 2, Sec. A.1.4)
- no QTA performed on 220 K and 298 K QCMs after 125°C Isothermal Test (Note 5, Sec. A.1.4)
- no QTA performed on 298 K QCM after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 298 K QCM after 25°C Isothermal Test (Note 8, Sec. A.1.4)
- interlock chamber evacuated with mechanical pump (Note 10, Sec. A.1.4)
- GC/MS data not available for this material (Note 5, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 600
- mass spectrometer sensitivity very low (Note 7, Sec. A.1.4)

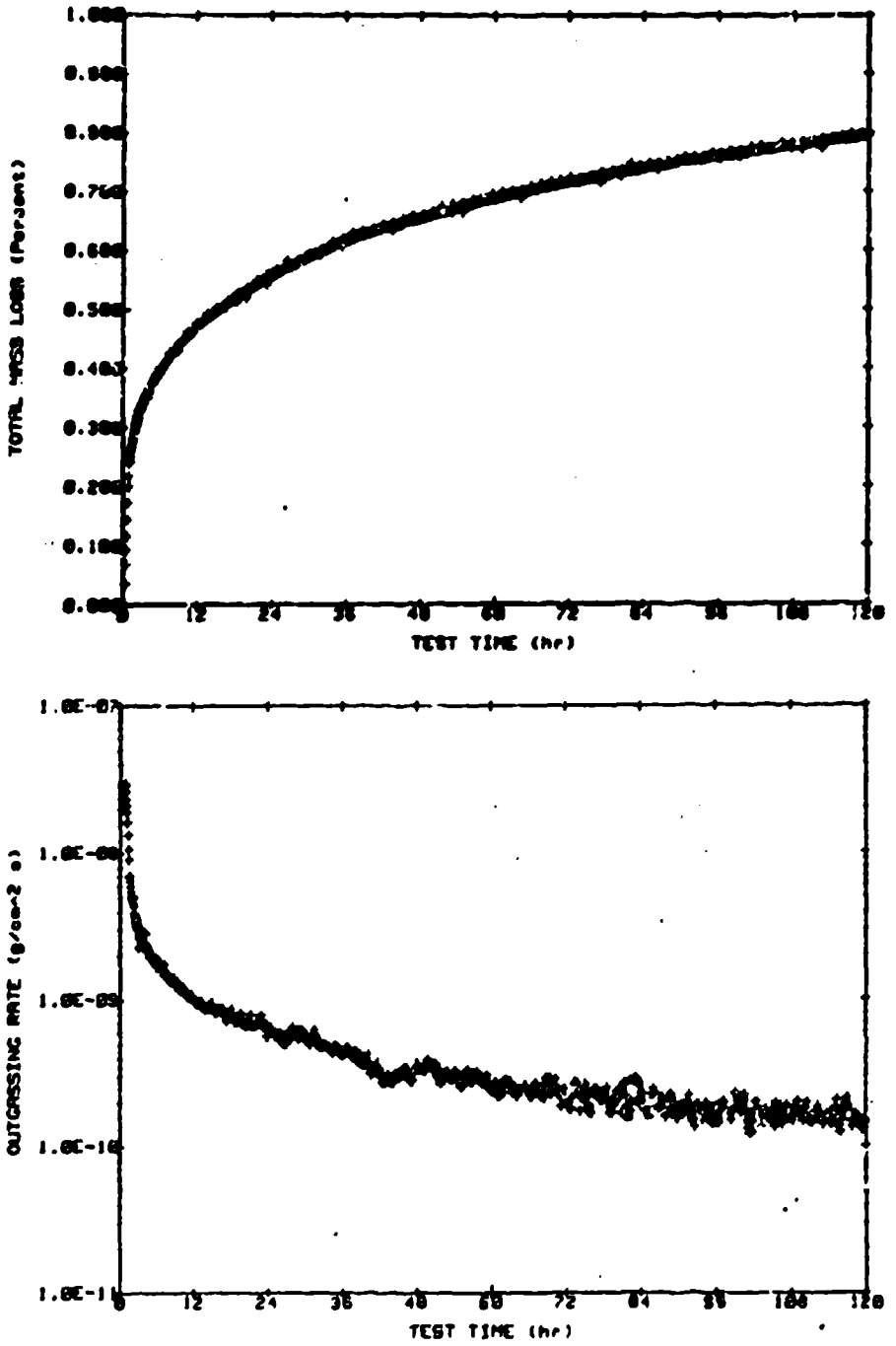


Fig. A-104 Total Mass Loss and Outgassing Rate as Functions of Time for a DC Q9-6313 Sample at 125°C.

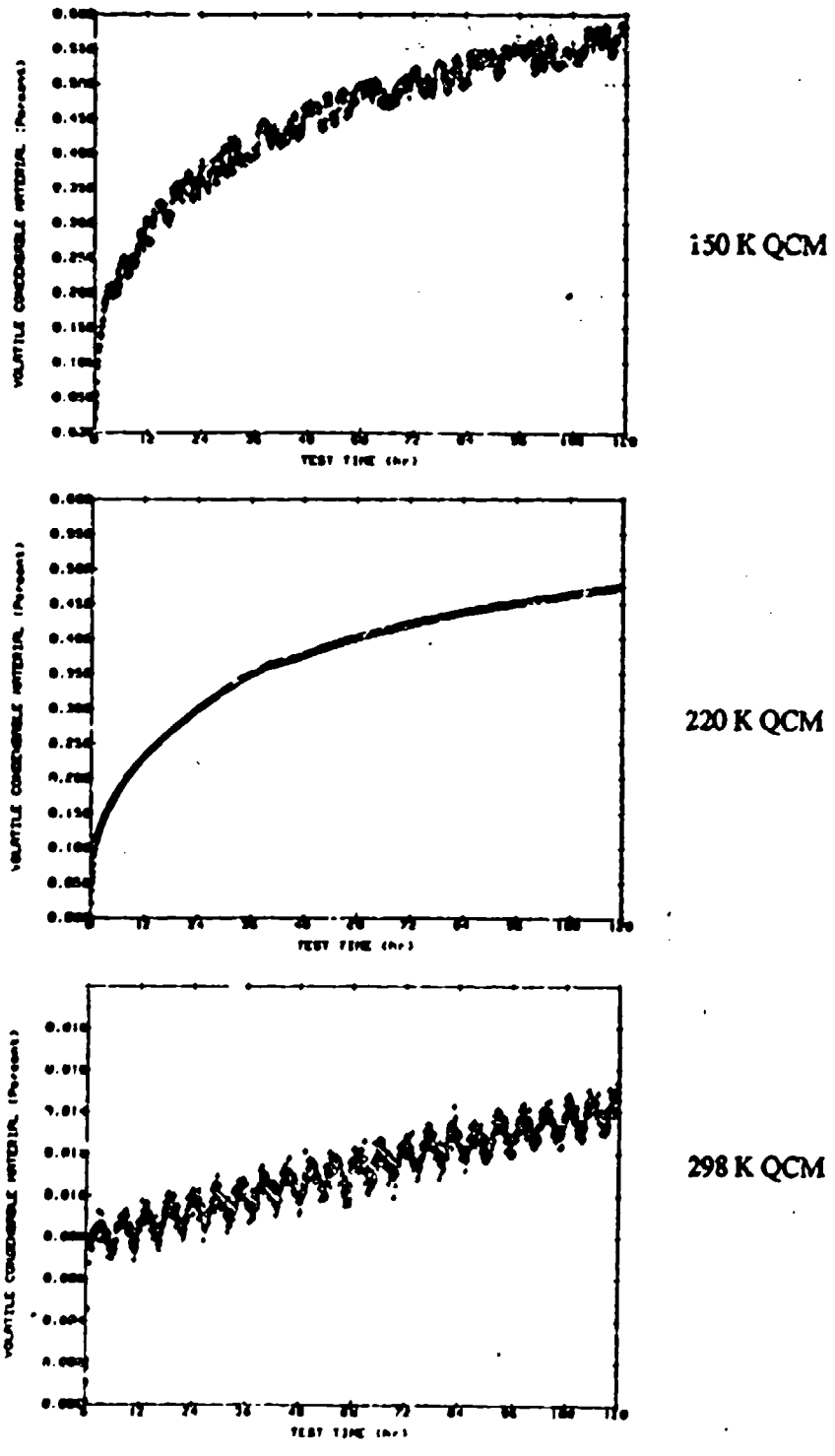


Fig. A-105 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC Q9-6313 Sample at 125°C.

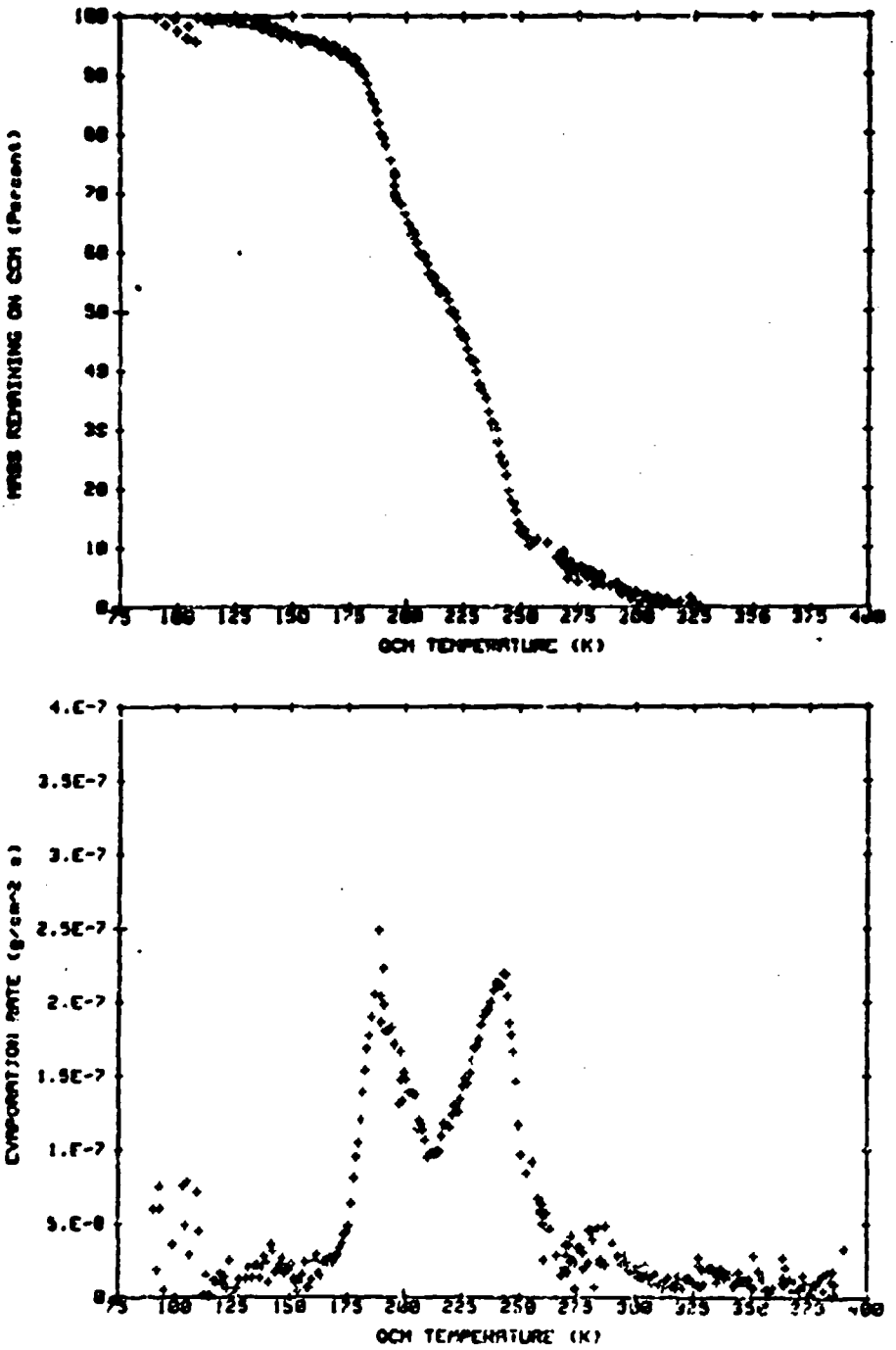


Fig. A-106 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC Q9-6313 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

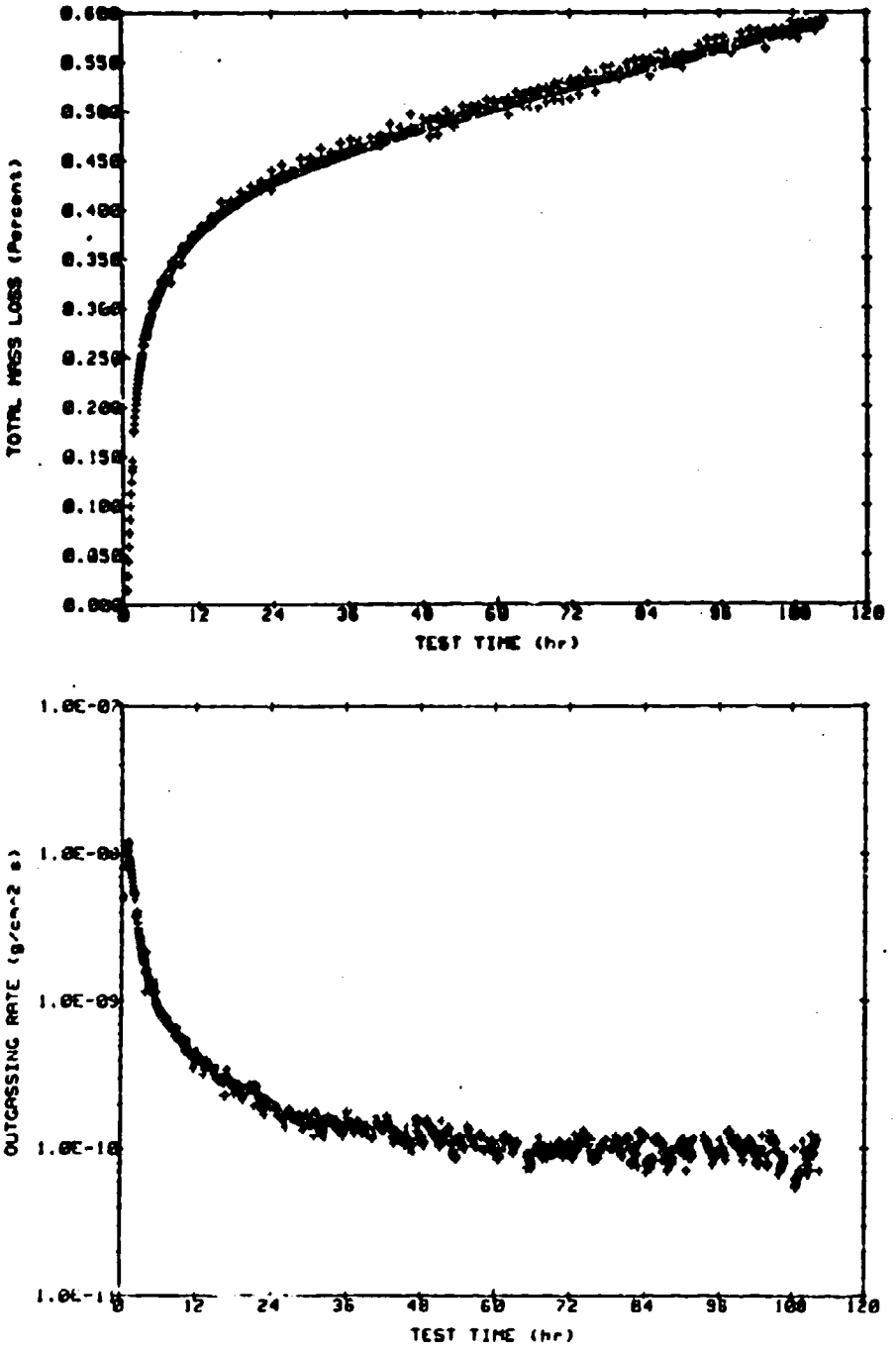


Fig. A-107 Total Mass Loss and Outgassing Rate as Functions of Time for a DC Q9-6313 Sample at 75°C.

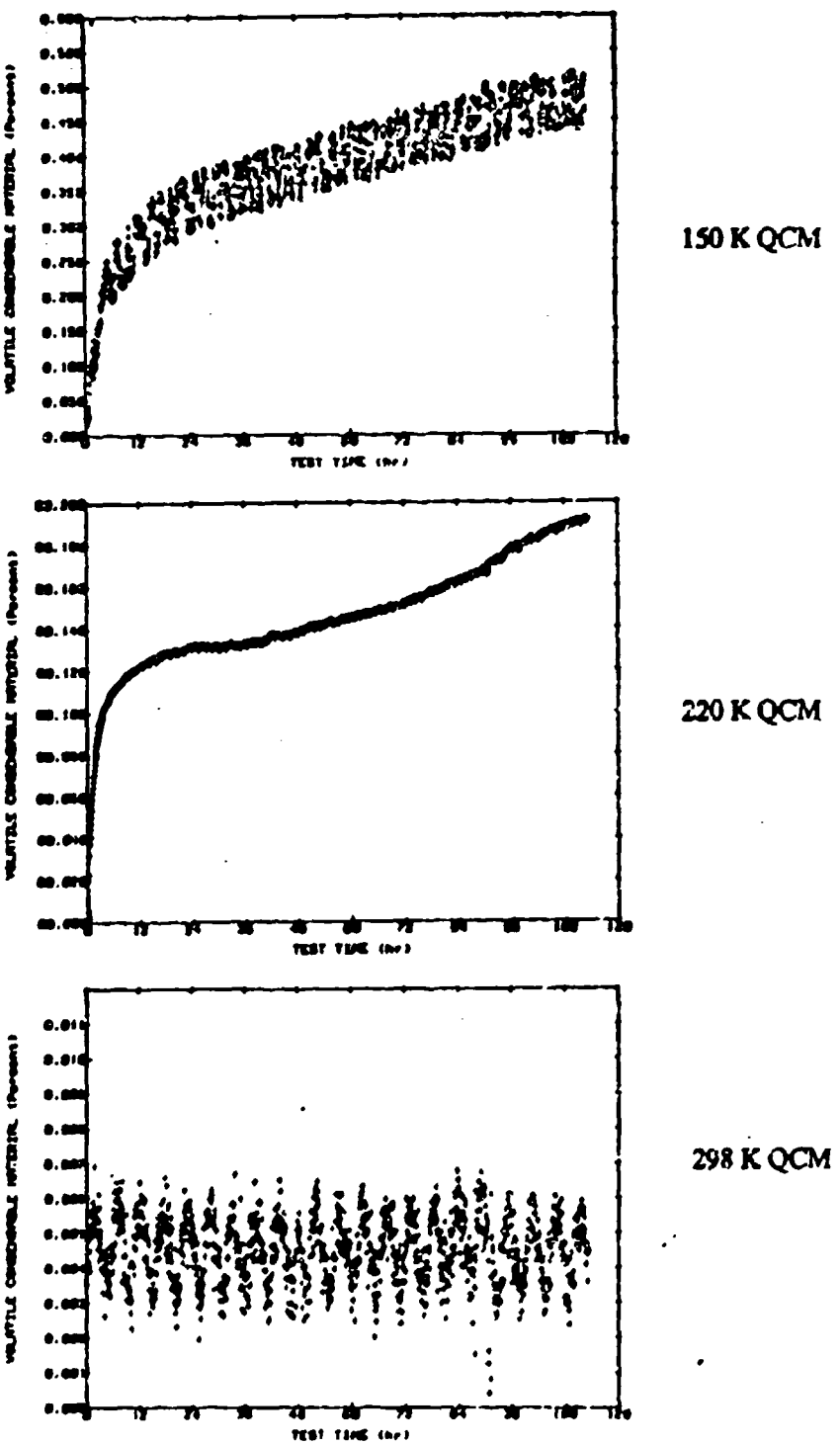


Fig. A-108 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC Q9-6313 Sample at 75°C.

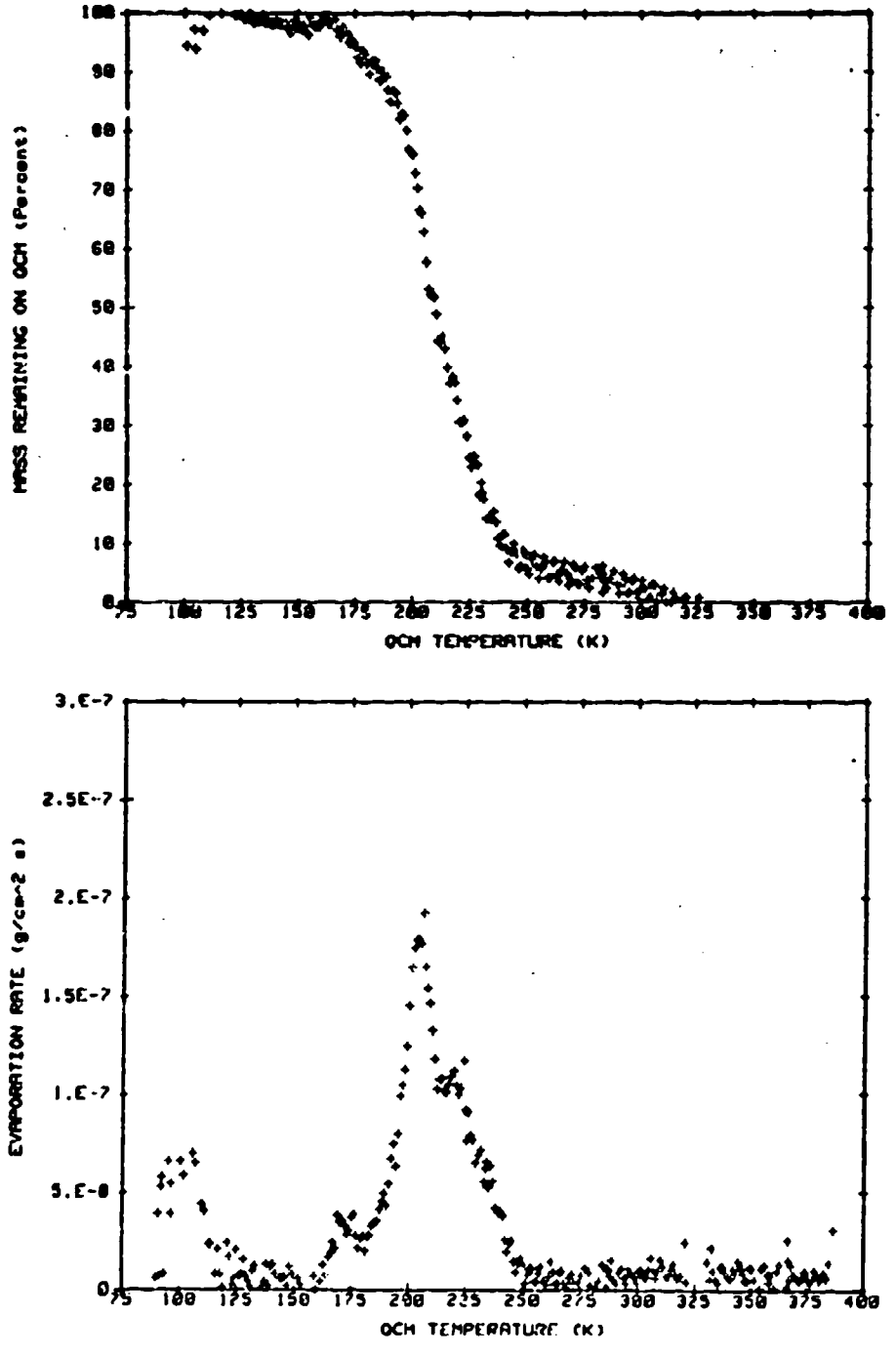


Fig. A-109 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC Q9-6313 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

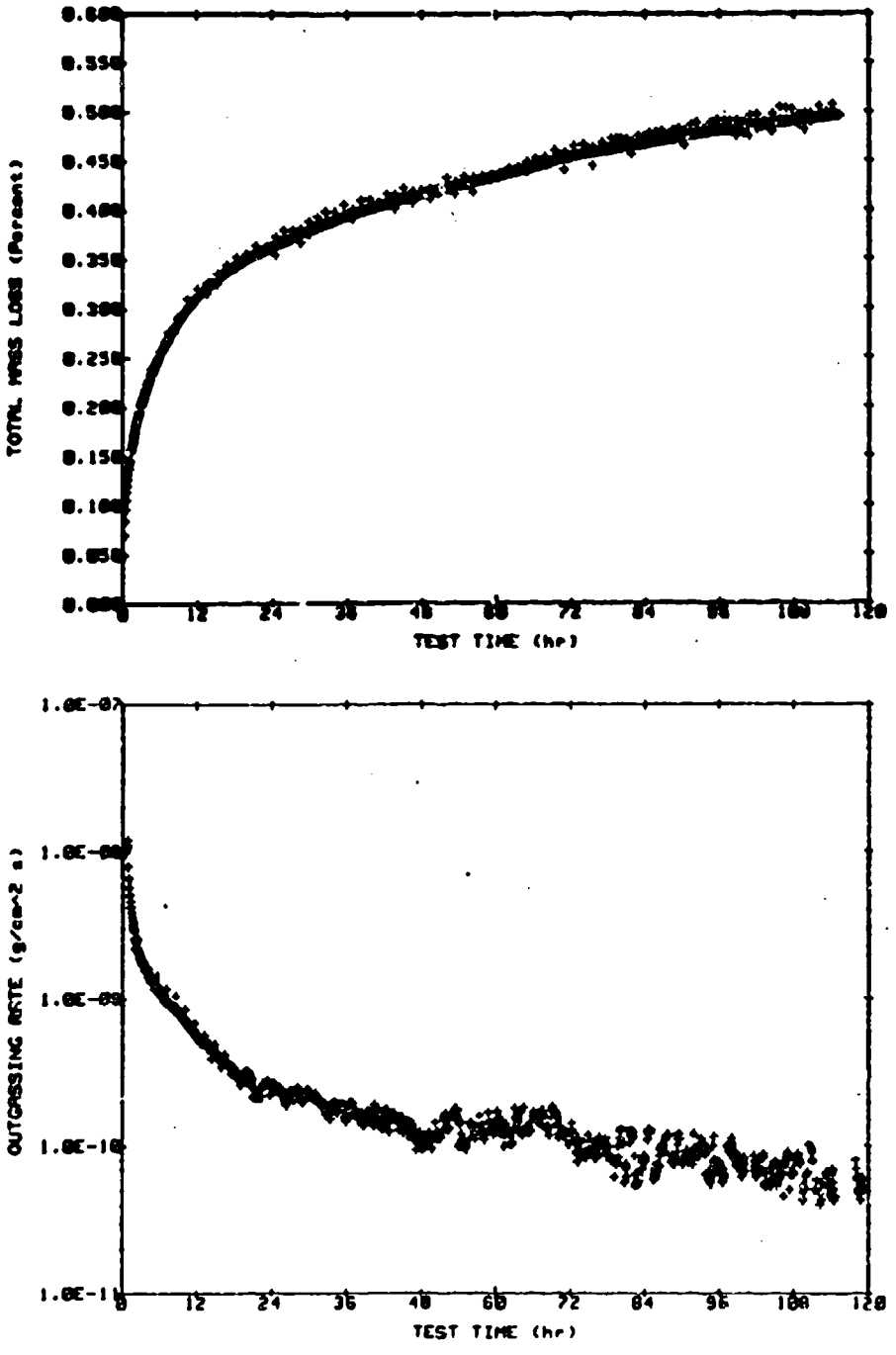


Fig. A-110 Total Mass Loss and Outgassing Rate as Functions of Time for a DC Q9-6313 Sample at 25°C.

