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INVESTIGATION OF SOURCE OF IRRITANT GAS PRODUCED BY PATRIOT MISSILE SYSTEM AIR CONDITIONERS

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Reported illnesses of persons working in PATRIOT Missile System equipment shelters were investigated and found to have been caused by exposure to Hydrolyzable Fluoride (HF). PATRIOT mil spec 18,000 BTUH Split-Package Air Conditioners (ACs) produced HF when their heater rod Teflon grommets outgassed upon being subjected to temperatures exceeding 400°F. A PATRIOT Support Project Office retrofit program for series '80 and '81 ACs and engineering changes to series '82 and later units eliminated the TFE grommets and solved the HF exposure problem.

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SUMMARY

On 5 April 1982 some Raytheon Corporation employees became ill while testing a PATRIOT Missile System Communications Relay Group (CRG) shelter. Raytheon is the prime contractor for the PATRIOT Missile System.

At the time of the test the shelter's military specification 18,000 BTUH Split-Package Air Conditioner was in its high heat mode of operation. Raytheon suspected this air conditioner to be the source of an irritant gas, and retained Skinner and Sherman Laboratories to sample and analyze the air conditioner's air output. This immediate effort indicated a significant level of acrolein in the air.

Following the Raytheon/Skinner and Sherman tests the VSE Corporation was tasked by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) PATRIOT Support Project Office to perform an investigation of the problem. VSE then retained the services of VERSAR, Incorporated, a Springfield, Virginia chemical analysis company to assist in the investigation. The investigation consisted of laboratory analyses of air samples, equipment inspections and tests, shelter tests, personnel interviews, conferences, and meetings. During the course of the investigation the U.S. Army Environmental Hygiene Agency provided input and guidance.

Extensive gas sampling of PATRIOT air conditioners at VSE during May, June and July of 1982, and VERSAR laboratory analyses of gasses from suspect materials, produced no indication of an irritant being generated in the air conditioner under normal operating conditions. In August 1982 representatives of VSE and VERSAR traveled to Fort Bliss, Texas to perform tests on the exact shelter and air conditioner that were involved in the initial incident at Raytheon facilities in Bedford, Massachusetts. Samples taken during these tests also failed to indicate the presence of an irritant.

In October 1982 VSE testing of an air conditioner with restricted air flow through the evaporator, which simulated a blocked return air filter, indicated much higher component temperatures than previously experienced. These temperatures were particularly high in the vicinity of the right internal condensate drain hose and at the back wall of the evaporator compartment. Scorching of the Tygon drain hose, at temperatures up to 385°F, and hardening of the foam rubber wall insulation, up to 340°F surface temperature, resulted. Simultaneously, fresh air entering the right side of the unit cooled the heater overtemperature switches which are located just above the right fresh air inlet. This prevented the overtemperature switches from sensing the excessive temperatures below them and thus turn off the heaters. Laboratory testing indicated that these elevated temperatures could cause outgassing of plastic materials in the unit and thus produce irritant gases. This finding was accepted initially as the elusive cause of all of the problems. The temporary solution was to post a sign near the return air filters in each shelter warning operators to be sure that the return air openings are never restricted. A proposed longer range fix involved relocating the overtemperature switches to be more responsive to temperatures in the lower evaporator compartment and less affected by the fresh air intake.

Just as this explanation of the irritant problem and proposed solutions were gaining acceptance, three other events took place: (1) On 3 November 1982 an irritant exposure occurred in a similar PATRIOT shelter at Fort Bliss where the return air was known to be unrestricted; (2) A similar irritant exposure occurred at Fort Huachuca, Arizona in an ANTSC 109 System communication shelter using a 36,000 BTUH horizontal compact military air conditioner; (3) VSE testing of heater elements revealed that the "cold area" at the end of the elements could attain temperatures above 1000°F where they are supported by Teflon grommets. Teflon begins to outgas a poisonous fluoride at temperatures around 400°F. The 36,000 BTUH horizontal compact military air conditioner also used Teflon grommets to support similar electric heater elements.

During November and December of 1982, and early January 1983, extensive air conditioner testing was performed, including sampling of the 3 November 1982 incident PATRIOT shelter at Fort Bliss, to determine whether or not fluoride from the Teflon grommets was the long sought-after irritant. All sampling indicated conclusively that fluoride from the hot Teflon heater grommets was the irritant which was plaguing that air conditioner, and others, under normal operating conditions. These tests also indicated that the Teflon outgassing is a time dependent function, with a high initial rate of outgassing which tapers off to an indiscernable rate after a few hours. It was this reducing rate characteristic and the type of contaminant which had eluded earlier discovery by chemical analysis.