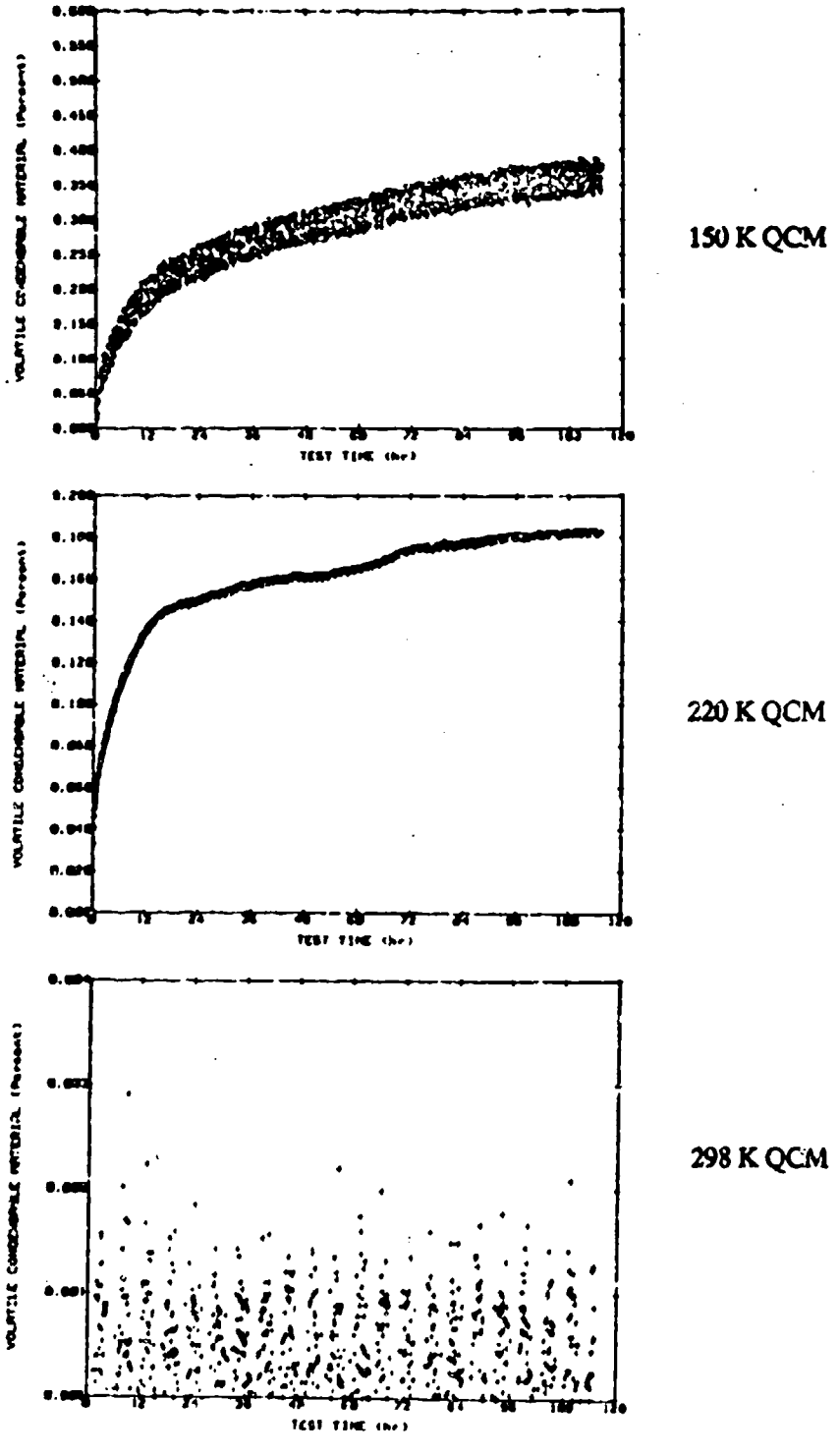


Fig. A-111 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for a DC Q9-6313 Sample at 25°C.

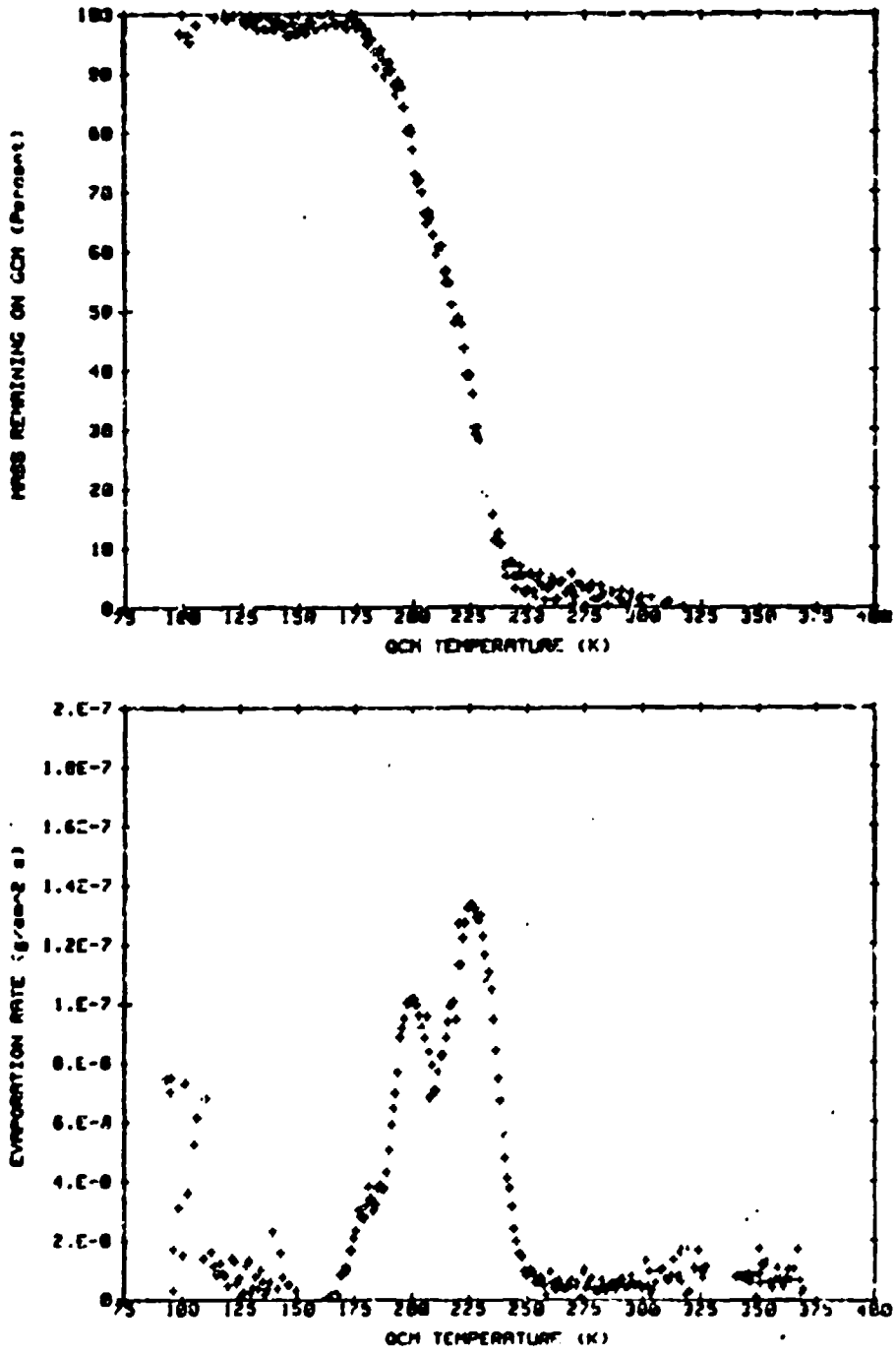


Fig. A-112 QTGA Data for Outgassing Products Collected on the 90 K QCM from a DC Q9-6313 Sample at 25°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-28

GC/MS Data for DC Q9-6313 at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
GC/MS D..	NOT AVAILABLE	

Table A-29

GC/MS Data for DC Q9-6313 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 125°C

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 200°C

Fig. A-113 Amount of Collected Volatiles Remaining in GC/MS Column from DC Q9-6313 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : Aremco 569 thermal control coating

DATE TEST STARTED : June 29, 1987

GC/MS DATA FILES :

125°C Test : data not available
200°C Test : data not available

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Sample Area (cm^2)	17.88	18.53	18.31
Weight, pretest (g)	0.44	0.78	0.80
Total mass loss (%)	3.58	2.28	1.39
ISOTHERMAL TEST DATA :			
Test duration (h)	25	24	24
QCM/Temperature Data File	G0629	G0701	G0706
Mass Spectrometer Data File	"	"	"
QCM THERMdAL ANALYSIS DATA :			
QCM/Temperature Data File	G0630Q	G0702Q	G0707Q
Mass Spectrometer Data File	"	"	"

COMMENTS :

- material is an inorganic, thermal control coating with aluminum oxide pigment and potassium silicate binder produced by Aremco Corp.
- samples supplied by H.B. Gjerde, LMSC Materials & Processes Engineering (O/62-92)
- sample substrates were aluminum discs 1.0 inch diameter by 0.1 inch thick
- sample configuration (125°C test): 3 Al discs sprayed on one side
- sample configuration (75°C test): 3 Al discs sprayed on one side
- sample configuration (25°C test): 3 Al discs sprayed on one side
- initial sample weights are ± 10% (Note 2, Sec A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 25°C Isothermal Test (Note 8, Sec. A.1.4)
- GC/MS data not available for this material (Note 5, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 600
- mass spectrometer sensitivity very low (Note 7, Sec. A.1.4)

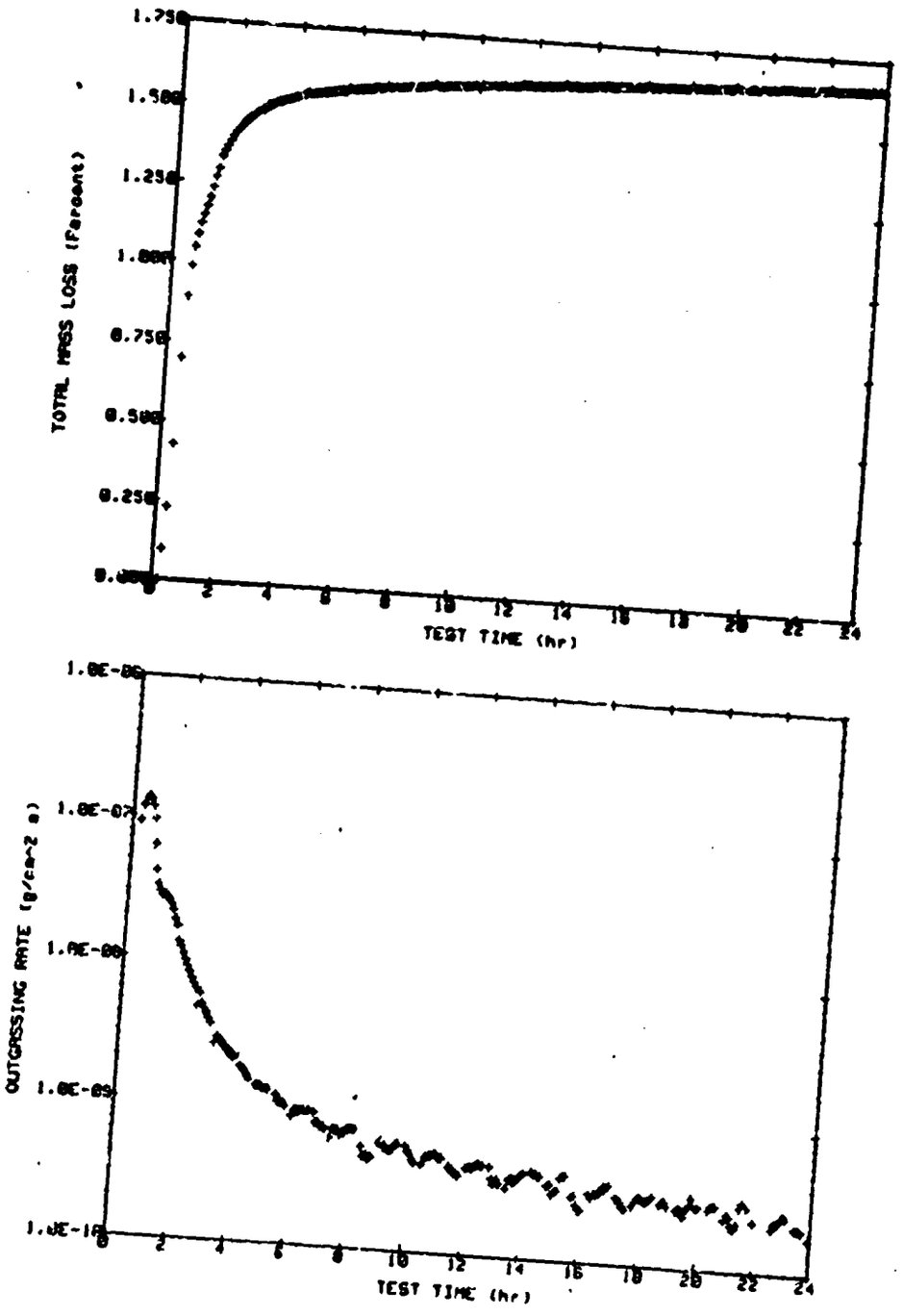


Fig. A-114 Total Mass Loss and Outgassing Rate as Functions of Time for an Aremco 569 Sample at 125°C.

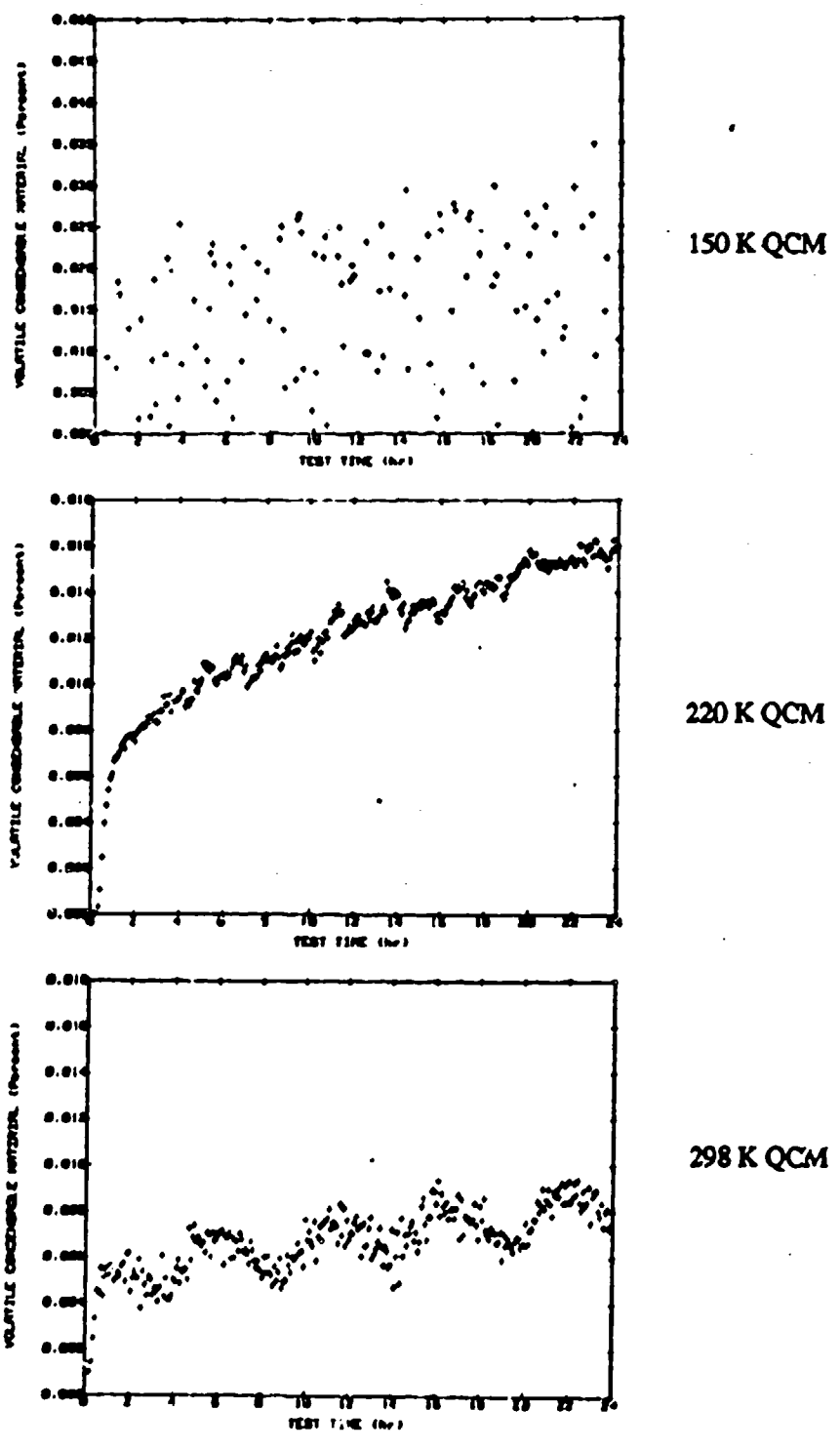


Fig. A-115 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an Aremco 569 Sample at 125°C.

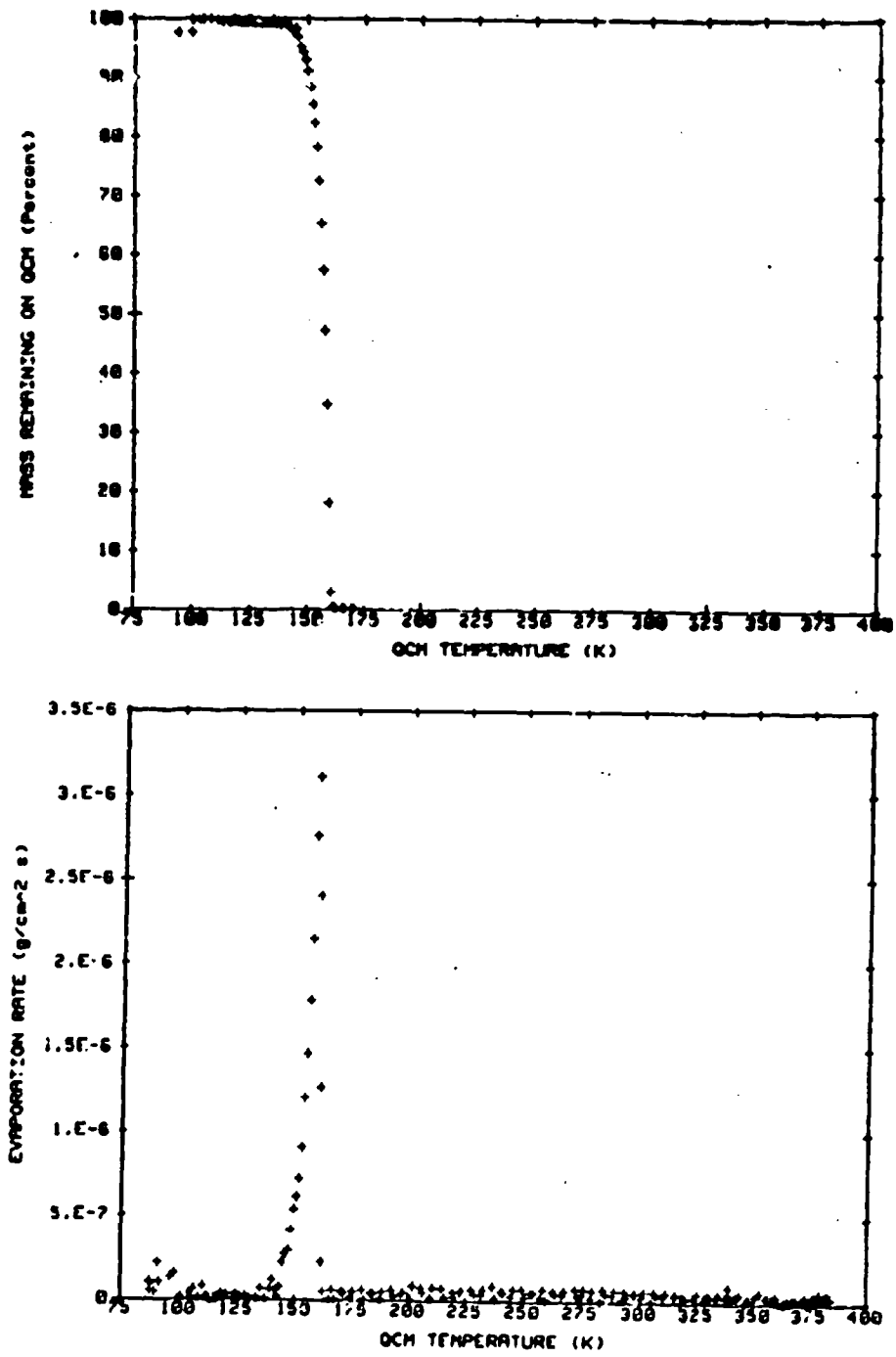


Fig. A-116 QTGA Data for Outgassing Products Collected on the 90 K QCM from an Aremco 569 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

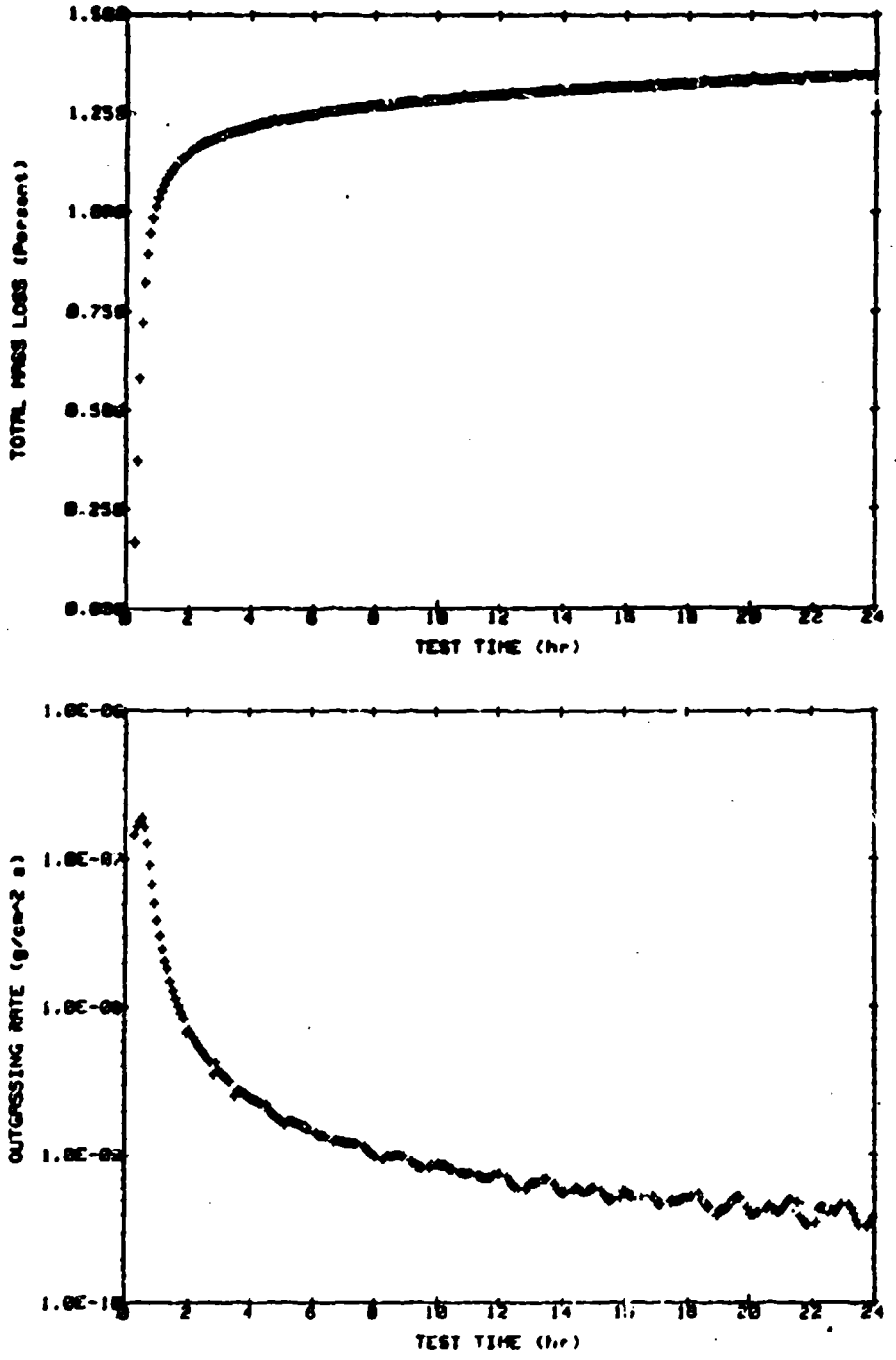


Fig. A-117 Total Mass Loss and Outgassing Rate as Functions of Time for an Aremco 569 Sample at 75°C.