Following completion of the investigation several recommendations were made to and accepted by MERADCOM. These recommendations resulted in retrofits and engineering changes which affected 473 '80, '81, '82 and later series PATRIOT Missile System air conditioners. Principal changes included:

1) Retrofit of 234 '80 and'81 series units to replace unfinned heater rod Teflon grommets with a metal retaining bracket, and to relocate overtemperature switches to be more responsive to temperatures near the heater rods.

2) Incorporation of engineering changes to '82 and later series units which replaced unfinned heater rods with finned rods, and relocated the overtemperture switches similar to the changes to the '80 and '81 series units.

Finally, on 29 June 1983 some Raytheon employees complained about a strong and offensive odor being produced by the air conditioner of another shelter undergoing testing. An investigation led to the conclusion that the paint coating on one manufacturers finned heater rod outgassed and produced the odor. It was determined to be nonhazardous, and also to become much weaker until no longer detectable after the heaters had been used for sometime. MERADCOM advised all PATRIOT personnel to have adequate shelter ventilation until the heater paint coating burned off.

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PREFACE

This report was prepared at the request of the PATRIOT Support Project Office (STRBE-FCP), U.S. Army Belvoir Research, Development and Engineering Center (BRDEC), Fort Belvoir, VA 22060-5606. BRDEC was known as the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) during the 5 April 1982 - 9 December 1983 investigative period concerning the subject air conditioners.

Investigations performed and described in this report were accomplished in accordance with Task Order 039 to MERADCOM Contract DAAK70-81-D-0109. This task order required VSE to provide engineering evaluation, documentation and testing service in support of the PATRIOT Program.

The authors of this report wish to acknowledge the very valuable guidance and contributions provided by the following persons:

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References used in this report are attached as appendices A through Q, and are identified in the Table of Contents.

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INVESTIGATION OF SOURCE OF IRRITANT GAS
PRODUCED BY PATRIOT MISSILE SYSTEM AIR CONDITIONERS

1. INTRODUCTION

1.1 Background. On 5 April 1982 several Raytheon Corporation employees became ill while working in a PATRIOT Missile System Communications Relay Group (CRG) Shelter located at Bedford, Massachusetts. The Raytheon Corporation is the prime contractor for the PATRIOT Missile System.

At the time of the onset of the Raytheon employees illness the CRG shelter air conditioner was providing heated air while functioning in the high heat mode of operation. PATRIOT Missile System equipment shelters are air conditioned by a government furnished 18,000 BTUH Split-Package military specification air conditioner.

Suspecting an airborne irritant to have caused their employees' illness, Raytheon retained Skinner and Sherman Laboratories, Inc., of Waltham, Massachusetts, a chemical analysis company, to sample and analyze the conditioned air in the CRG shelter. A sampling and analysis of conditioned air from a similar shelter and a separate air conditioner was also performed by Skinner and Sherman. Results of the Skinner and Sherman analyses showed a significant level of acrolein in the conditioned air provided by the three air conditioners.

Based upon the Skinner and Sherman analysis the VSE Corporation was tasked by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) PATRIOT Support Project Office to perform a thorough investigation of airborne irritants produced by PATRIOT Missile System air conditioners. To this end VSE retained the services of VERSAR, Incorporated, a Springfield, Virginia chemical analysis company.

1.2 Purpose of report. The purpose of this report is to summarize the results of an investigation to determine and correct the condition(s) causing persons to become ill while working in PATRIOT Missile System equipment shelters. This report was requested by the PATRIOT Support Project Office (STRBE-FCP) of the U.S. Army Belvoir Research, Development and Engineering Center (BRDEC), Fort Belvoir, VA 22060-5606. BRDEC was formerly known as MERADCOM.

1.3 Scope of report. This report covers the time period of 5 April 1982 through 9 December 1983. Major study investigation activities to include meetings, tests and findings are included within this report. Conclusions and recommendations of that time period are also a part of the report.

1.4 Reference to related work. Engineering Change Proposal number ECP 82HE0387 was initiated approximately at the beginning of November 1981 to correct an unnecessarily high heater element failure rate. This ECP changed the unfinned heater elements to finned elements, drastically reducing their surface temperature and therefore their resultant radiant heat. At the same

time, the overtemperature switches were relocated to be more responsive to heater and internal temperatures, and less affected by fresh air intake.

2. TEST PROGRAM AND TEST RESULTS

2.1 Preliminary tests. As a result of the irritant problem experienced by employees of the Raytheon Corporation on 5 April 1982, Skinner and Sherman Laboratories, Incorporated, of Waltham, Massachusetts were retained by Raytheon to sample and analyze the air in the subject Communications Relay Group (CRG) shelter and other PATRIOT air conditioners. During the analyses large quantities of constituents were found. The most important was acrolein. Although sampling indicated significant levels of acrolein, the results could not be substantiated or verified. The procedures used included mass spectroscopy and charcoal tube procedures. Results of Skinner and Sherman analyses are presented in Appendix A.

2.2 Expanded tests. To aid in investigation and analyzation of potential irritant sources and hazards associated with the PATRIOT air conditioner, VSE Corporation was tasked by the PATRIOT Support Project Office to complete a thorough study of the problem. To compliment VSE's capability, VERSAR Inc. was requested to provide their in-depth experience and chemical evaluation techniques to the effort.

In order to expedite the study, VERSAR was authorized to complete a series of initial tests. These involved organics and inorganics analysis and were directed toward detection of cyanide, fluoride, and chlorine. Fluoride was the only inorganic found, and the specific concentrations noted led to the conclusion that the air in the vicinity of the test area was being contaminated from another source and did not reflect changes due to the heater. Quantitative findings are presented in Appendix B.

Concurrent with VERSAR's analysis, VSE and VERSAR developed and documented a proposed test plan. The plan included physical inspections, operational checks, various temperature measurements, power consumption data, and a final physical inspection. In addition, VERSAR proposed further analysis of organic and inorganic substances given off during operation of the air conditioner and heater. The sampling methodology and procedures employed by VERSAR corresponded to those recommended by the National Institute for Occupational Safety and Health (NIOSH). Of prime concern were:

1) Chlorine based substances.
2) Fluorine based substances.
3) Acrolein.
4) Other aldehydes.
5) HCN or other cyanogen based.
6) HCL.
7) Paint, adhesive components.
8) Plastic, insulation, elastomer components.

Physical inspections of subject air conditoners included:

1) Insulation.
2) Wiring near heater elements.
3) Heater elements.
4) Heater grommets.
5) Any debris evident in the compartment.
6) All other items, particularly any non-metal parts.

The proposed test plans as submitted to the U.S. Army Mobility Equipment Research and Development Command are presented in Appendix C.

2.3 Coordination meeting at VSE Corporation. During the same time frame several conversations between representatives of MERADCOM, the PATRIOT Missile Systems Office, the Army Environmental Hygiene Agency (AEHA), and Raytheon were effected. As a result, it was agreed that the MERADCOM PATRIOT Support Project Office would promulgate a draft test plan which would be thoroughly reviewed for its adequacy for identifying the content of gases present in the air flow from PATRIOT air conditioners when operating in the heat mode. To effect this procedure, a meeting of cognizant representatives was scheduled to be held at VSE on 8 June 1982.

Minutes of the meeting are in Appendix D. Much of the discussion was directed towards results of outgassing tests conducted by Raytheon/Skinner and Sherman and MERADCOM (VSE/VERSAR) on the PATRIOT 18,000 BTUH air conditioner and AEHA on the Army military specification 18,000 BTUH air conditioner. Interestingly, the data concerning content of the gases present in the air flow of the air conditoners was entirely different. This prompted the PATRIOT Office to request MERADCOM to take the lead in finalizing a test plan and initiating testing of new production air conditioners.

2.4 Coordinated test plan development for follow-on gassing tests. The remainder of the meeting was spent finalizing the proposed draft test plan. It was agreed that the plan would effectively incorporate procedures to verify existence of the large quantities of constituents found in the Skinner and Sherman tests. The agreed upon plan required sampling of four new air conditioners for a period of three hours, with three one-hour samples taken during that time. It included the following parameters:

CONSTITUENTS	SAMPLING METHOD	ANALYSIS
Acrolein	Tenax (cooled)	HRGC/MS
Aromatics	Tenax (cooled)	HRGC/MS
Phalates-Universal (others)	Charcoal	HRGC/MS
Formaldehide	Std-NIOSH-bislfides	Standard
Hydrogen Cyanide	Std-NIOSH-OLIN NAOH	Standard

VERSAR was tasked with drafting the sampling plan, coordinating it with AEHA and Raytheon/Skinner and Sherman, and delivering it to MERADCOM.