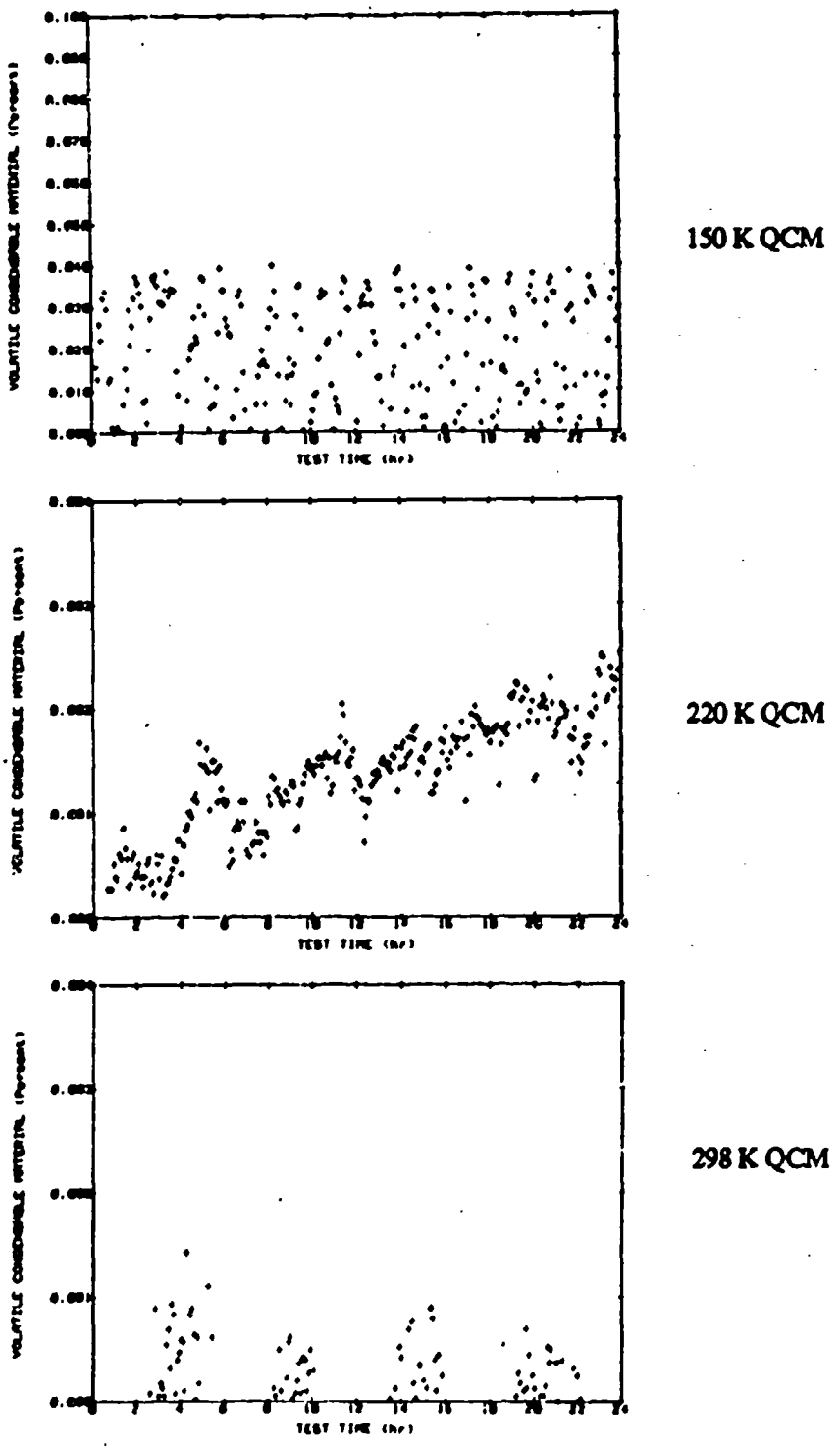


Fig. A-118 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an Aremco 569 Sample at 75°C.

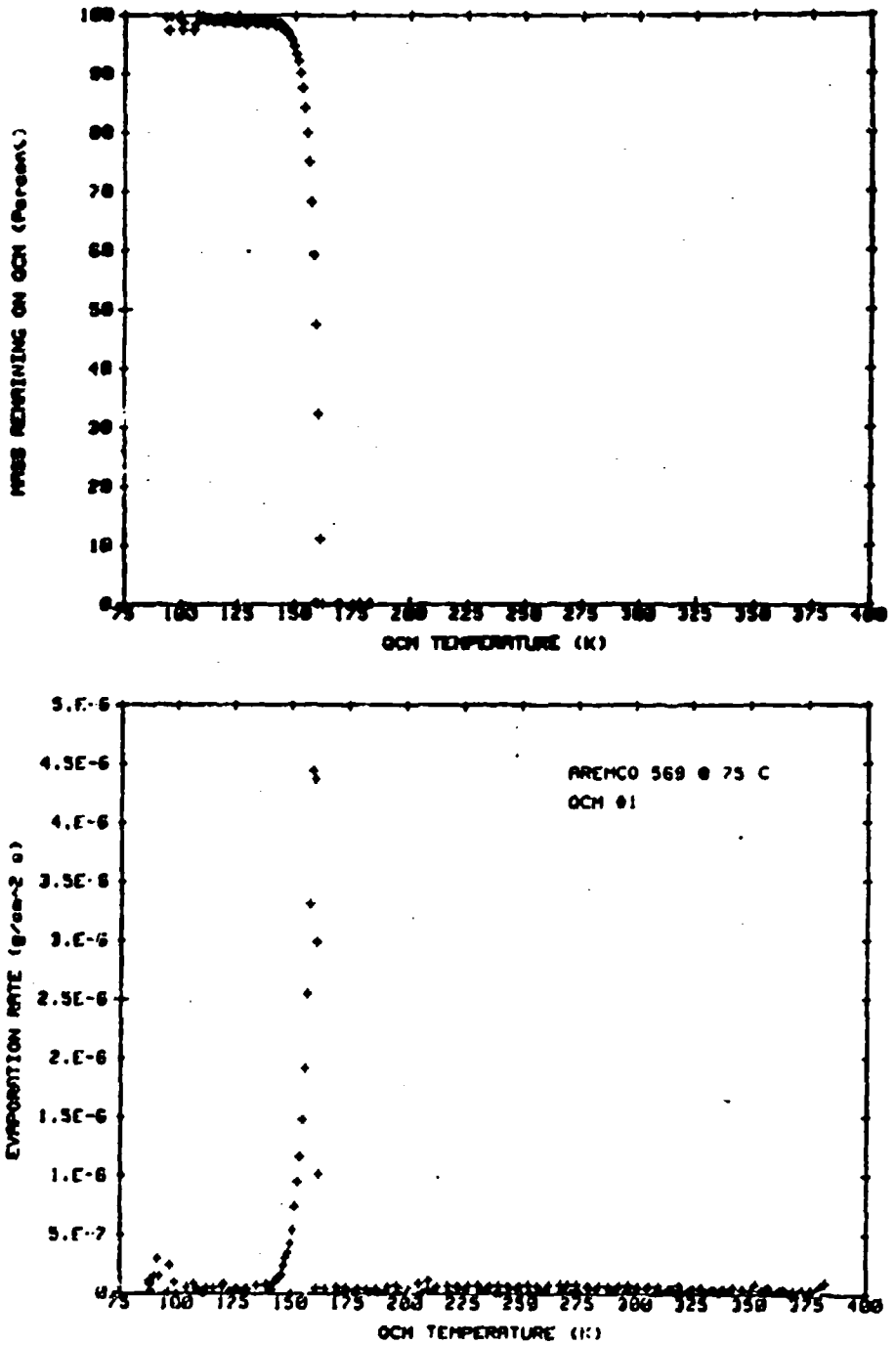


Fig. A-119 QTGA Data for Outgassing Products Collected on the 90 K QCM from an Aremco 569 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

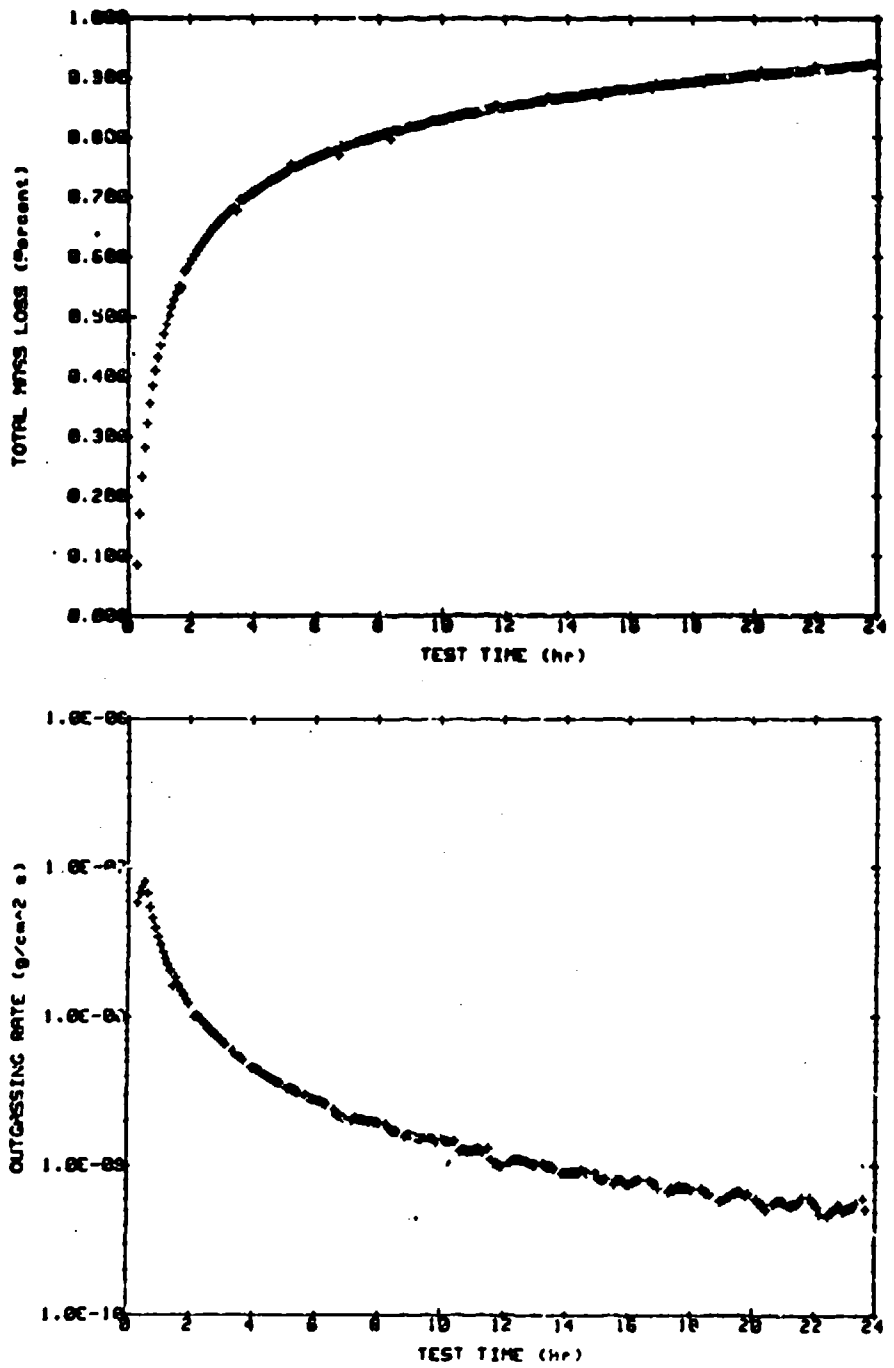


Fig. A-120 Total Mass Loss and Outgassing Rate as Functions of Time for an Aremco 569 Sample at 25°C.

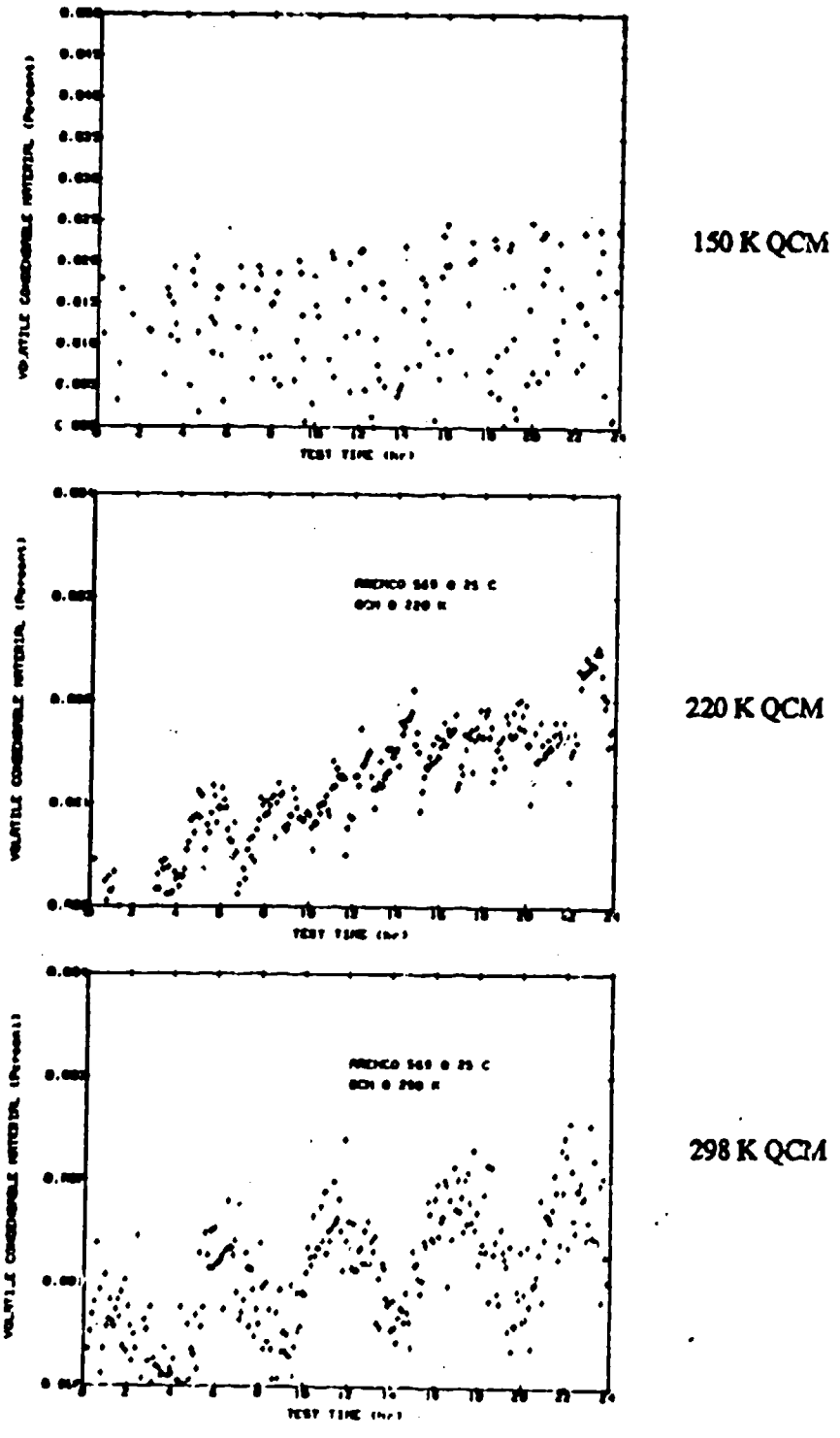


Fig. A-121 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an Arenco 569 Sample at 25°C.

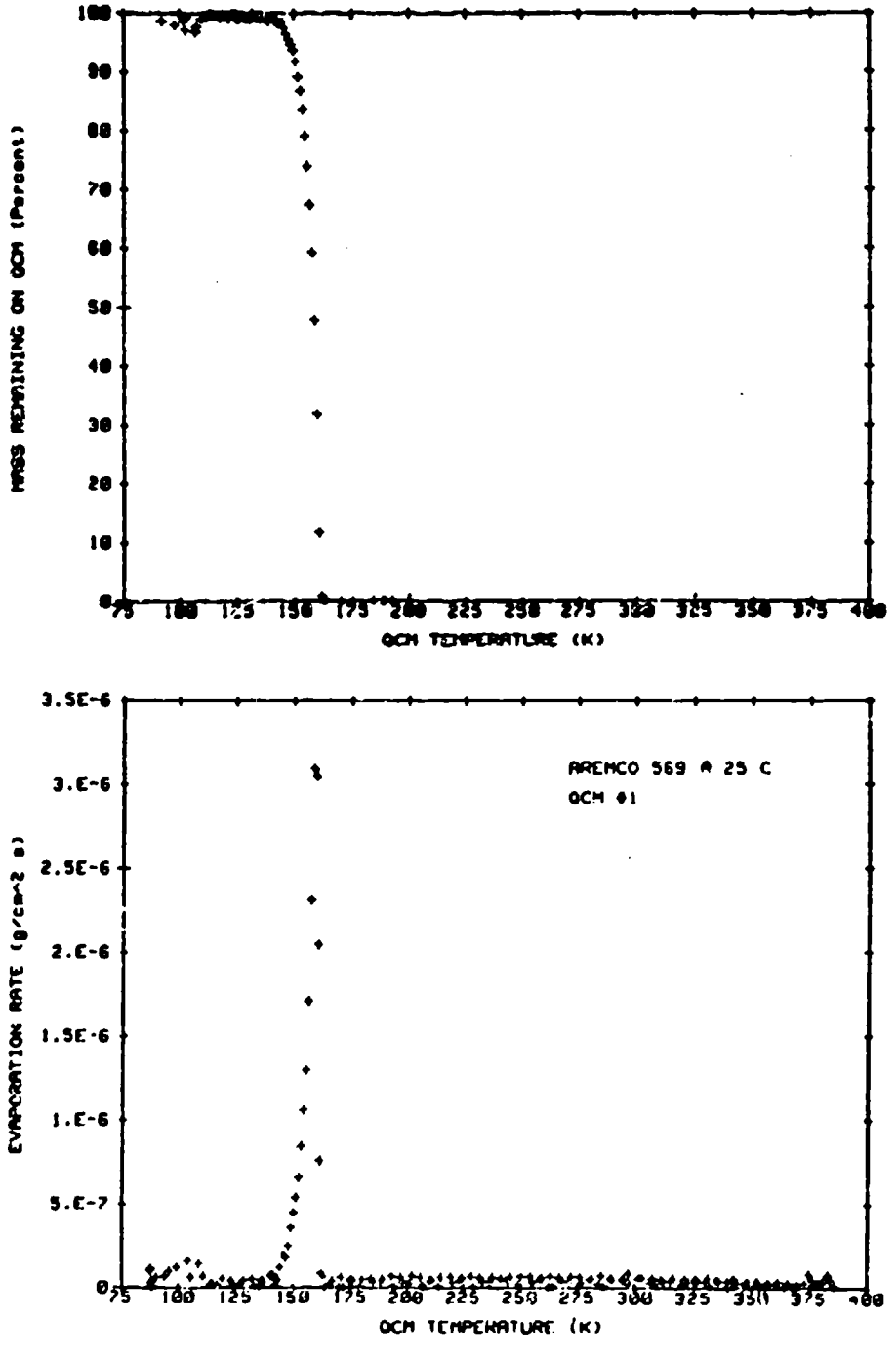


Fig. A-122 QTGA Data for Outgassing Products Collected on the 90 K QCM from an Aremco 569 Sample at 25°C Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-30

GC/MS Data for Aremco 569 at 125°C
Quantitation Report

SCAN TIME (min)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

Table A-31

GC/MS Data for Aremco 569 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 125°C

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 200°C

Fig. A-123 Amount of Collected Volatiles Remaining in GC/MS Column from Aremco 569 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : LMSC 1170 thermal control coating

DATE TEST STARTED : July 9, 1987

GC/MS DATA FILES :

125°C Test : data not available
200°C Test : data not available

	Test Temperature (°C)		
	125	75	25
MATERIAL SAMPLE DATA :			
Area (cm^2)	18.53	18.31	18.53
Weight, pretest (g)	0.29	0.41	0.35
Total mass loss (%)	2.89	1.88	0.86
ISOTHERMAL TEST DATA :			
Test duration (h)	24	24	23
QCM/Temperature Data File	G0709	G0713	G0715
Mass Spectrometer Data File	"	"	"
QCM THERMAL ANALYSIS DATA :			
QCM/Temperature Data File	G0710Q	G0714Q	no data
Mass Spectrometer Data File	no data	"	no data

COMMENTS :

- material is a transparent silicate thermal control coating with aluminum oxide and zinc oxide pigments and potassium silicate binder produced by LMSC
- samples supplied by H.B. Gjerde, LMSC Materials & Processes Engineering (O/62-92)
- sample substrates were aluminum discs 1.0 inch diameter by 0.1inch thick
- sample configuration (125°C test): 3 Al discs sprayed on one side
- sample configuration (75°C test): 3 Al discs sprayed on one side
- sample configuration (25°C test): 3 Al discs sprayed on one side
- initial sample weights are ± 10% (Note 2, Sec. A.1.4)
- no 25°C isothermal outgassing test data after 18 hrs due to liquid nitrogen failure (Note 9, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on QCMs after 25°C Isothermal Test due to liquid nitrogen failure (Note 9, Sec. A.1.4)
- interlock chamber evacuated with mechanical pump (Note 10, Sec. A.1.4)
- GC/MS data not available for this material (Note 5, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 600
- mass spectrometer sensitivity very low (Note 7, Sec. A.1.4)

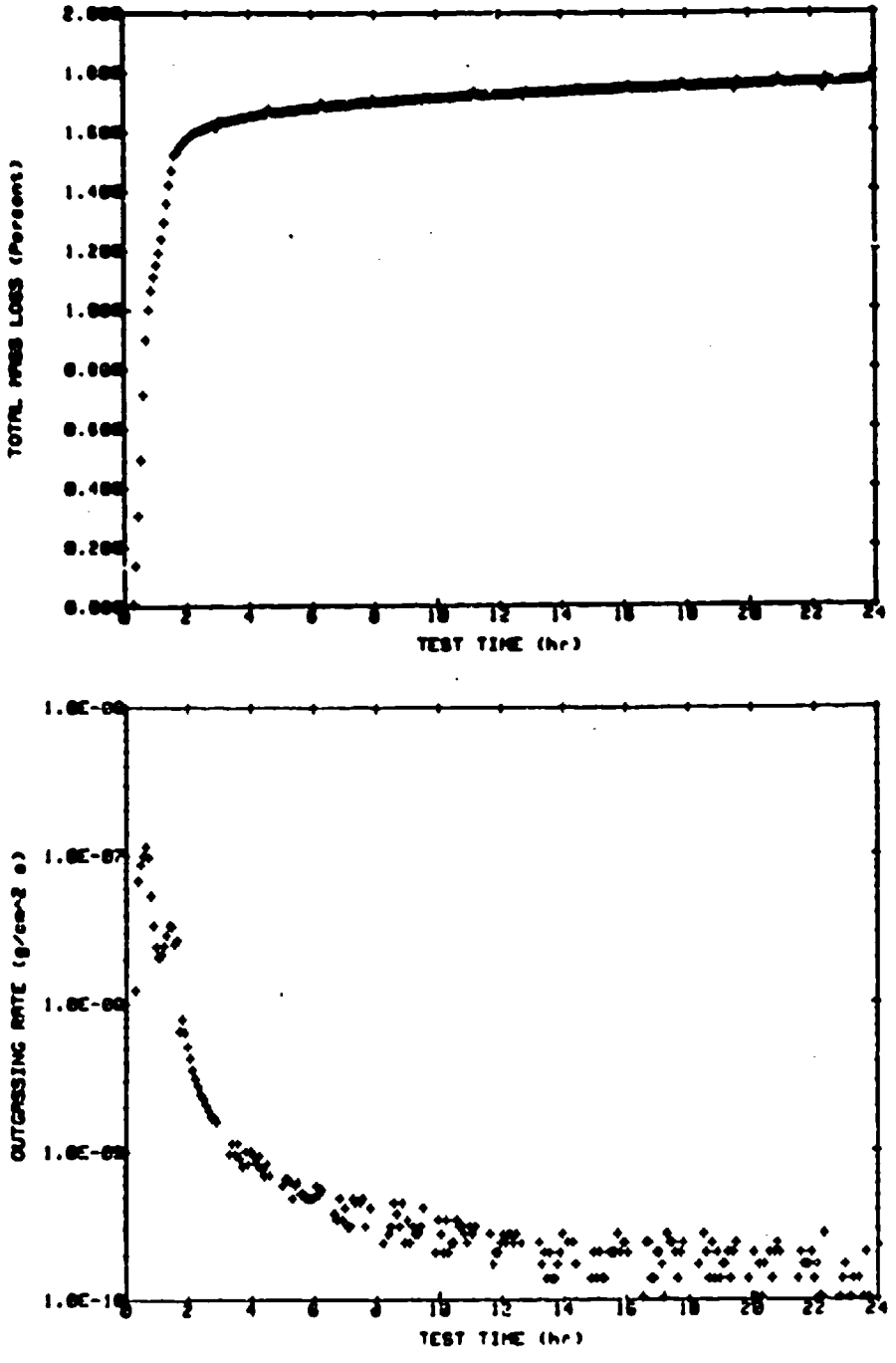


Fig. A-124 Total Mass Loss and Outgassing Rate as Functions of Time for an LMSC 1170 Sample at 125°C.

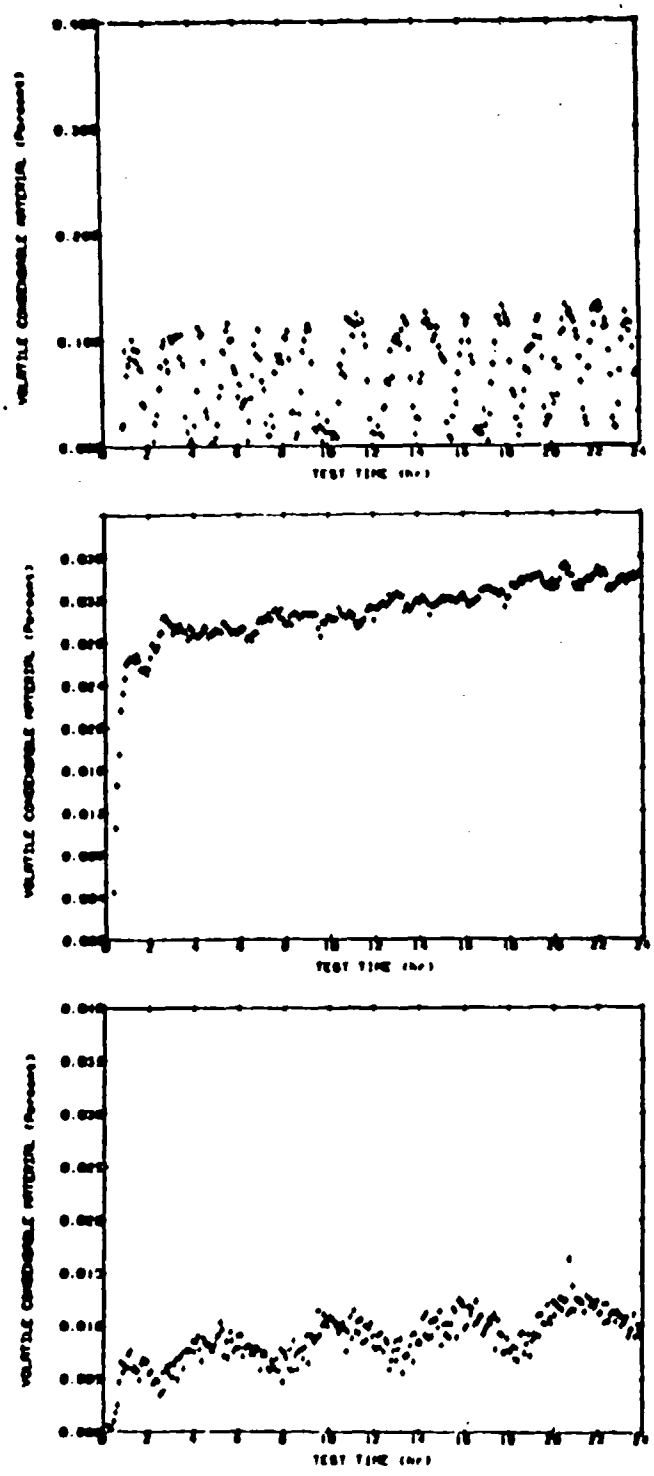


Fig. A-125 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an LMSC 1170 Sample at 125°C.