On 18 June 1982 the finalized test plan was distributed with intention to begin VSE/VERSAR preliminary validation studies during the week of 21 June 1982. Testing of the air conditioners was to begin the week of 28 June 1982 with a Draft Final Report due NLT 28 July 1982. A copy of the finalized test plan is presented in Appendix E.

2.5 Coordinated tests

2.5.1 Four air conditioners - VSE Corporation. Testing of the four air conditioners began on 30 June 1982 and was completed on 2 July 1982. Tests were conducted at VSE's facility in Alexandria, Virginia. The effort was performed with each air conditioner/heater operating continuously during sampling in the high heat mode. Sampling techniques used would allow detection of the target parameters acrolein, aromatics, a broad range of organic compounds, formaldehyde, and hydrogen cyanide.

Actual testing of the air conditioners was conducted by VERSAR personnel. Three one-hour tests were conducted on each unit. During sampling activities, data concerning ambient, unit intake, and unit exhaust temperatures were recorded at 15-minute intervals. Also recorded were the voltage, wattage, Hobbs Hours Meter recordings, and static pressure created by the unit in operation.

Sample collection equipment, sampling methods and areas, a summary of total samples collected, and analysis procedures and results are presented in Appendix F, Section 2.0 and 3.6.

2.5.2 Fifth air conditioner - VSE Corporation. On 15 July 1982 a fifth air conditioner (unit SN 801160) was subjected to the same methods applied to the intensive analysis of the four new units tested during the 30 June - 2 July 1982 time period. This unit was the one tested previously by Skinner and Sherman for Raytheon; however, MERADCOM decided it would be beneficial to test the unit using the same sampling and analysis techniques applied to the other units. Procedures employed for testing the unit and recorded results are presented in Appendix G, Sections 2.0 through 3.2.

2.5.3 Test sample analyses - all five air conditioners. Following the test plan measurements, triplicate samples were taken during the first hour of operation of each unit. Samples were sent to AEHA, Skinner and Sherman, and VERSAR for analysis. Upon completion of preliminary analyses virtually no differences existed between the findings although the Skinner and Sherman report listed acrolein found in the first hour of one unit (SN 801193). Briefly, the findings indicated:

1) With the exception of the one unit, acrolein was not produced by or from any units tested.

2) Benzene and toluene were observed at extremely low levels. No other aromatic organic compounds were observed. Thus, aromatic organic compounds were not produced by or from any of the four new units tested.

3) With the exception of the laboratory/field contaminations, no organics were found in discharged air at any substantial levels. Levels of trichloroetheylene were always slightly higher in exhaust than intake in the four new units.

4) Formaldehyde was not produced by or from any of the four new units tested.

5) Hydrogen cyanide was not produced by or from any of the four new units tested.

The fifth unit, tested at the request of MERADCOM, continued to show a real contamination of intake air by toluene. As with the other units the exhaust air toluene was somewhat higher, thus indicating possible generation by the unit but not at a level which would cause probable concern. Aside from this, results of the other target parameters were akin to the four new units; i.e., non-found.

The report providing in depth discussion of analytical methods, findings and conclusions is presented in Appendix H. (Note: Pertinent parts extracted from VERSAR/Skinner and Sherman/AEHA, and put into Appendix H).

2.5.4 Interim conclusion. Based on the results, the conclusion was drawn that none of the target parameters set forth in the test plan were present in the sampling configurations tested. This prompted VERSAR to recommend a two-fold approach to find and isolate possible chemical irritants:

1) One previously tested unit should be moved into a controlled chemical environment and disassembled by a knowledgeable investigative team. Selected components/materials should then be singled out for thermal irritant generation potential. A prime target for this was the acrylonitrile-vinyl chloride black foam.

2) The unit should be tested in an enclosure typical of the type in use when Raytheon personnel became ill. The test location should be free of environmental contaminents, have a relatively low moisture content, and should have ambient air temperatures requiring use of the heater. A meeting to review the sampling results and establish future efforts was set for 21 July 1982.

2.6 Test meeting at VSE Corporation. The primary focus of the 21 July 1982 meeting was to discuss results of irritant testing of the four new production air conditioners and the single air conditioner which was in use at the time the Raytheon personnel became ill and which had been tested by Skinner and Sherman in April 1982.

Explanations of the precautions taken to assure that gas samples taken were truly representative of the content of the air as it entered and exited the subject air conditoners were offered. In addition, discussion of the coordinated efforts required to take and analyze the samples was initiated.

It was generally agreed that the results were valid, and that they presented no indication of the target parameters identified in the test plan. Minutes of the 21 July 1982 meeting are presented in Appendix I.

2.7 Improved coordinated test plan development. Failure of the samples to show any significant amounts of toxicity resulted in the development of new tests to resolve the potential problem of irritant gases. Results of the 21 July 1982 meeting identified two major categories of new tests; those involved with the PATRIOT air conditioner and those involved with the CRG shelter. Essentially, these tests included the following efforts and were presented as the Consensus Recommendations for PATRIOT Heater/Air Conditioner Developed at the 21 July 1982 Review Meeting.

1) Disassembly of unit by investigative team - develop and work detailed plan (Include MERADCOM, AEHA, Raytheon, Skinner & Sherman, VSE and VERSAR).

a) Verify adherance to specifications (mechanical, electrical and material).

b) Find specific materials that could add irritants to discharge air.

c) Study temperature ranges - Normal high heat mode.
- Safety switch high heat mode.
- 50% discharge air, normal high heat mode.

d) Test suspect materials by "headspace" or equivalent GC/MS methods (temperature range to be determined).

e) Measure air flow characteristics.

f) Do worst case analysis of materials - i.e., destroy and evaluate thermal degradation products.

2) Review manufacturing process of acrylonitrile-vinyl chloride black foam.

a) General review of manufacture of foam.

b) Determine possibility of acrolein carry over (Raytheon hypothesis).

c) Investigate hardware degreasing as potential sources of acrolein (VSE hypothesis).

3) Test entire "original incident" CRG enclosure.

a) Develop detailed plan (MERADCOM, AEHA, Raytheon, Skinner and Sherman, VSE and VERSAR).

b) Improve Sampling and Analysis techniques as indicated by reports.

c) Control input air (major concern is dryness).

4) Validate standard NIOSH method 211 for Acrolein.

5) Possible expansion of target parameters (i.e., amines, polyamines, carbon dioxide, carbon monoxide).

At a minimum it generally was agreed that upon completion of these recommendations it would be possible to use the PATRIOT heater/air conditioners in the high heat mode or, failing that, at least know the corrective actions which would be required in order to use the units safely.

As a direct result of the meeting and development of the Consensus Recommendations VCRSAR developed a test plan which focused on efforts to comprehensively address each of the major areas. It was separated into two distinct tasks with Task 1 covering recommendation nos. 1 and 2 and Task 2 covering the remaining recommendations.

Task 1 primarily focused on investigation of potential production of chemical irritants through material and mechanical evaluation; whereas, Task 2 was a sampling, analysis and method validation plan of the entire CRG enclosure from which the first personnel complaints originated. A more detailed discussion of the plan is presented in Appendix J.

2.8 Improved coordinated tests

2.8.1 VSE test. Having reached agreement on the procedures to be used, the investigative team met at VSE on 9 August 1982 to inspect one of the PATRIOT air conditioners, thus initiating Task 1 as identified above. The team inspected two heater/air conditioner units and noted design and manufacturing problems. The team also identified materials in the units which could conceivably release irritants or toxic materials when heated. One of the units inspected was missing a piece of reflective aluminum intended to protect the insulating foam from high heat. The team concurred that that was a serious omission and that the manufacturer's quality control procedures should be tightened to prevent further omissions.

The temperatures attained in various areas of the heater box were measured under a variety of condtions. The maximum temperature measured on any surface in the unit was 246°F.

A number of materials used in the units were heated and tested for the presence of outgassing products. At normal operating temperatures, only two materials released any compounds of concern. The adhesive released toluene, and the insulating foam released carbonyl sulfide, carbon disulfide and benzene. The quantities of products released were determined to be probably nonhazardous at normal operating temperatures.