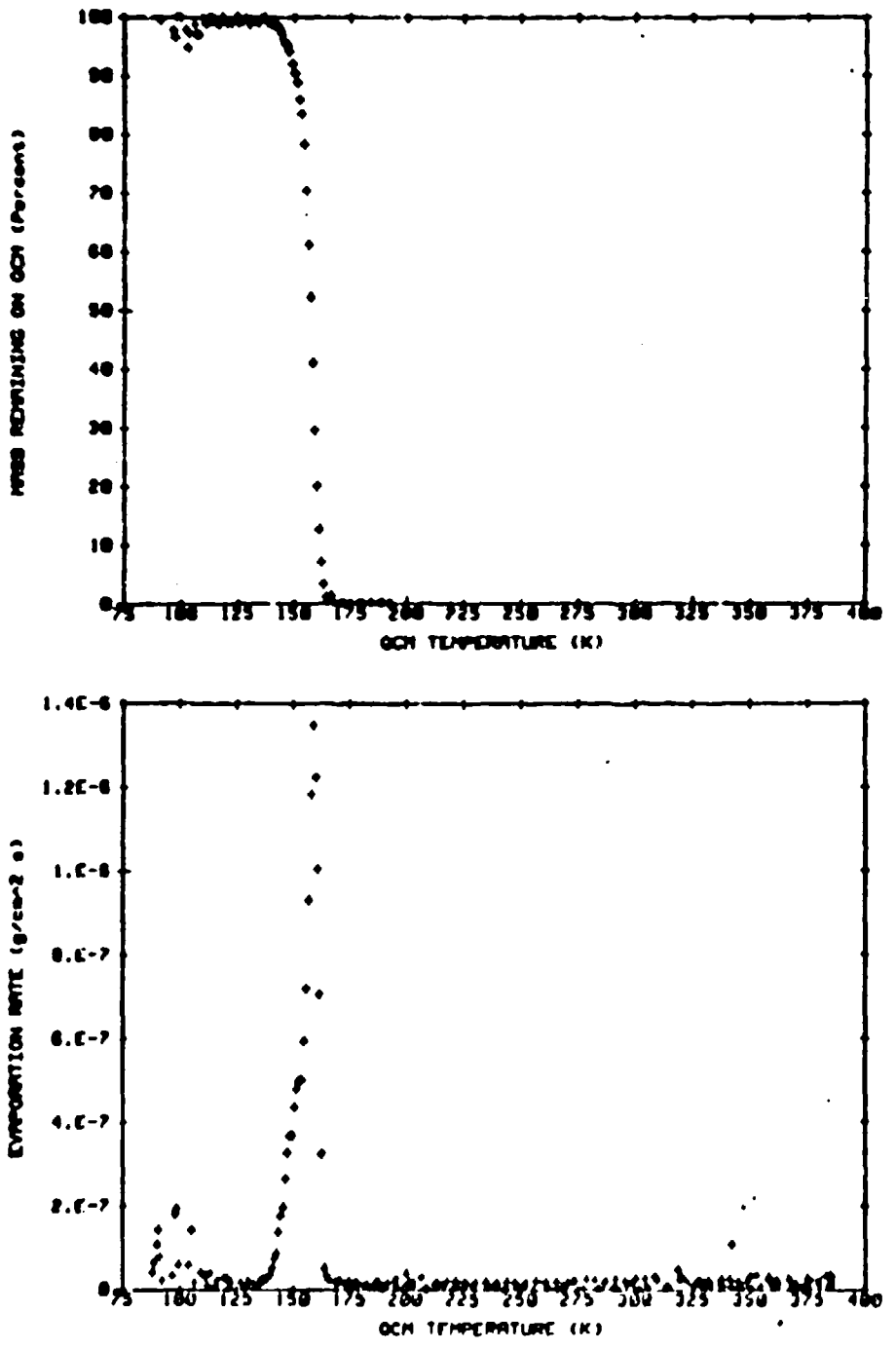


Fig. A-126 QTGA Data for Outgassing Products Collected on the 90 K QCM from an LMSC 1170 Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

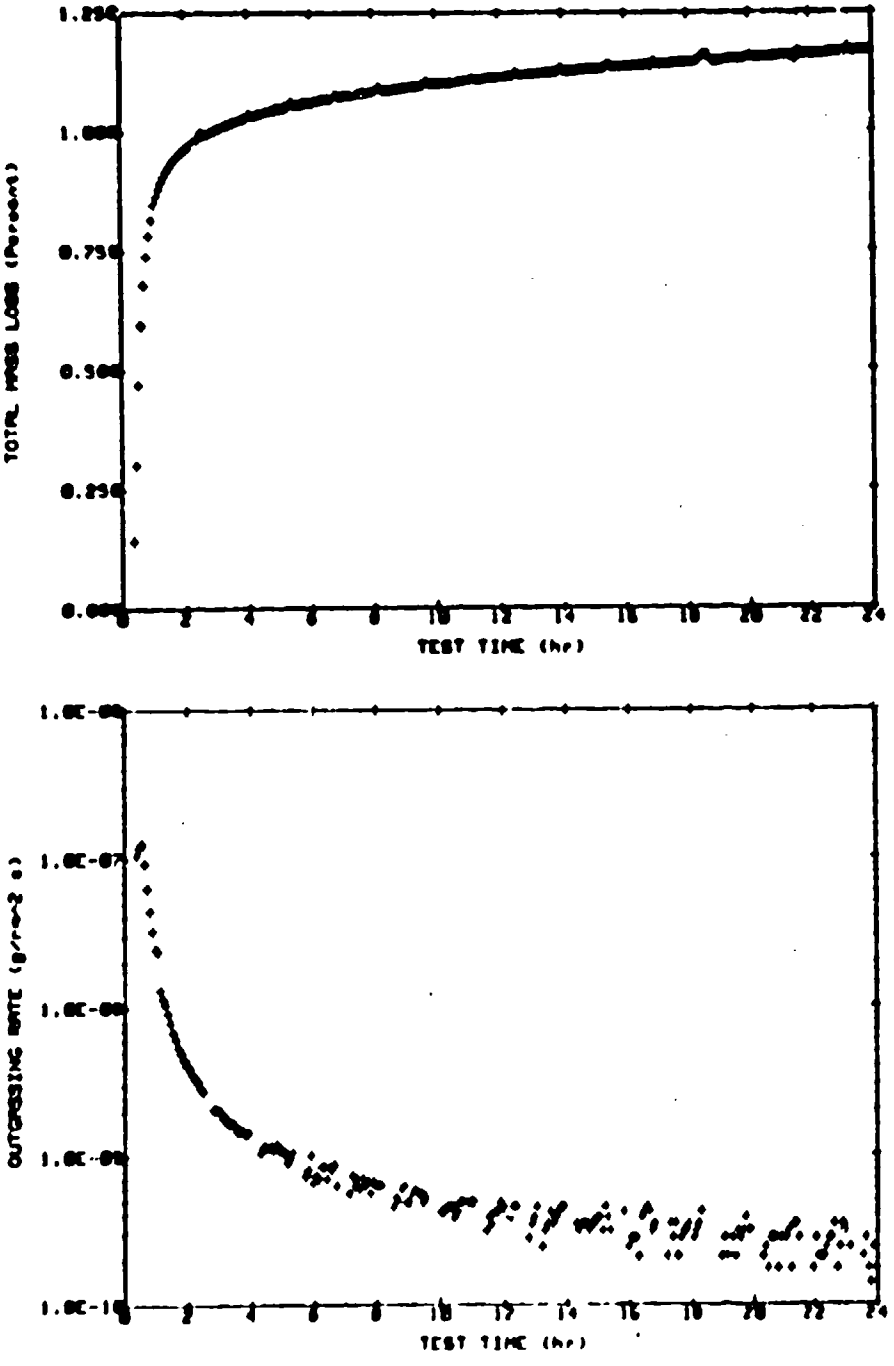


Fig. A-127 Total Mass Loss and Outgassing Rate as Functions of Time for an LMSC 1170 Sample at 75°C.

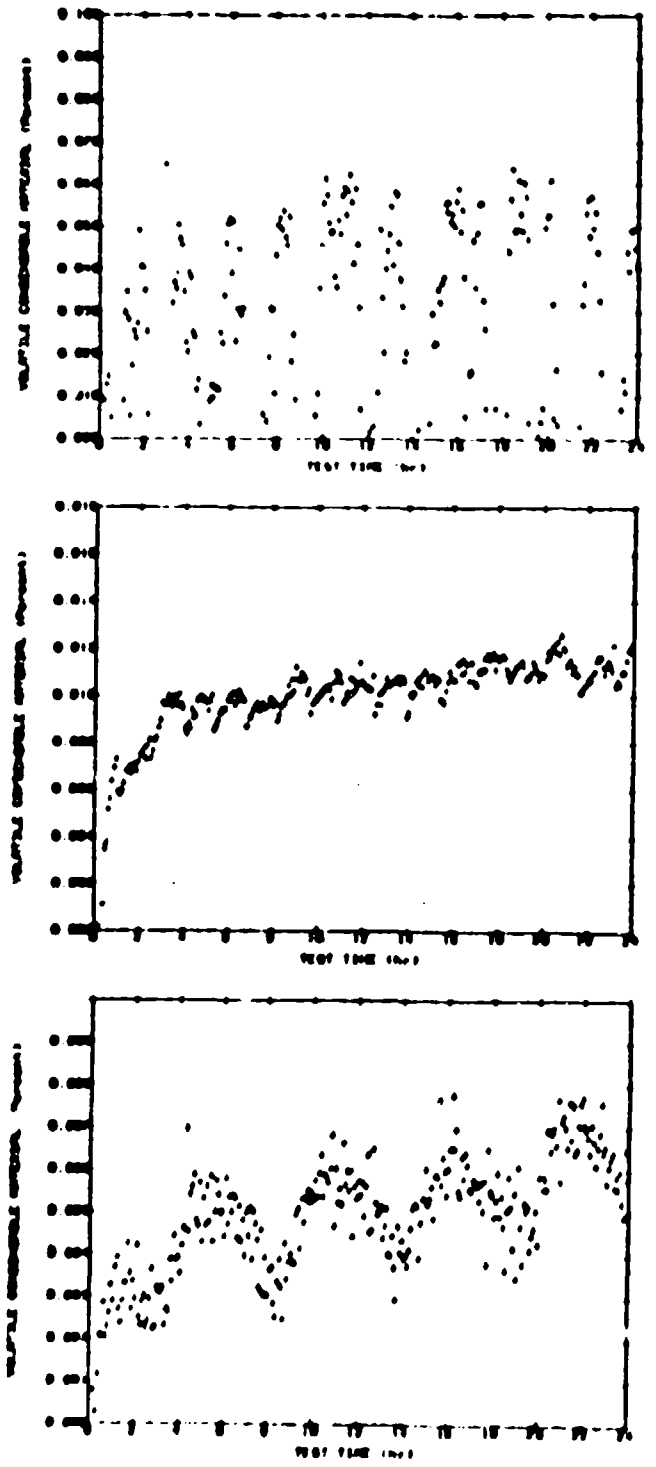


Fig. A-128 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an LMSC 1170 Sample at 75°C.

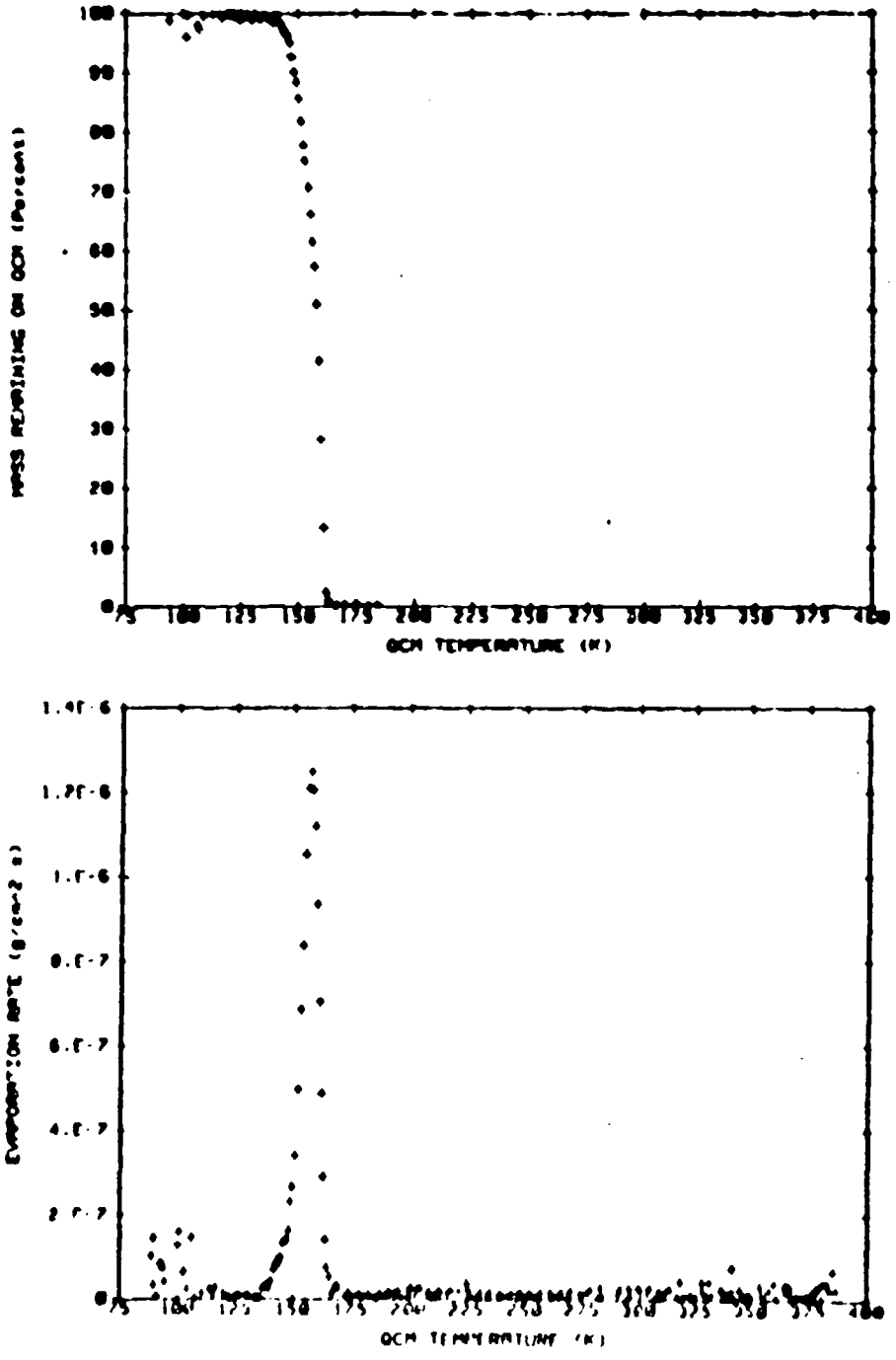


Fig. A-129 QTGA Data for Outgassing Products Collected on the 90 K QCM from an LMSC 1170 Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

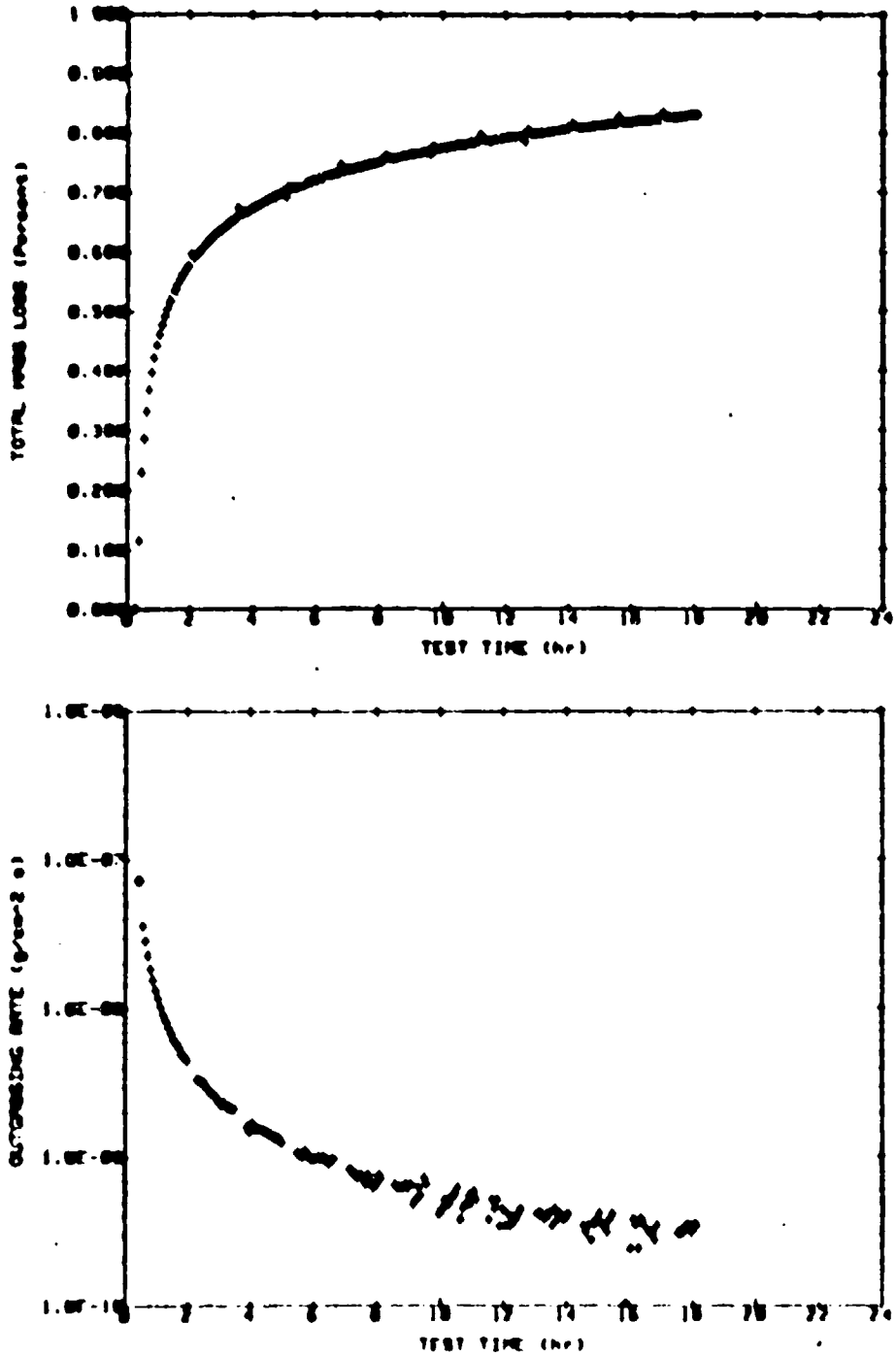


Fig. A-130 Total Mass Loss and Outgassing Rate as Functions of Time for an LMSC 1170 Sample at 25°C.

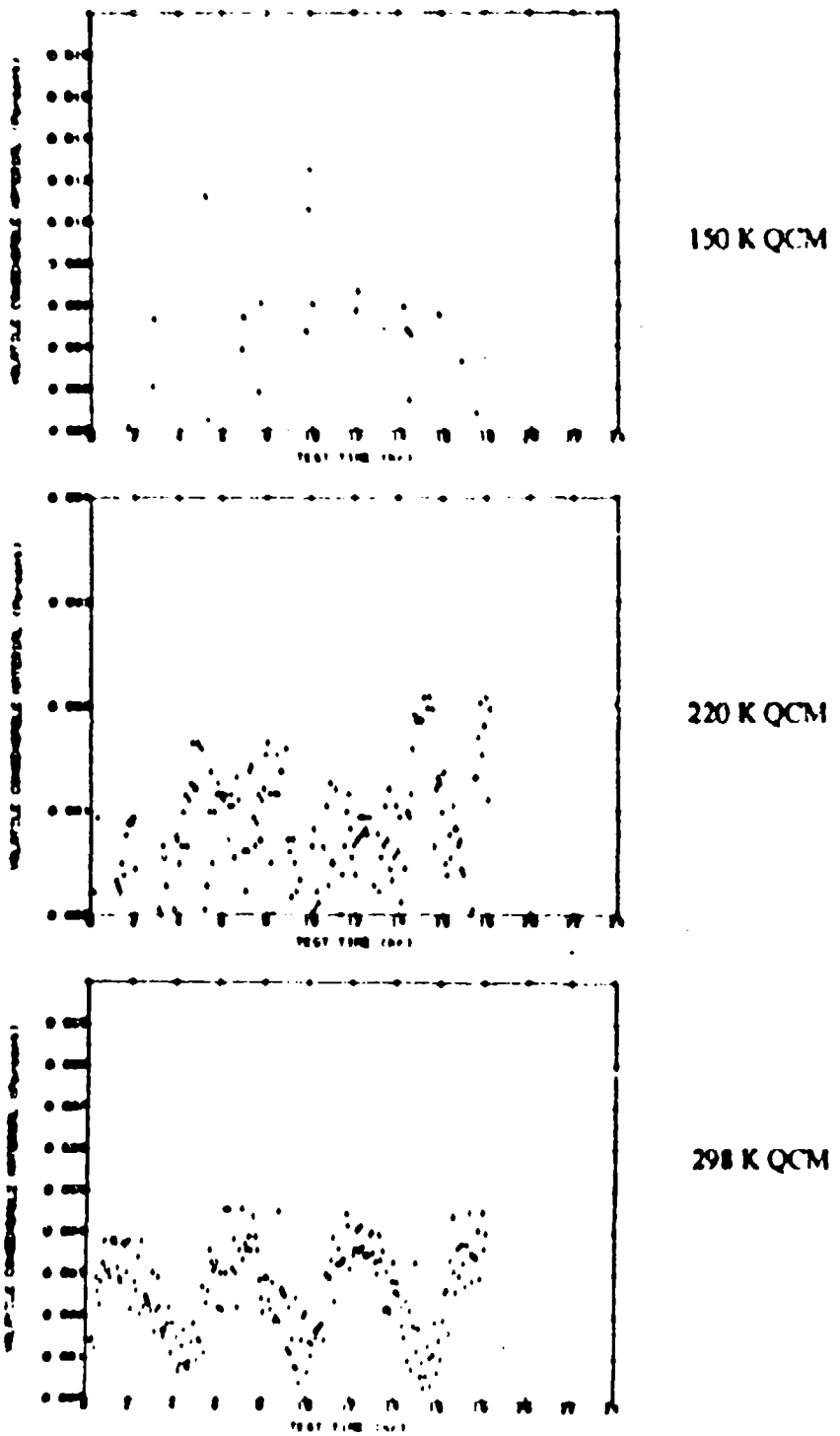


Fig. A-131 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an LMSC 1170 Sample at 25°C

No Data Available - QCM Thermal Analysis Not Performed

Fig. A 132 QTGA Data for Outgassing Products Collected on the QCK QCM from an LMSC 1120 Sample at 25°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature

Table A-32

GC/MS Data for [illegible] at 125°C
Quantitation Report

SCAN TIME (sec)	ASSIGNED IDENTITIES (percent)	SPECTRUM SIMILARITY

GC/MS DATA NOT AVAILABLE

Table A-33

GC/MS Data for LMSC 1170 at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION

GC/MS DATA NOT AVAILABLE

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 125°C

NO GC/MS DATA AVAILABLE
FOR THIS SAMPLE AT 200°C

Fig. A-133 Amount of Collected Volatiles Remaining in GC/MS Column from LMSC 1170 at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : AS4/PEEK (carbon fiber/thermoplastic resin)

DATE TEST STARTED : April 1, 1988

GC/MS DATA FILES :

125°C Test : JG18DEC87F
200°C Test : JG22DEC87C

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	51.47	51.23
Weight, pretest (g)	6.46845	6.43252
Total mass loss (%)	0.04	0.03
ISOTHERMAL TEST DATA :		
Test duration (h)	48	48
QCM/Temperature Data File	G0401	G0403
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0403Q	G0405Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a composite using AS4 carbon fiber and a 'Victrex' polyetheretherketone thermoplastic matrix produced by Imperial Chemical Industries Ltd.
- samples supplied by R.G. Rudness, Martin Marietta Energy Systems, Inc.
- sample configuration (125°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- sample configuration (75°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- samples were cleaned with isopropyl alcohol 24 hours before start of test
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 150 K, 220 K, and 298 K QCMs after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

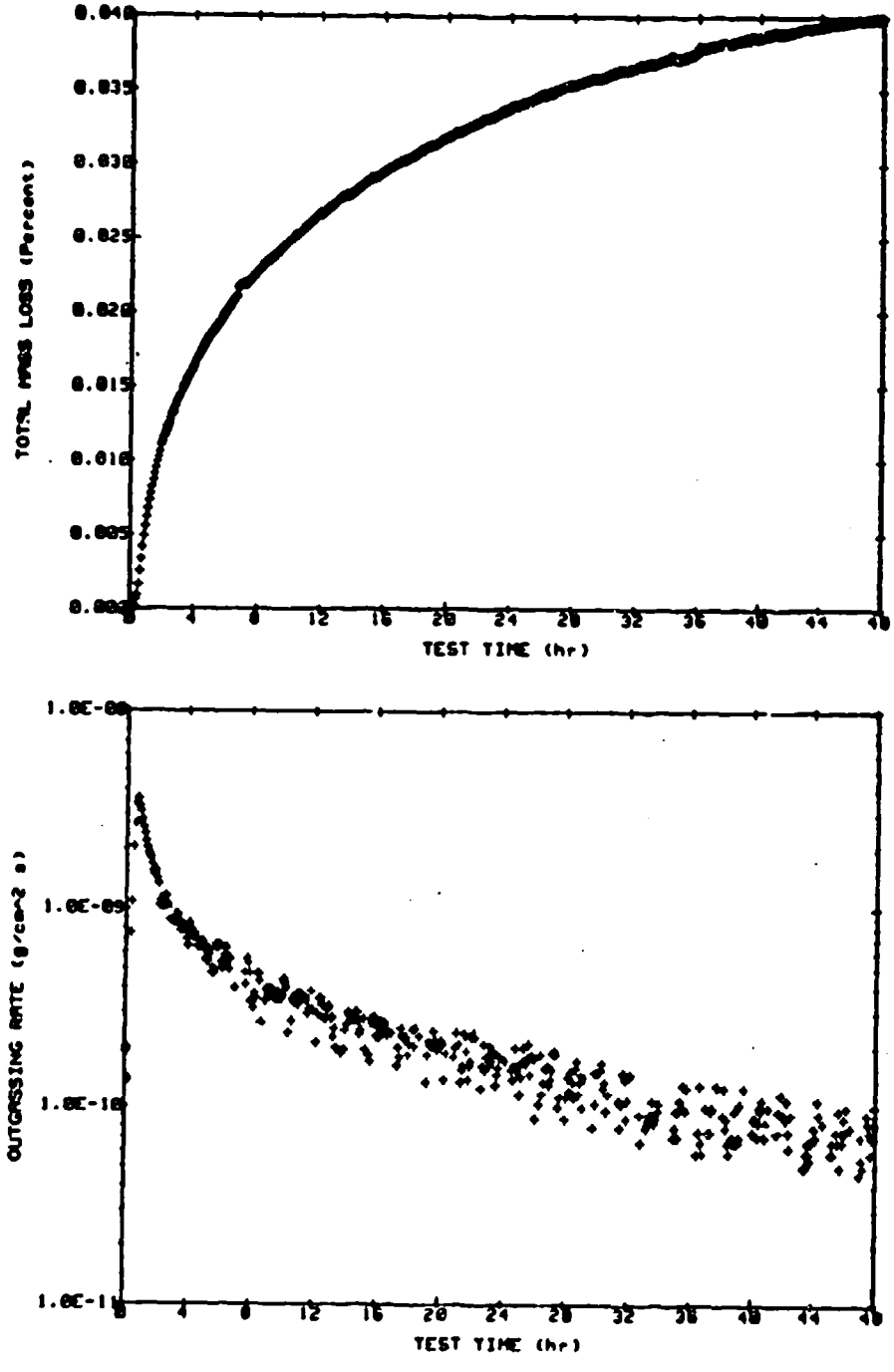


Fig. A-134 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/PEEK Sample at 125°C.

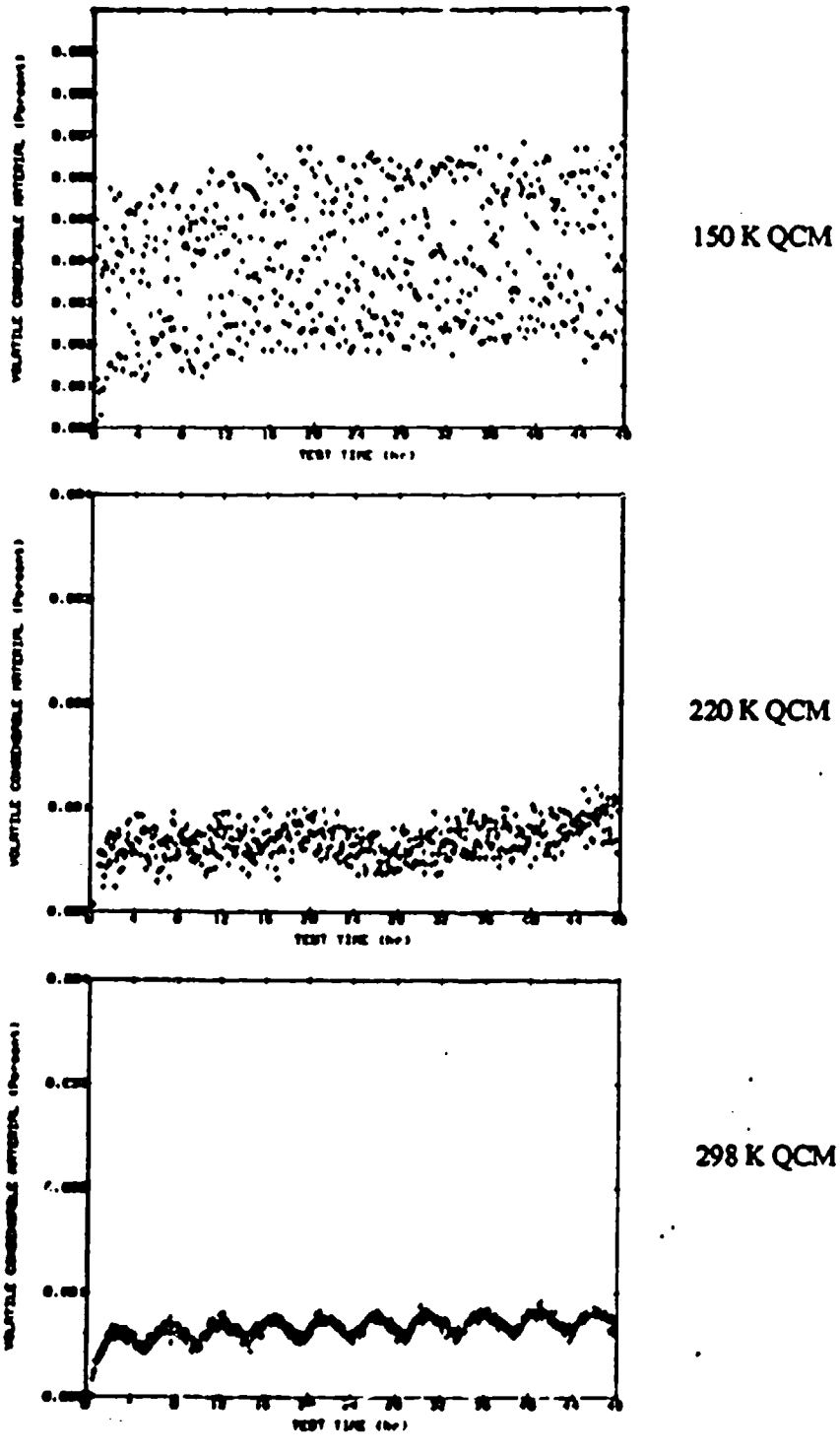


Fig. A-135 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/PEEK Sample at 125°C.

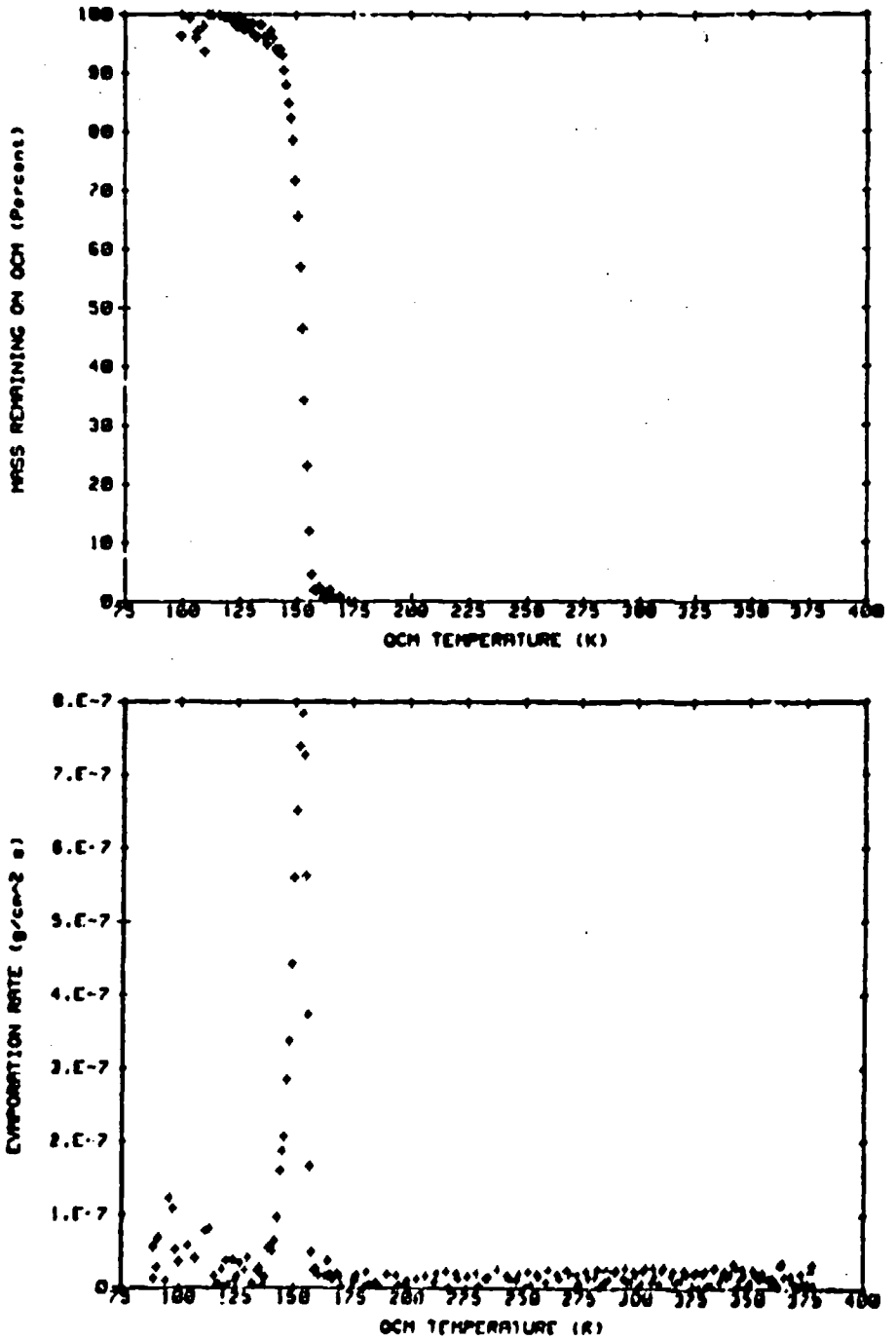


Fig. A-136 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/PEEK Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

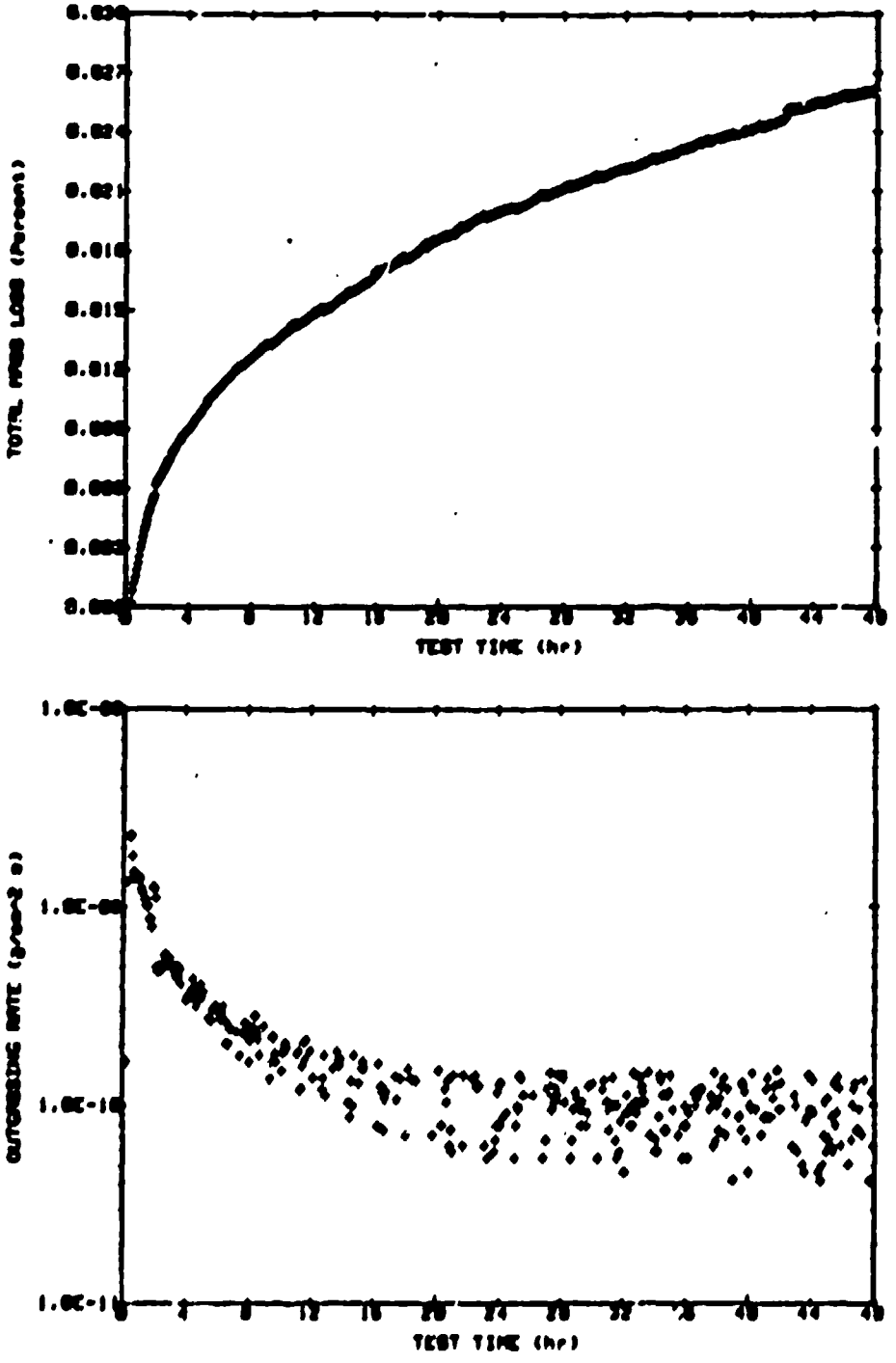


Fig. A-137 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/PEEK Sample at 75°C.

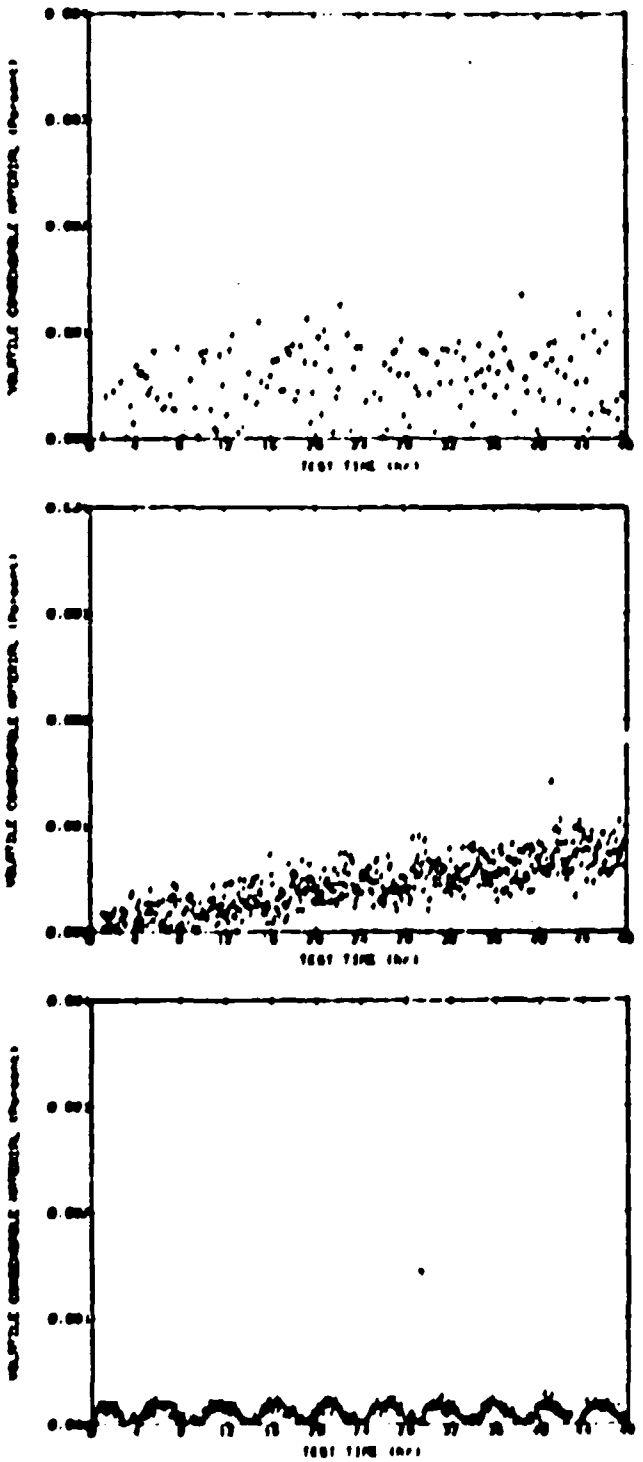


Fig. A-138 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/PEEK Sample at 75°C.

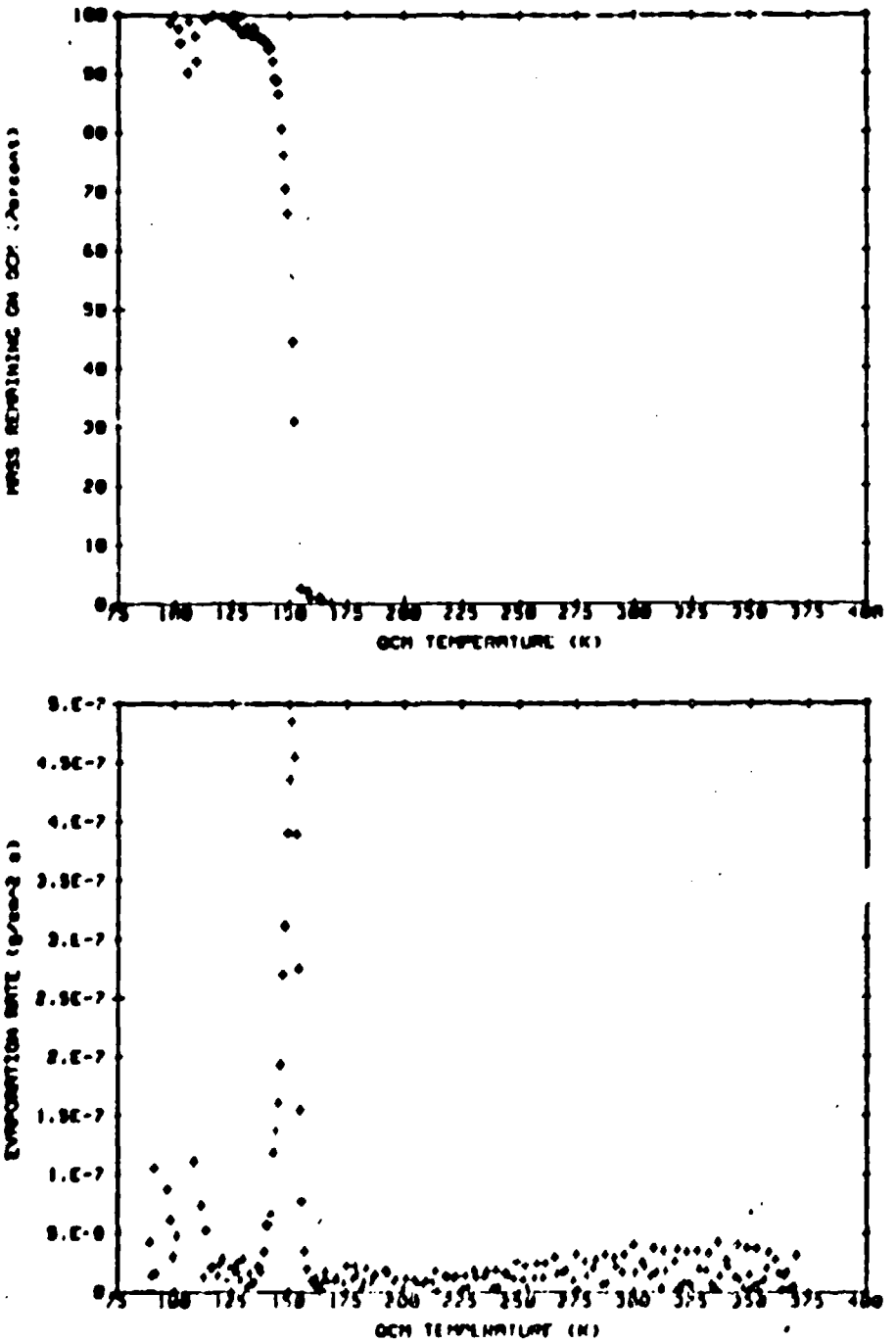


Fig. A-139 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/PLEK Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-34

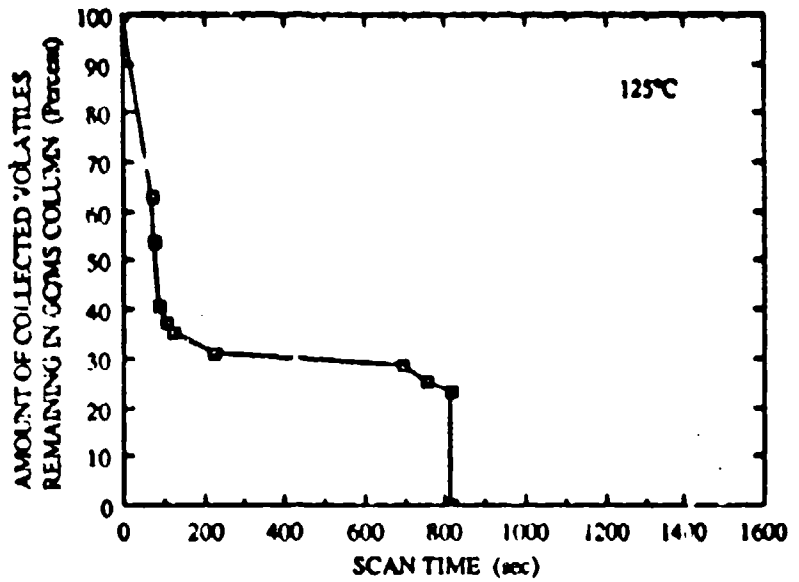
GC/MS Data for AS4/PEEK at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
73	37.35	CO_2 artifact
75	9.23	
90	12.64	isopropanol
106	3.41	n-propanol
127	2.04	chloroform
225	4.47	toluene
693	2.44	$C_{14}H_{30}$, MW198, hydrocarbon, tetradecane?
754	3.45	$C_{15}H_{32}$, MW 212, hydrocarbon, pentadecane?
812	1.65	
815	23.31	$C_{16}H_{30}O_4$ diester

Table A-35

GC/MS Data for AS4/PEEK at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
86	4.70	isopropanol
103	1.46	n propanol
122	1.03	chloroform
214	1.79	toluene
593	0.64	
658	1.03	$C_{14}H_{30}$, MW 198, hydrocarbon, e.g. tetradecane
717	2.31	$C_{16}H_{32}$, MW 212, hydrocarbon, e.g. pentadecane
775	14.66	$C_{16}H_{30}O_4$ diester
951	59.93	1,1' sulfonyl bisbenzene
1092	1.20	
1146	1.43	bis(2-ethylhexyl)adipate
1207	1.76	
1243	2.17	phthalate diester, m/z 149 base peak
1283	2.08	
1377	3.74	



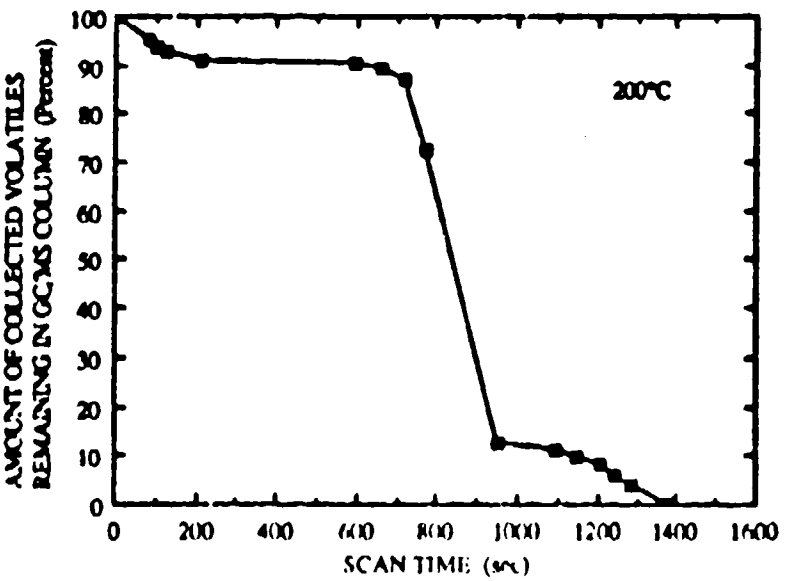


Fig A-140 Amount of Collected Volatiles Remaining in GC/MS Column from AS4/PEEK at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : AS4/PPS (carbon fiber/thermoplastic resin)

DATE TEST STARTED : November 20, 1987

GC/MS DATA FILES :

125°C Test : JG21DLC87B
200°C Test : JG22DLC87D

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	26.12	26.12
Weight, pretest (g)	6.81730	6.84348
Total mass loss (%)	0.06	0.03
ISOTHERMAL TEST DATA :		
Test duration (h)	57	53
QCM/Temperature Data File	G1120	G1124
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G1122Q	G1126Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a composite using AS4 carbon fiber and a Ryton polyphenylene sulphide thermoplastic matrix produced by Phillips Petroleum
- samples supplied by R.O. Rudness, Martin Marietta Energy Systems, Inc.
- sample configuration (125°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- sample configuration (75°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- samples were cleaned with isopropyl alcohol 24 hours before start of test
- no QTA performed on 298 K QCM after 125°C Isothermal Test (Note 8, Sec. A.1.4)
- no QTA performed on 298 K QCM after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

Fig A 101 Total Stress Paths and Change in Pore Pressure as Functions of Time for an ASAWPS Sample at 125 f

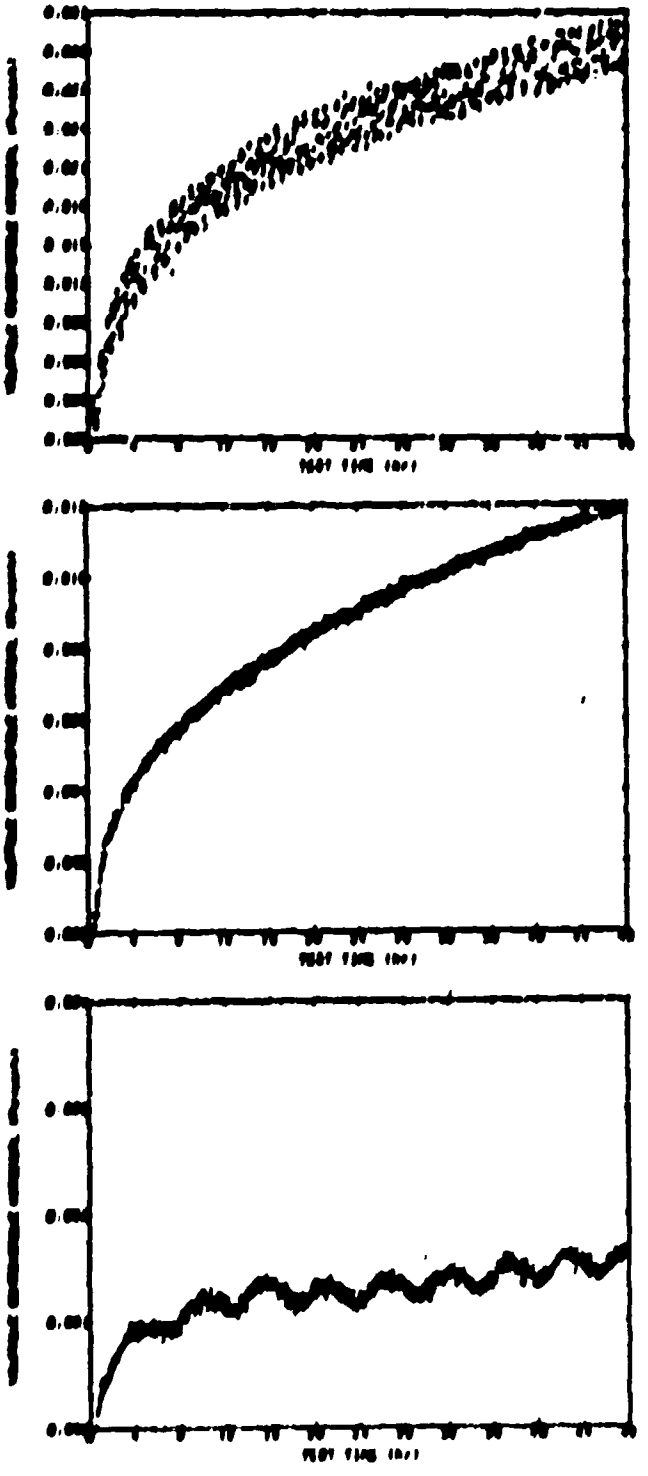


Fig. A-142 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an Ab4/PPS Sample at 125°C.

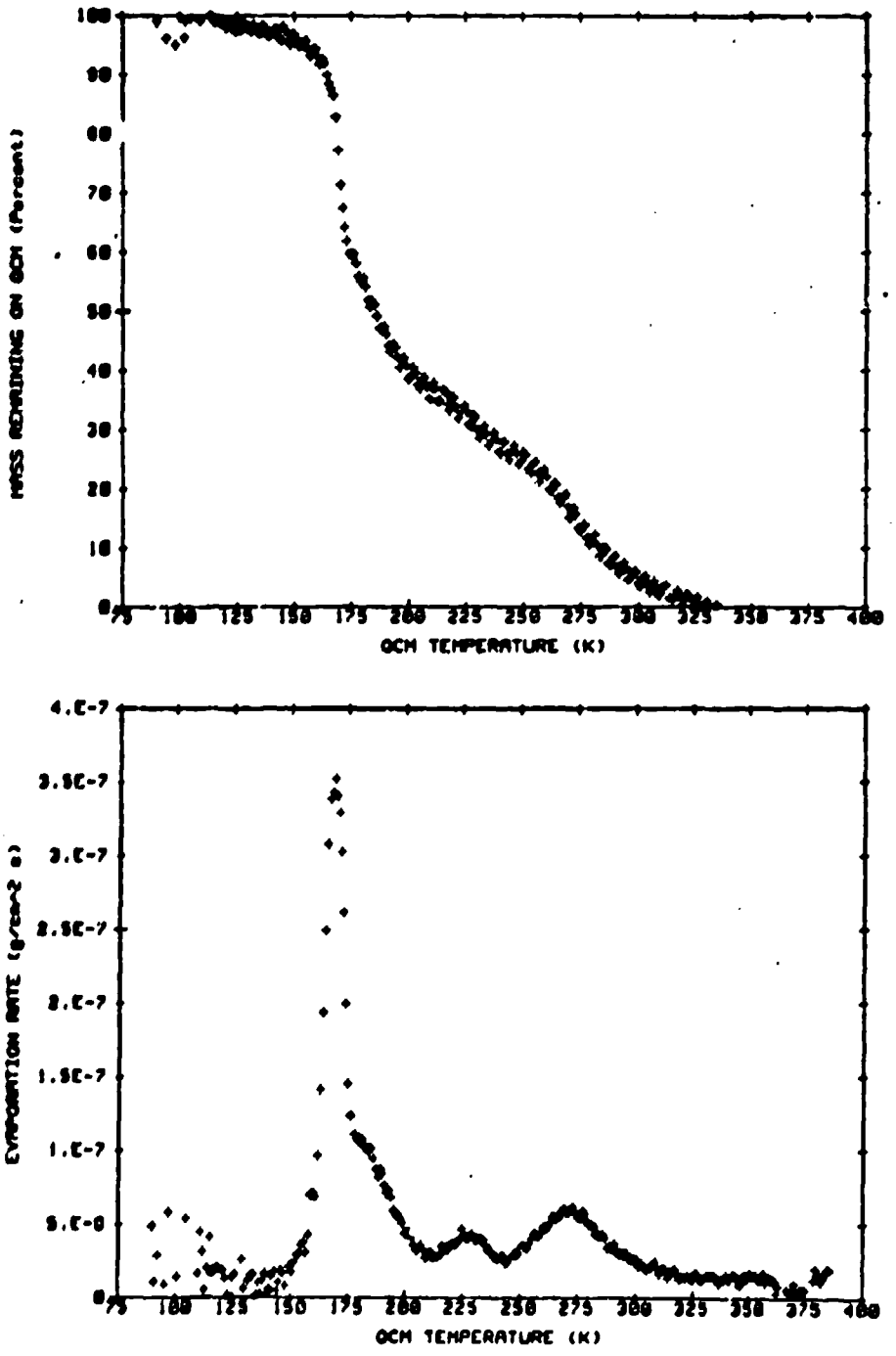


Fig. A-143 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/PPS Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

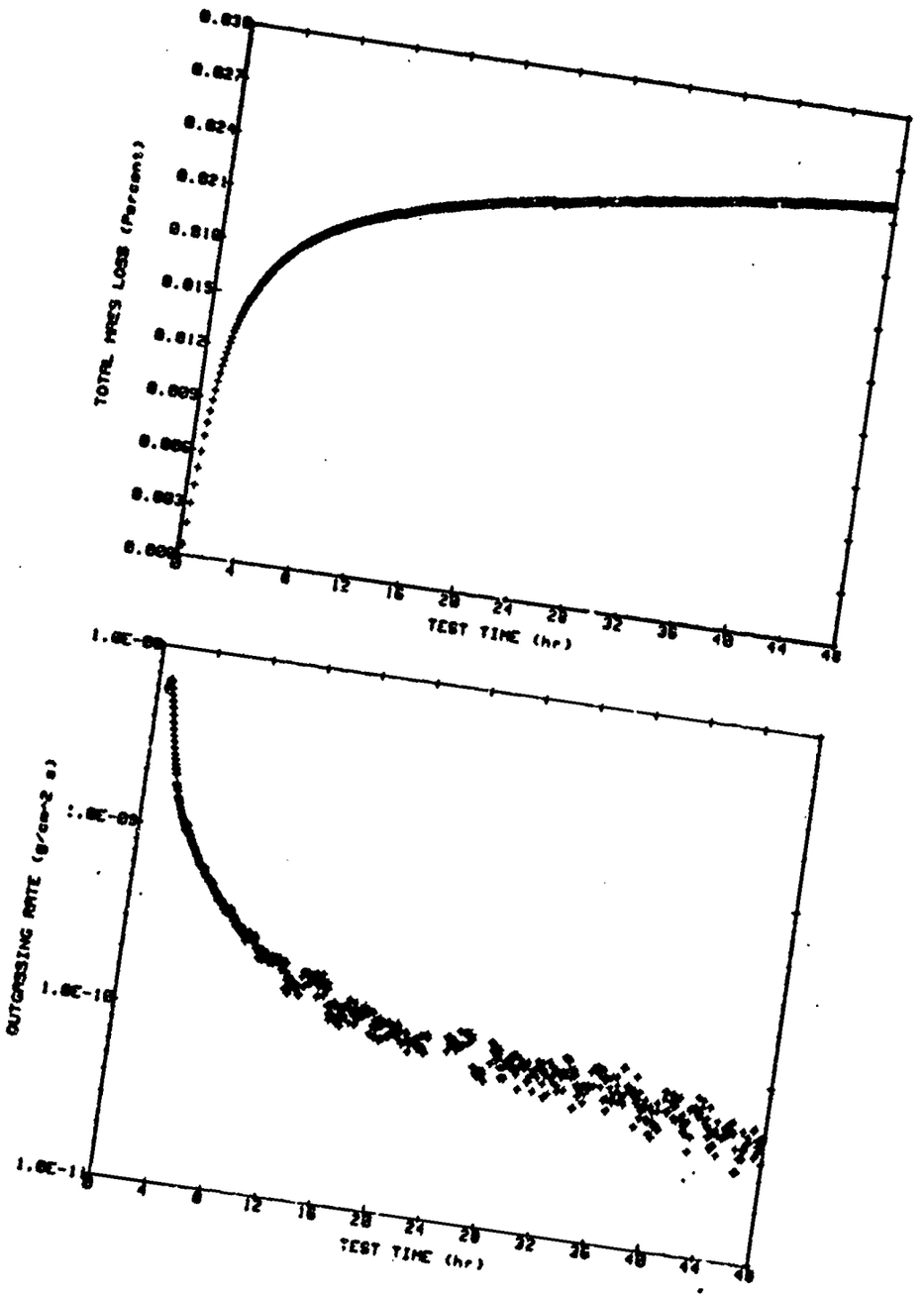


Fig. A-144 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/PPS Sample at 75°C.

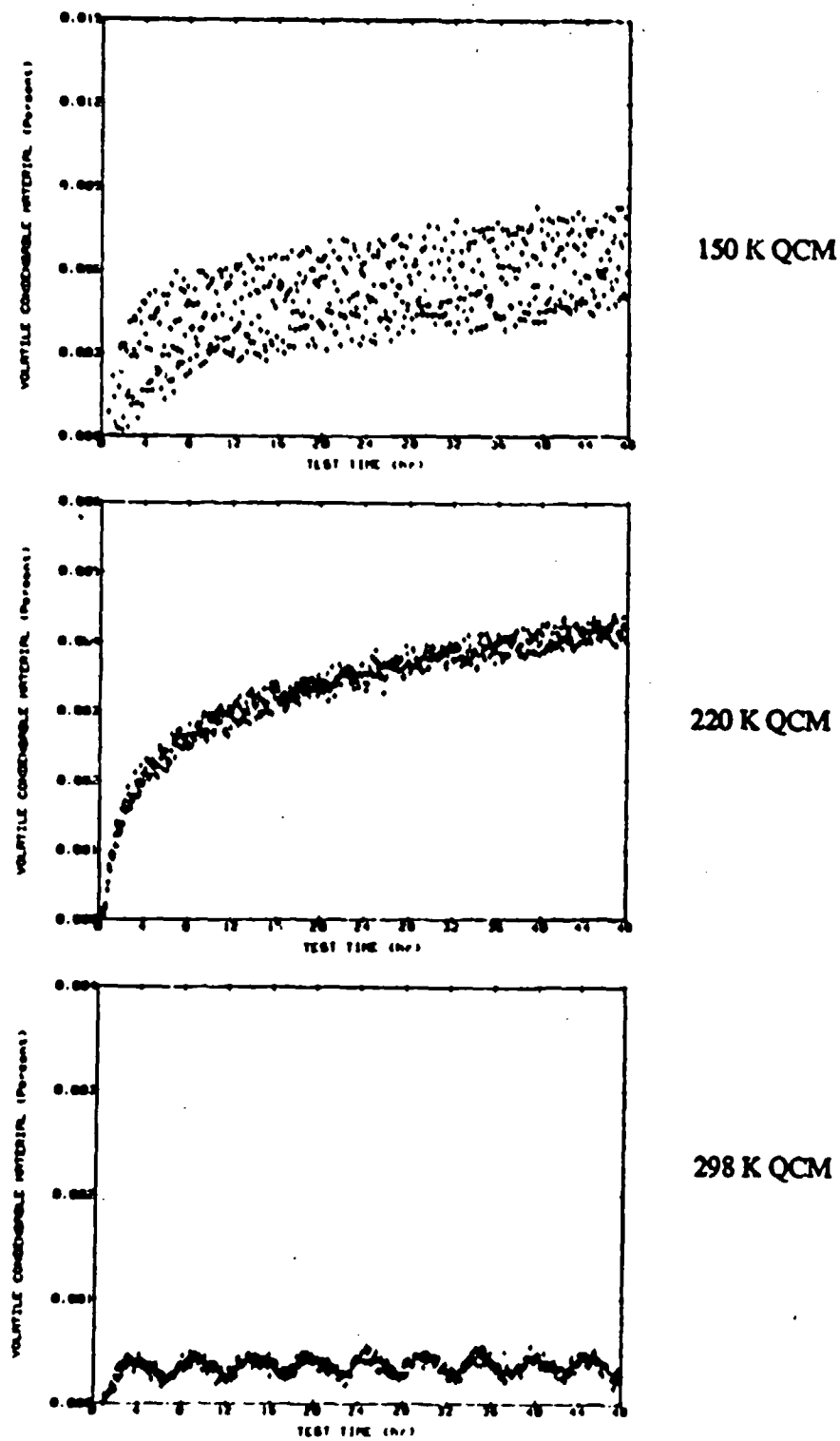


Fig. A-145 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/PPS Sample at 75°C.

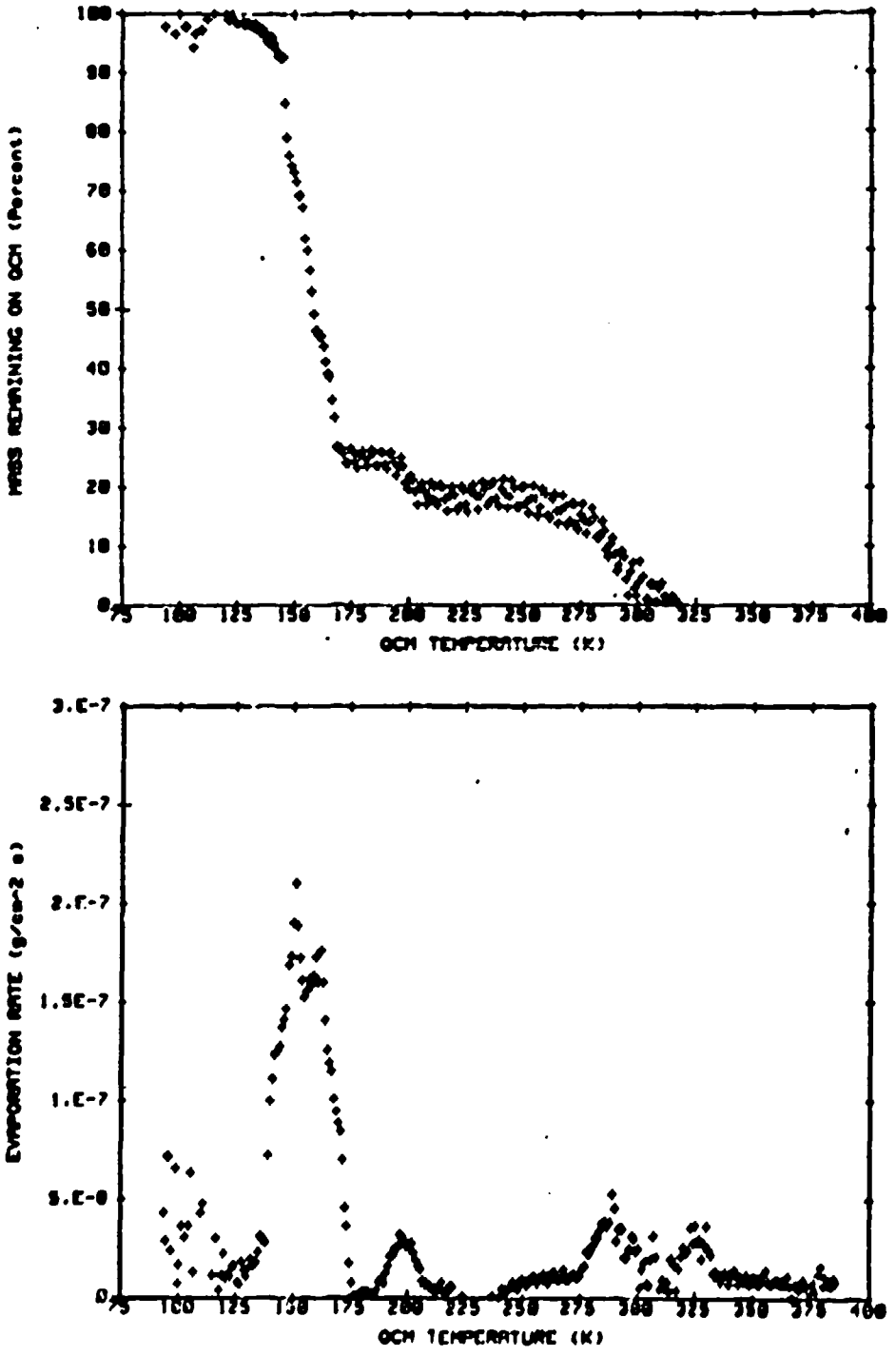


Fig. A-146 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/PPS Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-36

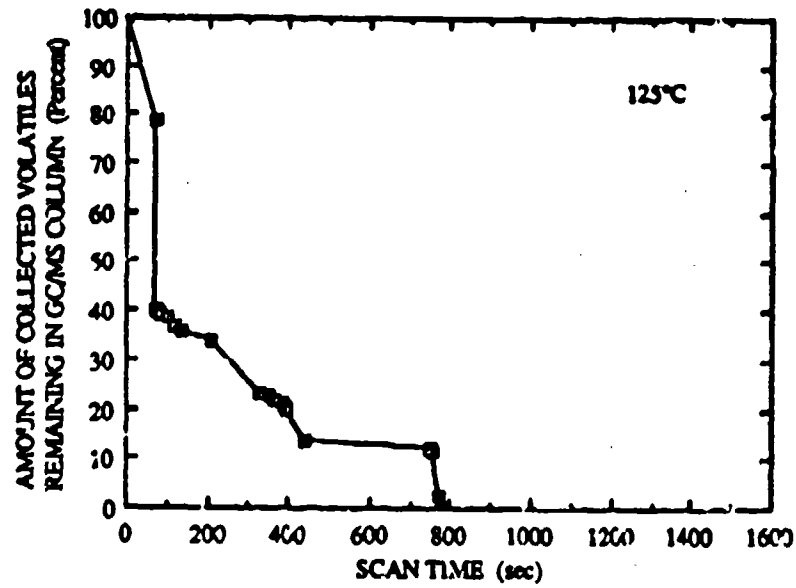
GC/MS Data for AS4/PPS at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
70	21.40	
72	38.37	CF_2Cl_2 (dichlorodifluoromethane)
75	0.44	CO_2 artifact
86	0.65	isopropanol, acetone, hydrocarbon
100	0.65	n-propanol
119	1.89	$CHCl_3$ (chloroform)
135	0.76	2-methyl-1, 3-dioxolane
211	2.15	toluene
328	10.76	dihydro-2-furanone
348	0.41	
361	0.99	2-methyl-1, 3, 6-trioxocane
384	0.39	
387	0.58	3-methyl-dihydro-2-furanonone
390	0.42	
393	0.45	trimethyl benzene
441	6.16	N-methyl benzamine
747	1.54	$C_{15}H_{24}O$ phenolic, MW 220
757	0.36	
774	9.54	$C_{16}H_{30}O_4$, diester
780	2.36	$C_{14}H_{22}O$ phenolic, MW 206

Table A-37

GC/MS Data for AS4/TPS at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
86	0.68	butane
122	0.57	chloroform
139	1.70	2-methyl-1, 3-dioxolane
215	0.64	toluene
347	14.44	dihydro-2 furanone
352	0.82	
358	0.83	2-methyl-1, 3, 6-trioxocane
369	1.35	tetrahydropyran-2-one
387	4.43	aniline
396	0.69	phenol
405	1.11	2(2-ethoxyethoxy)ethanol
434	0.85	1-metayl-2-pyrolidinone
448	12.19	N-methyl benzenamine
461	0.87	
550	2.00	2-[2-(2-methoxyethoxy)ethoxy]ethanol
566	1.53	
573	0.75	
592	1.68	2-[2-(2-ethoxyethoxy)ethoxy]ethanol
599	3.06	2-chloro-4-methyl benzenamine
717	0.58	artifact from previos run
725	1.68	similar to 2-[2-(2-ethoxyethoxy)ethoxy]ethanol
737	1.28	similar to 2-[2-(2-ethoxyethoxy)ethoxy]ethanol
750	3.30	$C_{15}H_{24}O$ phenolic, MW 220
758	1.97	$C_{17}H_{28}$ aromatic compound
776	4.76	$C_{16}H_{30}O_4$, diester
785	7.58	$C_{14}H_{22}O$ phenolic, MW 206
809	1.42	1-phenyl-2-pyrolidinone
871	1.13	similar to 2-[2-(2-ethoxyethoxy)ethoxy]ethanol
900	2.71	
915	2.77	
929	1.10	
999	0.47	
1014	1.09	1-nitro-4-phenoxybenzene
1030	1.63	
1043	1.45	
1054	0.60	
1107	2.23	8-chlorophenothiazin-4-ol
1165	0.98	
1186	0.99	$C_{20}H_{34}O_4$ polyethoxyphenylether ?
1199	0.76	
1312	0.59	
1380	1.63	
1420	1.75	phthalate diester
1441	1.23	



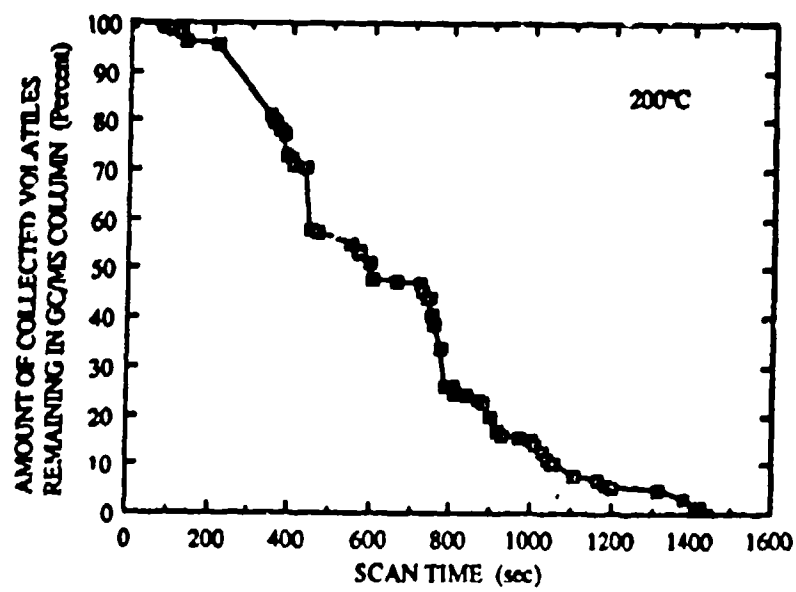


Fig. A-147 Amount of Collected Volatiles Remaining in GC/MS Column from AS4/PPS at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : AS4/3501-6 (Source A) (carbon fiber/thermoset epoxy)

DATE TEST STARTED : December 3, 1987

GC/MS DATA FILES :

125°C Test : JG18DEC87D
200°C Test : JG22DEC87B

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	26.22	26.2
Weight, pretest (g)	5.91837	5.84784
Total mass loss (%)	0.20	0.08
ISOTHERMAL TEST DATA :		
Test duration (h)	50	48
QCM/Temperature Data File	G1203	G1207
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G1205Q	G1209Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a composite using AS4 carbon fiber and a DEGBA resin (MY720) thermoset epoxy matrix produced by Hercules/Ciba Geigy
- samples prepared and supplied by R.G. Radness, Martin Marietta Energy Systems, Inc.
- sample configuration (125°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- sample configuration (75°C test): 4 squares, each 1.0 inch by 1.0 inch by 0.060 inch
- samples were cleaned with isopropyl alcohol 24 hours before start of test
- no QCA performed on 150 K, 220 K, and 298 K QCMs after 75°C Isothermal Test (Note 8, Sec. A.1.4)
- mass spectrometer scanning m/e = 10 to 500

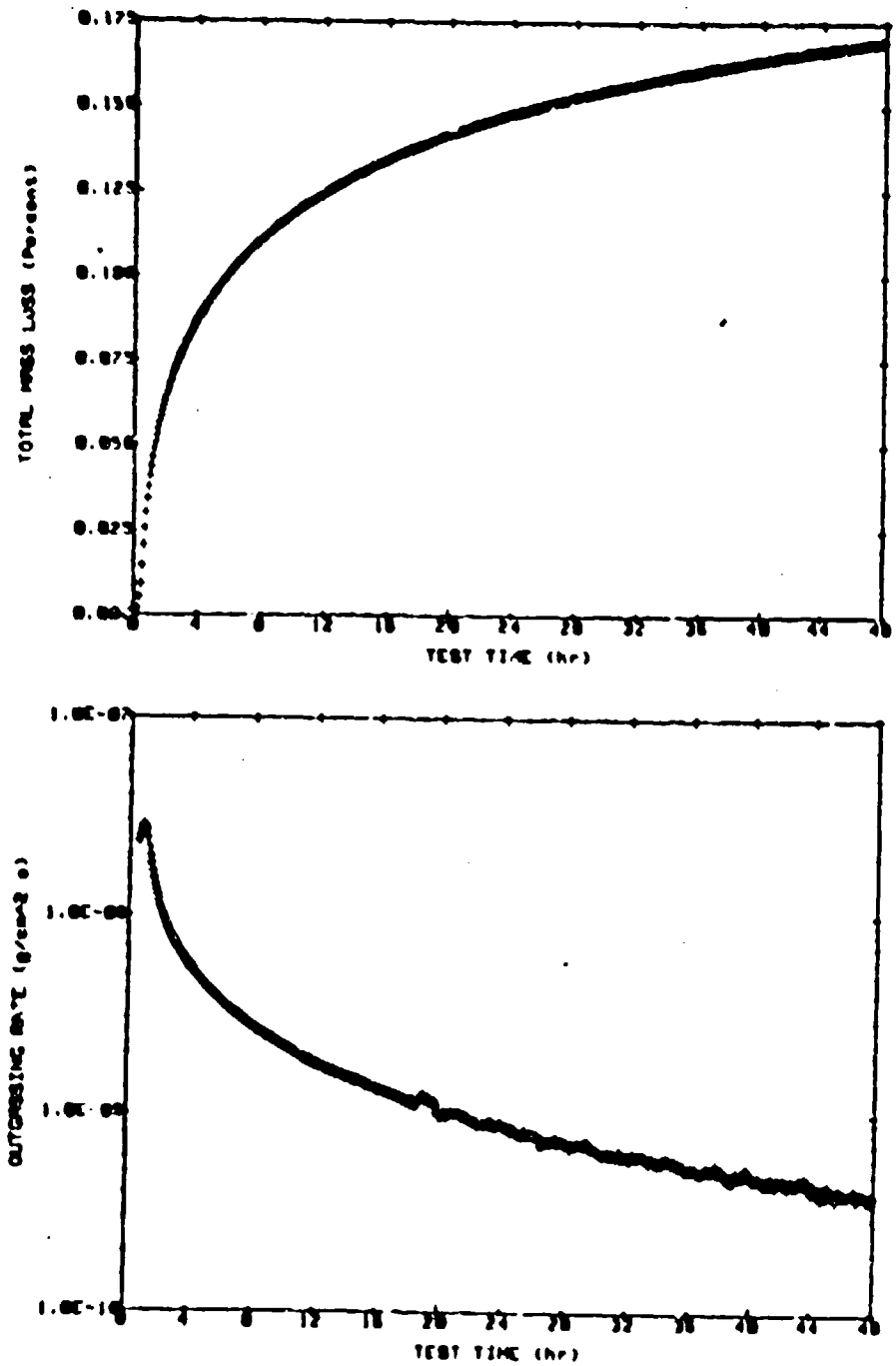


Fig. A-148 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/3501-6 (Source A) Sample at 125°C.

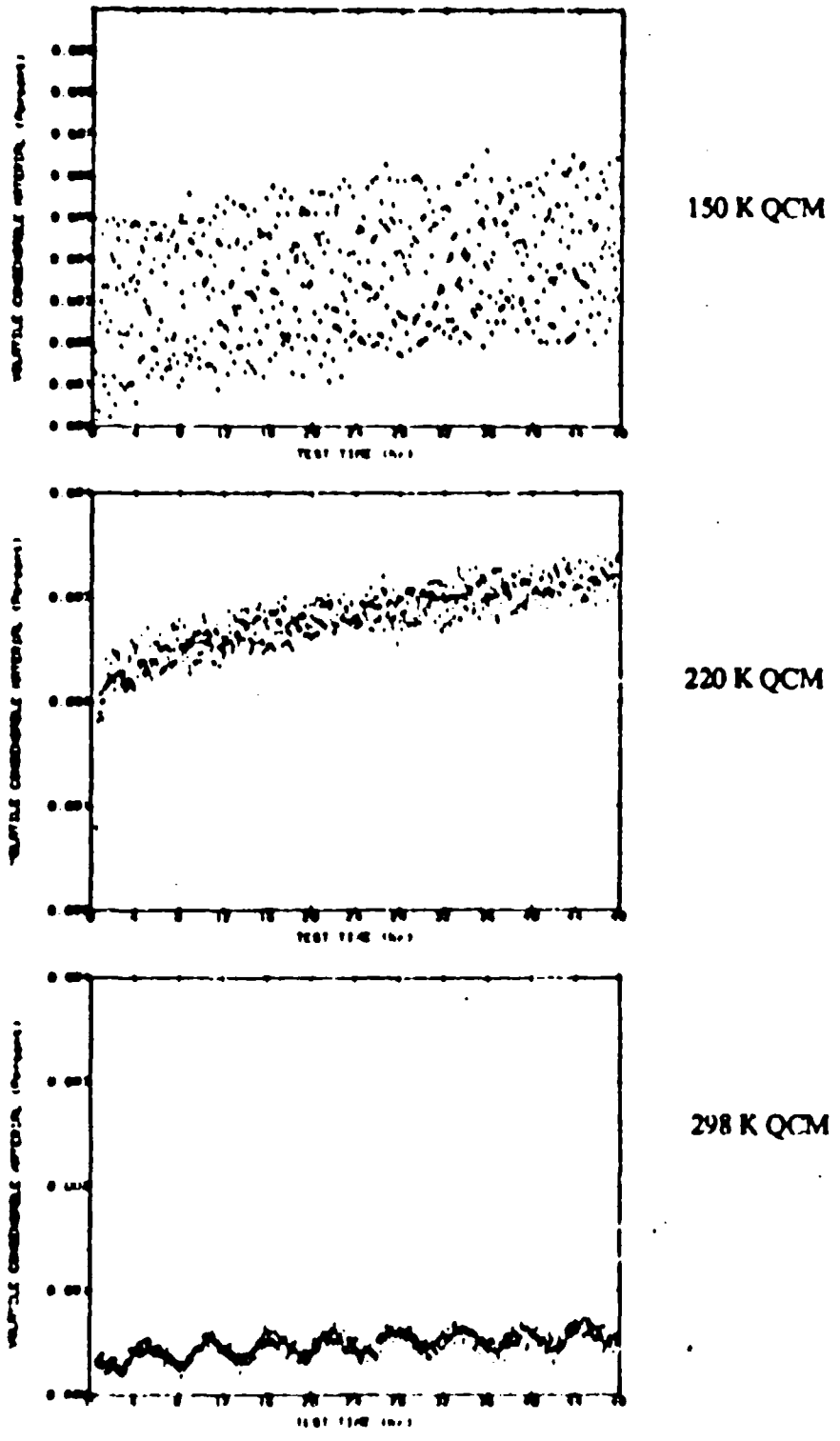


Fig. A-149 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/3501 6 (Source A) Sample at 125°C.

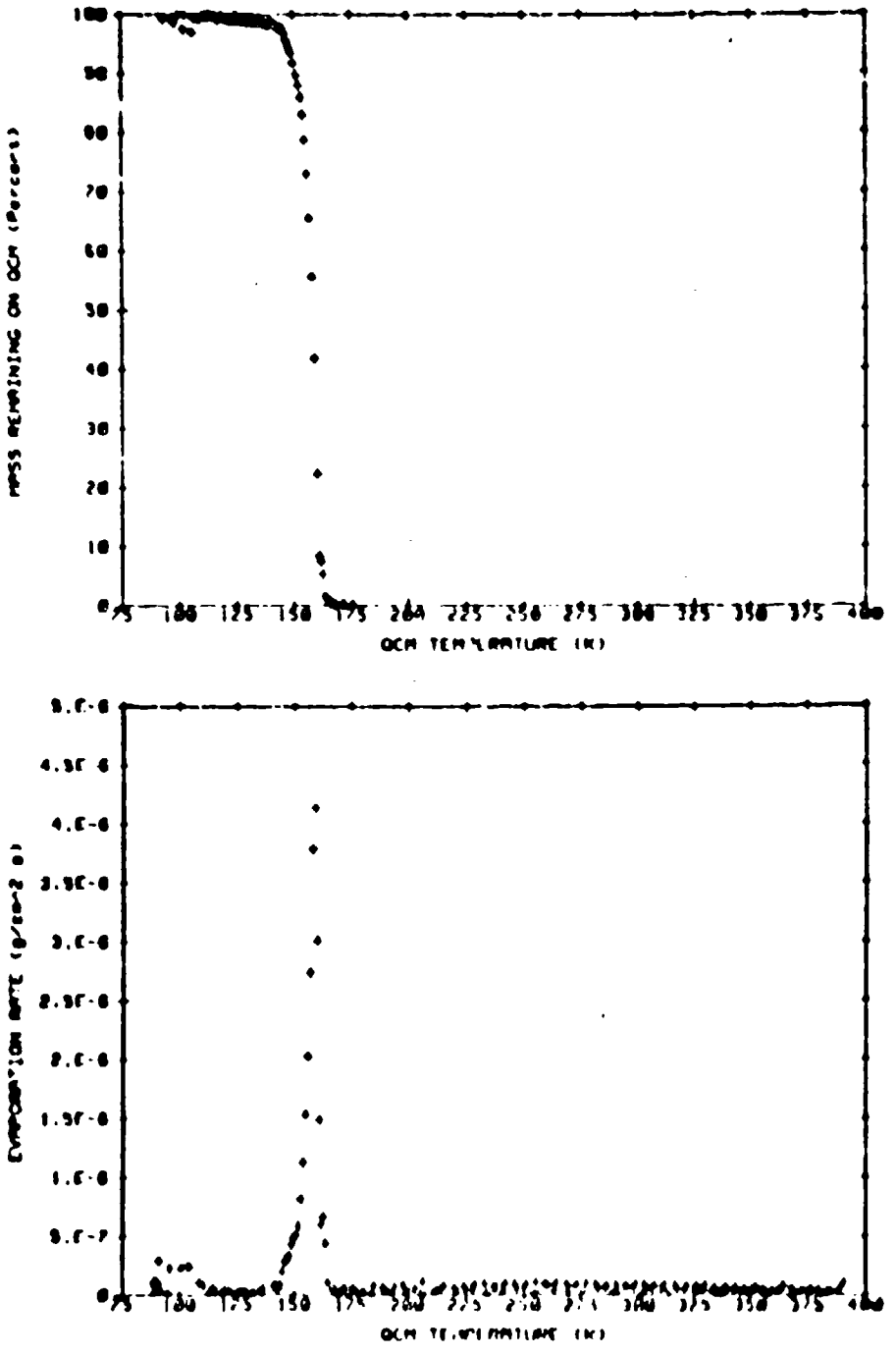


Fig. A-150 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/3501-6 (Source A) Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature

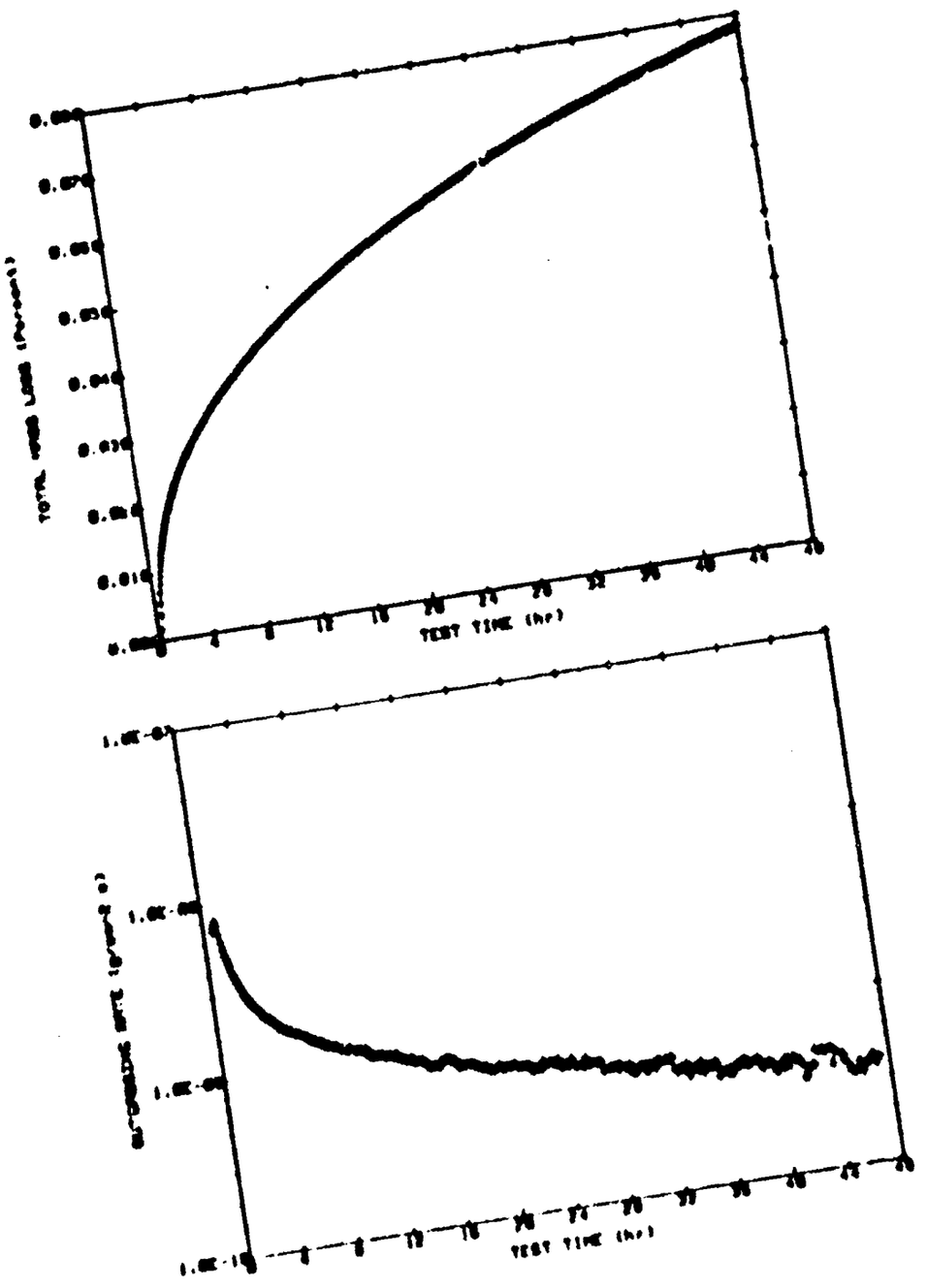


Fig. A-151 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/3501 6 (Source A) Sample at 75°C.

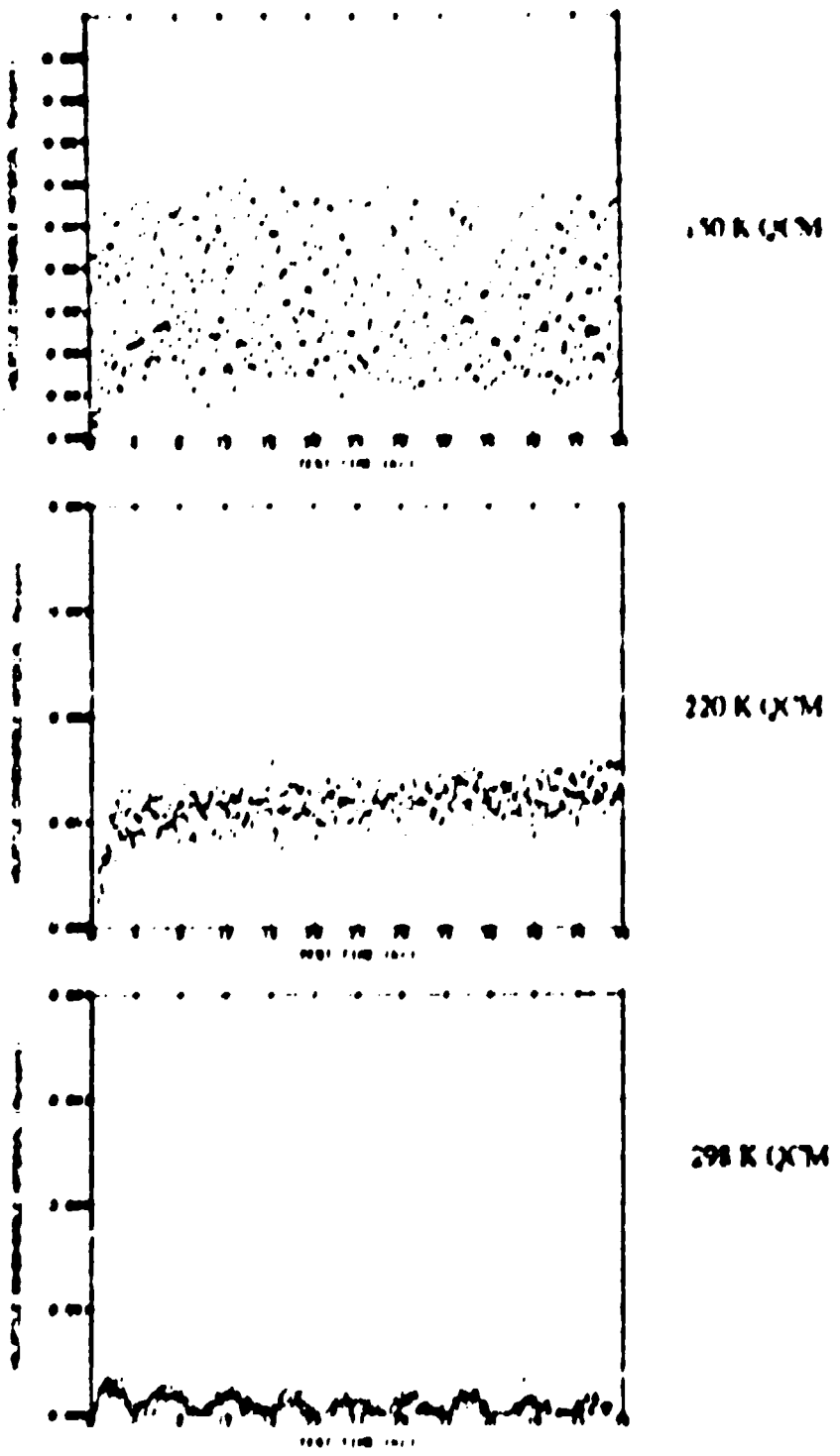


Fig. A-192 Volatile Condensable Material on Collector QCM at 140 K, 220 K, and 298 K as a Function of Time for an AS4/1501-6 (Sample A) Sample at 75°C

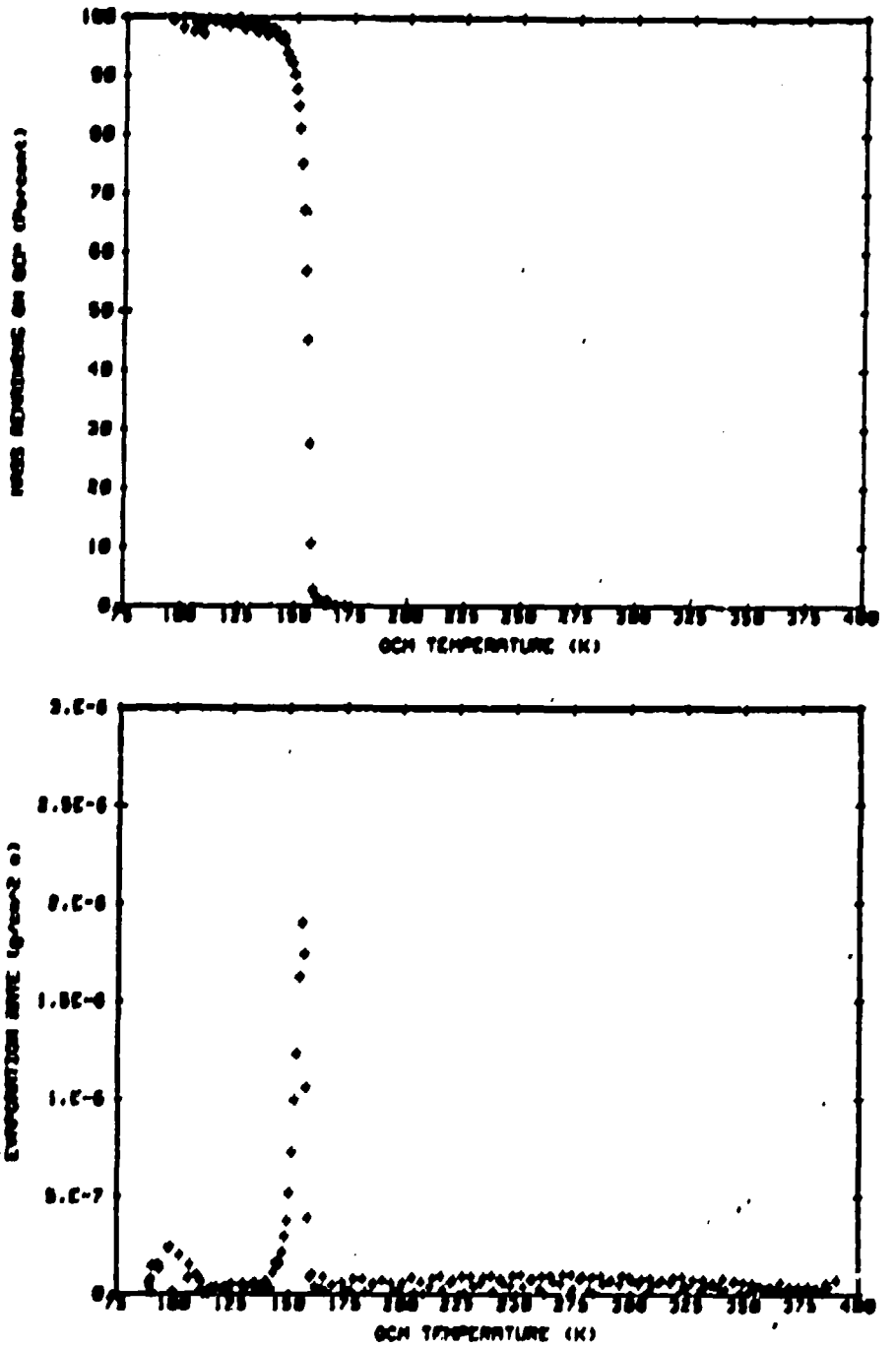


Fig. A-153 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/3501-6 (Source A) Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-38

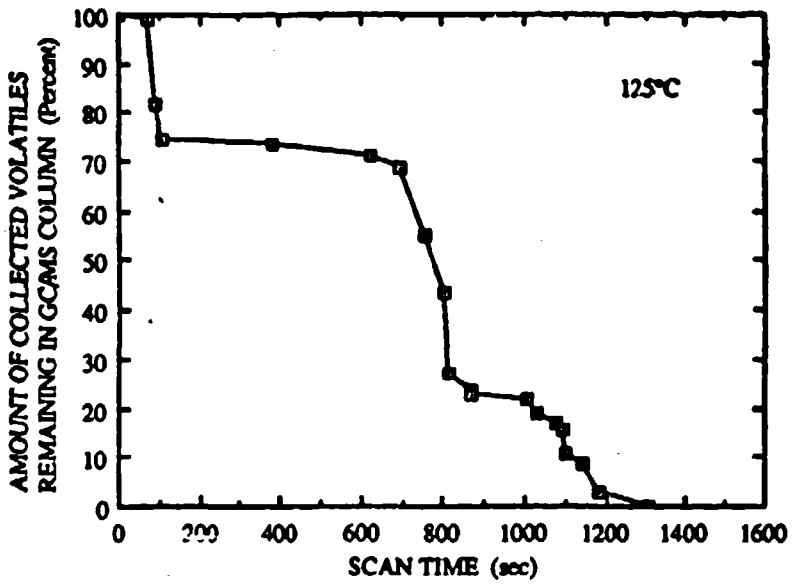
GC/MS Data for AS4/3501-6 (Source A) at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
74	0.89	CO_2 artifact
90	17.39	isopropanol
105	7.43	n-propanol artifact
381	1.02	artifact
625	2.13	artifact
693	2.60	$C_{14}H_{30}$, MW 198, hydrocarbon
754	13.57	$C_{15}H_{32}$, MW 212, hydrocarbon
803	11.63	Dodecanoic Acid artifact
812	16.49	$C_{16}H_{34}$, MW 226, hydrocarbon
867	3.37	$C_{17}H_{36}$, MW 240, hydrocarbon
870	0.75	
1003	1.03	
1029	2.72	artifact
1077	2.03	polydimethyl siloxane artifact
1095	1.50	
1102	4.91	artifact
1142	1.65	
1184	6.11	artifact
1309	2.80	dioctyl phthalate isomer

Table A-39

GC/MS Data for AS4/3501-6 (Source A) at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
73	5.25	CO_2 artifact
75	0.59	CF_2Cl_2
78	0.27	
87	4.44	propanol
408	0.30	
410	0.40	3-cyclohexene-1-methanol
489	0.90	
505	6.85	
509	0.34	
520	0.51	
544	7.59	
591	0.74	
597	0.30	
659	0.38	tetradecane
663	0.58	
703	1.12	long chained hydrocarbon
717	1.28	pentadecane
772	1.43	hexadecane
814	0.27	long chained hydrocarbon
824	0.38	heptadecane
845	0.48	
933	0.88	
943	5.39	
954	0.68	phthalate diester
1005	0.55	
1029	13.37	
1040	7.19	
1047	0.34	
1050	0.19	
1195	1.49	diheptyl phthalate isomer
1254	35.44	dioctyl phthalate isomer



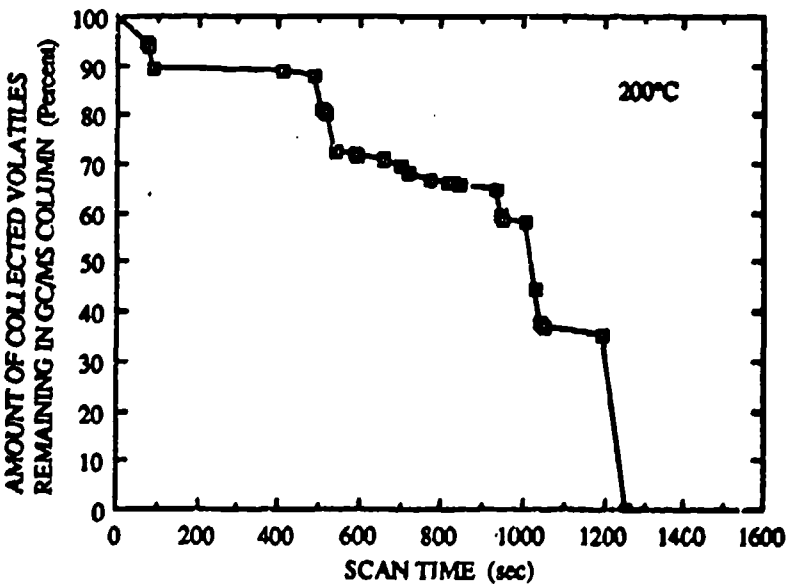


Fig. A-154 Amount of Collected Volatiles Remaining in GC/MS Column from AS4/3501-6 (Source A) at 125°C and 200°C

TEST INFORMATION

MATERIAL TESTED : AS4/3501-6 (Source B) (carbon fiber/thermoset epoxy)

DATE TEST STARTED : February 5, 1988

GC/MS DATA FILES :

125°C Test : JG8APR88B
200°C Test : JG7APR88B

	Test Temperature (°C)	
	125	75
MATERIAL SAMPLE DATA :		
Area (cm^2)	39.51	37.51
Weight, pretest (g)	6.98689	6.51814
Total mass loss (%)	0.24	0.13
ISOTHERMAL TEST DATA :		
Test duration (h)	48	48
QCM/Temperature Data File	G0205	G0208
Mass Spectrometer Data File	"	"
QCM THERMAL ANALYSIS DATA :		
QCM/Temperature Data File	G0207Q	G0210Q
Mass Spectrometer Data File	"	"

COMMENTS :

- material is a composite using AS4 carbon fiber and a DEGBA resin (MY720) thermoset epoxy matrix produced by Hercules/Ciba Geigy
- samples prepared by D.M. Carlin, USAF/AFWAL/MLBC
- samples supplied by Lt. P.M. Falco, USAF/AFWAL/MLBT
- sample configuration (125°C test): 1 square 1.765 inch by 1.735 inch by 0.092 inch
- sample configuration (75°C test): 1 square 1.710 inch by 1.700 inch by 0.090 inch
- samples were cleaned with isopropyl alcohol 24 hours before start of test
- mass spectrometer scanning m/e = 10 to 500

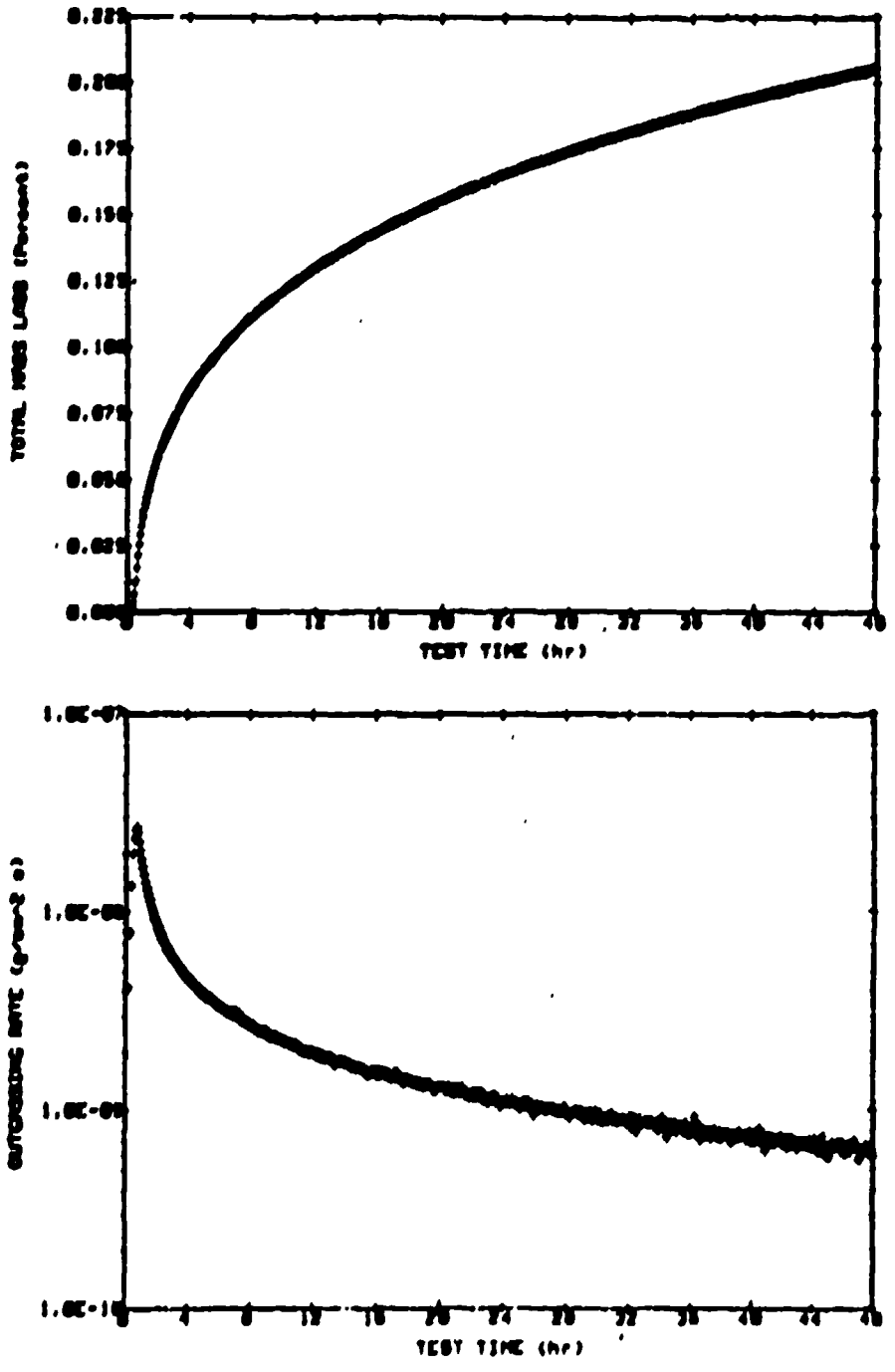


Fig. A-155 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/3501-6 (Source B) Sample at 125°C.

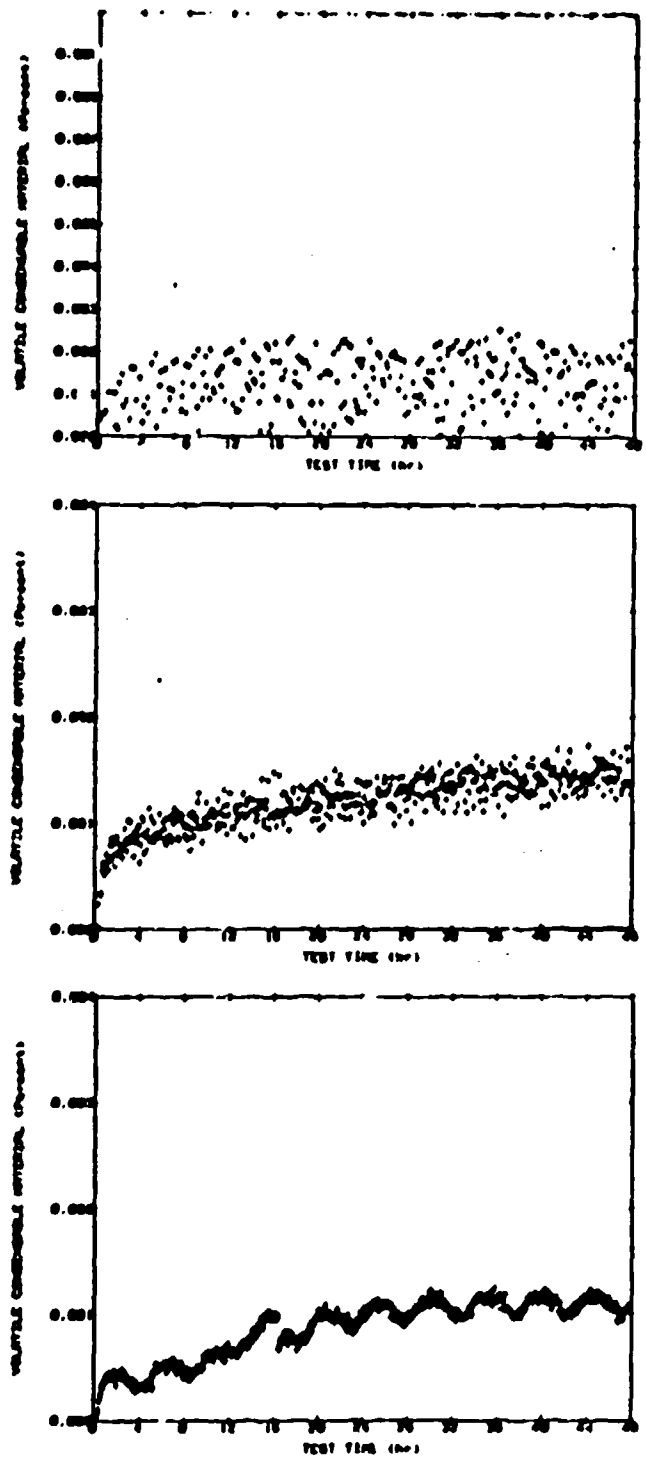


Fig. A-156 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/3501-6 (Source B) Sample at 125°C.

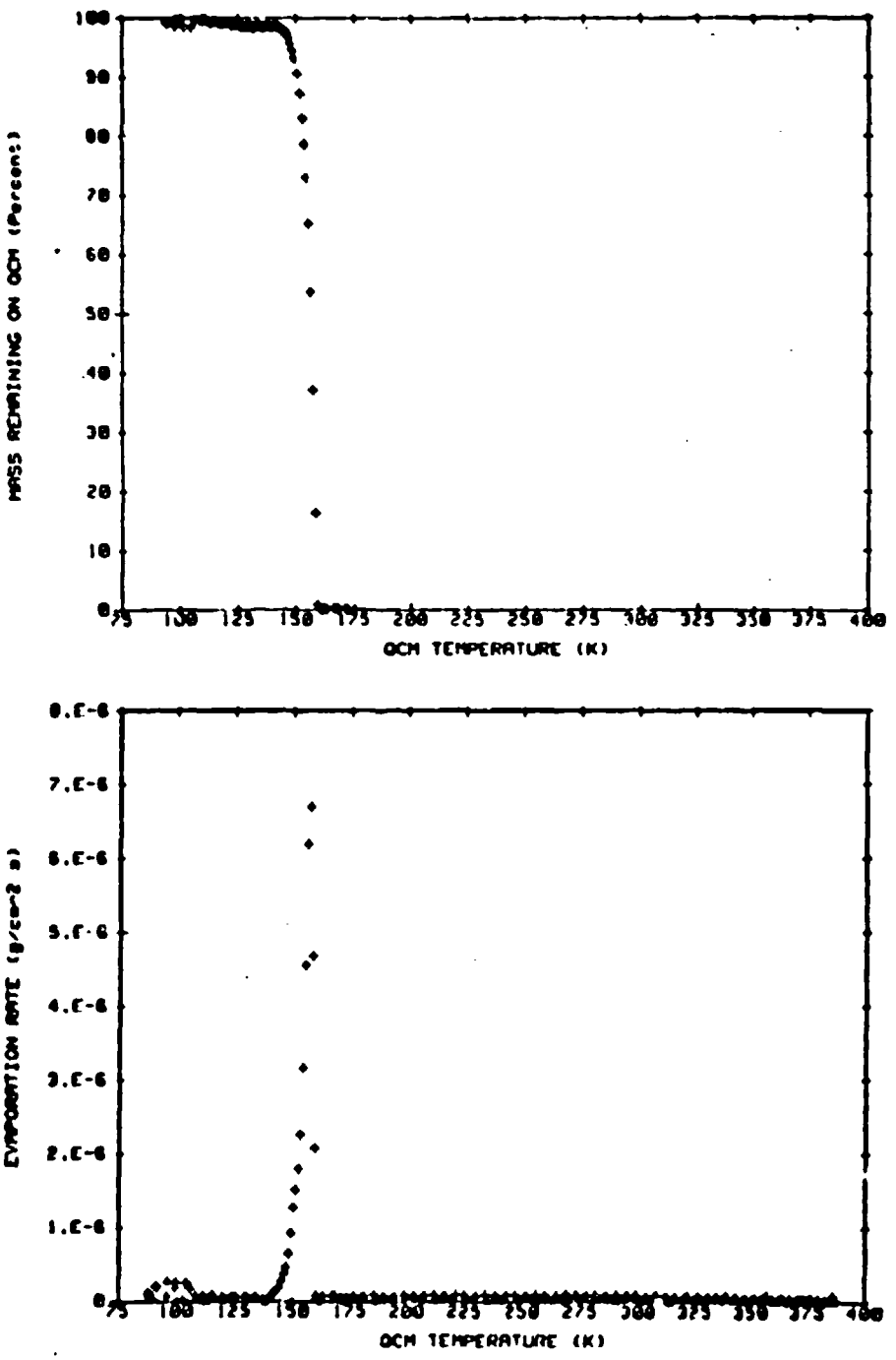


Fig. A-157 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/3501-6 (Source B) Sample at 125°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

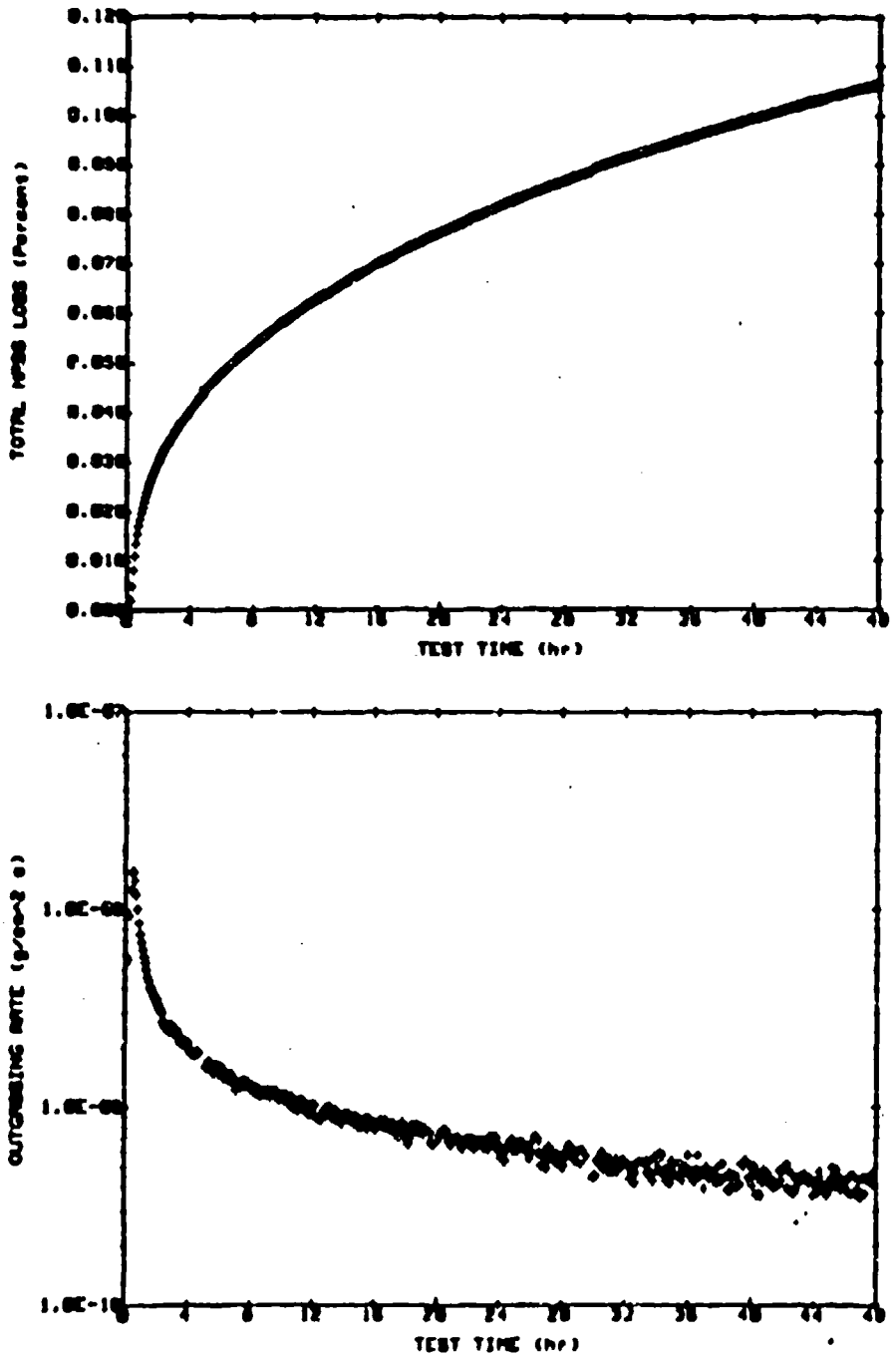


Fig. A-158 Total Mass Loss and Outgassing Rate as Functions of Time for an AS4/3501-6 (Source B) Sample at 75°C.

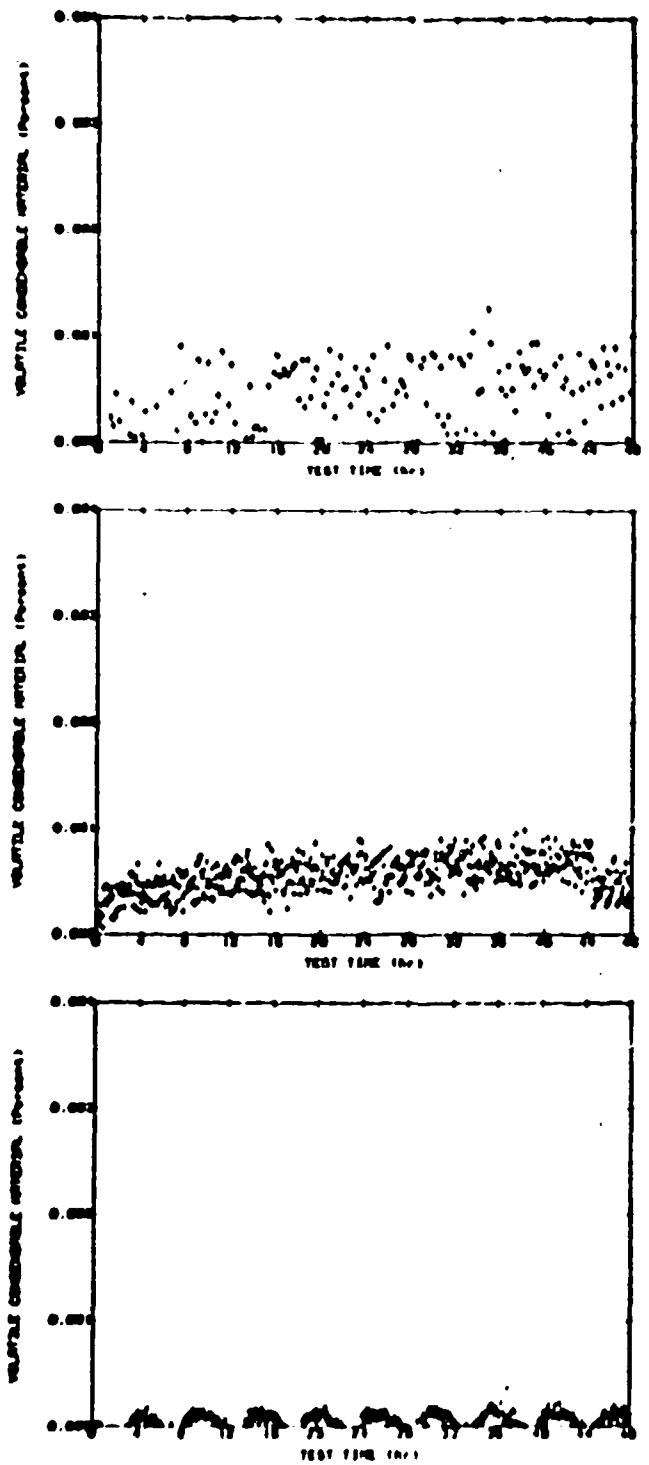


Fig. A-159 Volatile Condensable Material on Collector QCMs at 150 K, 220 K, and 298 K as a Function of Time for an AS4/3501-6 (Source B) Sample at 75°C.

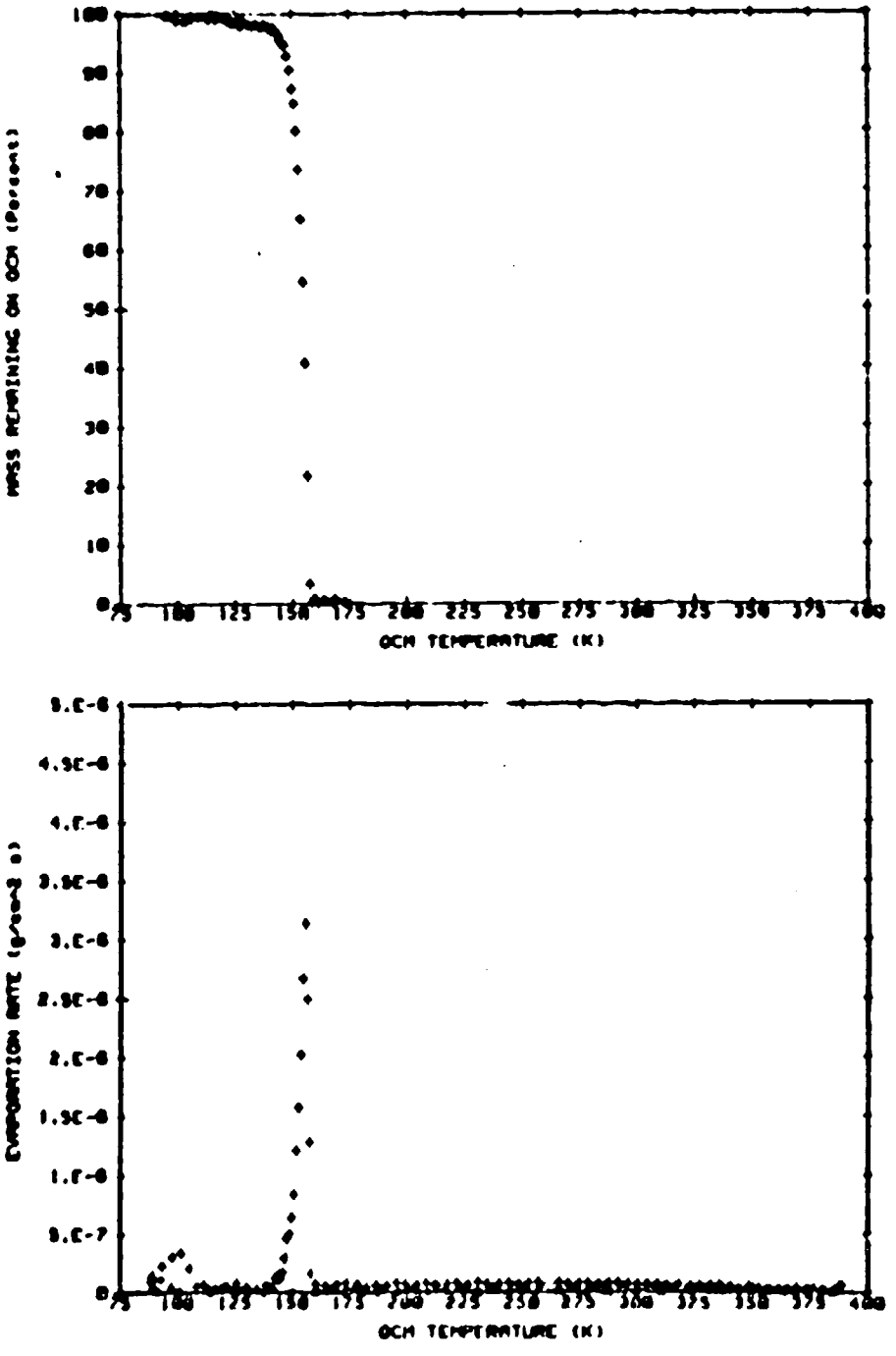


Fig. A-160 QTGA Data for Outgassing Products Collected on the 90 K QCM from an AS4/3501-6 (Source B) Sample at 75°C. Mass of Collected Outgassing Products Remaining on the QCM and Evaporation Rate from the QCM as Functions of Temperature.

Table A-40

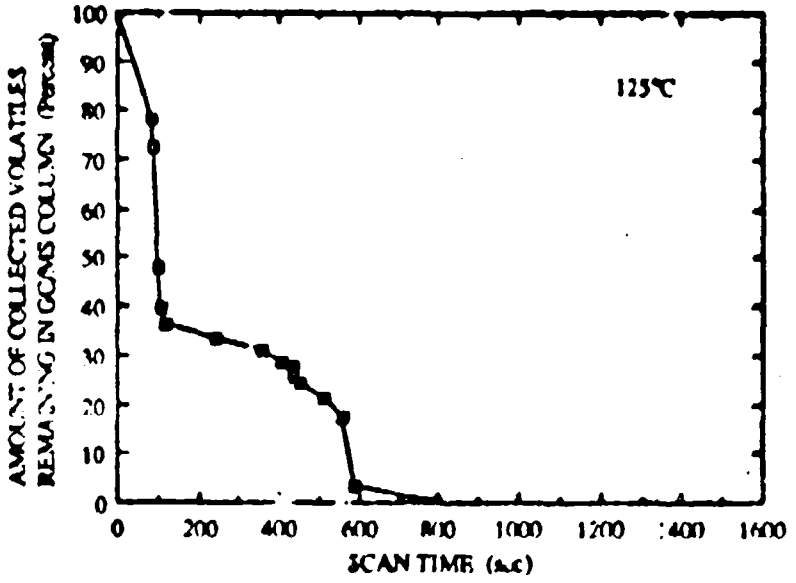
GC/MS Data for AS4/3501-6 (Source B) at 125°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
82	21.65	CO_2 artifact
88	5.69	propane
100	24.66	2-propenal (acrolein)
110	8.62	CH_2Cl_2
121	3.29	2-methyl-2-propenal
243	2.72	toluene artifact
354	2.35	aliphatic hydrocarbon
404	2.70	artifact
434	0.95	artifact
436	1.79	artifact
454	1.51	artifact
514	2.64	
557	3.80	
588	14.18	unspecified aldehyde
791	3.46	butylated hydroxy toluene (B.H.T.)

Table A-41

GC/MS Data for AS4/3501-6 (Source B) at 200°C
Quantitation Report

SCAN TIME (sec)	AMOUNT OF DETECTED SPECIES (percent)	SPECIES IDENTIFICATION
81	2.33	
85	1.28	SO_2
88	3.85	propene
100	55.77	2-propenal (acrolein)
111	7.21	methylene chloride (CH_2Cl_2)
122	4.88	2-methyl 2-propenal
185	0.40	
209	1.30	
225	0.88	
245	4.50	toluene artifact
299	0.83	
348	1.21	
401	3.60	
405	3.00	
653	1.02	1-methyl-3-cyclohexene-1-carboxaldehyde
683	0.96	



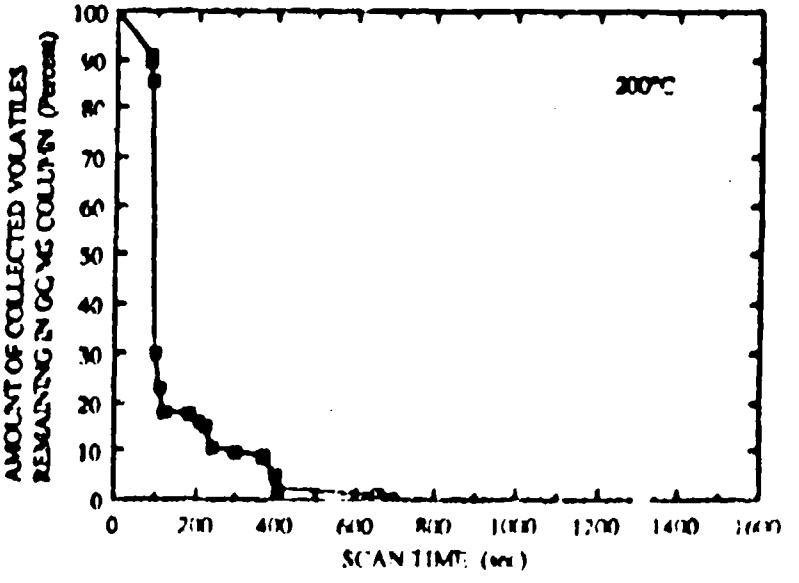


Fig. A 161 Amount of Collected Volatiles Remaining in GC/MS Column from ASA(1941-6 (Source B) at 125°C and 200°C