Two materials, tubing and foam, were tested for outgassing products at temperatures significantly higher than the worst case temperature agreed to by the investigative team (i.e., 340°F rather than 280°F). These tests were undertaken to simulate possible outgassing effects when major overheating

occurred as was apparent in the first units tested at Fort Bliss, Texas. It was determined that the quantities of compounds released from the foam at 340°F could pose a hazard to personnel in the CRG shelter.

With respect to recommendations nos. 3; 4 and 5 a final list of target parameters for sampling at Ft. Bliss was finalized and included:

1) Acrolein.
2) Formaldehyde.
3) Cyanide.
4) Amines.
5) Hydrogen Chloride.
6) Carbon Dioxide.
7) Carbon Monoxide.
8) Semi-volatile organics and aromatics collected on charcoal.
9) Volatile organics and aromatics collected on Porapak N.

The results of analysis and sampling showed that no acrolein, cyanide or hydrogen chloride were present in the air in the CRG shelter. All samples were below the detection limit of the methods. Traces of formaldehyde were found both inside and outside the CRG shelter, but the levels found were so low that they were not considered a hazard. An unknown compound which interfered with the analysis for amines was present in the ambient air at Fort Bliss. Therefore, no results were obtained for amines. Carbon dioxide and carbon monoxide levels inside the CRG shelter were not significantly different from the levels found in the ambient air outside the shelter. The charcoal tube test for semi-volatile organics and aromatics did not detect any contaminants at hazardous levels. Trace quantities of volatile organic and aromatic compounds were found in the Proapak N sampling tubes, but below levels which were thought to be hazardous.

For a comprehensive discussion of the investigative procedures sampling methods, analyses and findings of Task 1 and 2 testing, refer to Appendix J.

2.8.2 Interim conclusion. Interestingly, the Task 1 and 2 tests proved, for all practical purposes, to be inconclusive in their findings. As a result, the conclusion at this point was that there was nothing which would prevent using PATRIOT air conditioners in the high heat mode if operated in accordance with prescribed procedures.

2.8.3 Fort Bliss test. The PATRIOT air conditioner involved in the irritant emissions incident (serial number 801198) was shipped from VSE to Fort Bliss in El Paso, Texas. This was to facilitate testing of two air conditioners while mounted on a shelter during the period 23-26 August 1982. Air Conditioner S/N 81013, mounted on a CRG shelter, was inspected through the fresh air opening located on the curb side of the unit. This inspection was performed by VSE personnel. Several of the Teflon bushings which separate the heater elements from their mounting bracket had melted and were found in the bottom of the evaporator section. The right hand drain hose located below the heater elements had melted to the extent that it was badly misshapen and

flattened on the bottom where it rested on the bottom of the unit. In addition, the hose top was scorched and had a hole melted or burned into it. The initial indication was that the heater area had been extremely hot. The only reasonable explanation for this was that the return air intake became severely restricted as a result of a dirty air filter or a piece of newspaper or packing paper being sucked against the return air opening. The return air opening is located at floor level in the shelter. It was also apparent that some of the heater elements had burned out when the air conditioner was replaced by air conditioner S/N 801198. This new unit had better heating capacity than its counterpart. Air conditioner S/N 801198 was fully inspected at VSE's facility in Alexandria, VA during the week of 9 August 1982. A brief visual inspection at Fort Bliss revealed no apparent problems.

The exhaust air from both PATRIOT air conditioners were sampled for the following inorganic and organic compounds:

1) Acrolein.
2) Formaldehyde.
3) Cyanide.
4) Amines.
5) Hydrogen Chloride.
6) Carbon Dioxide.
7) Carbon Monoxide.
8) Semi-volatile organics and aromatics collected on charcoal.
9) Volatile organics and aromatics collected on Porapak N.

The samples were collected inside the shelter using techniques which would allow detection of the target parameters. Sample sets were also collected outside the shelter to establish baseline ambient conditions for comparison. Two 2-hour sample sets were collected with S/N 801198 unit operating with the heater off, in the air conditioning mode. This was done to verify that none of the target parameters were present inside the CRG shelter when the Heater/Air Conditioner was operating in other than the high heat mode.

In subsequent sampling, both air conditioners (S/N 801198, 81013) were operated with the main switch on high heat and the thermostat set at the highest heat setting. The over-temperature switch and thermostat were not bypassed in this sampling because: 1) the ambients at Ft. Bliss (65-85°F) were not characteristic of temperatures encountered during winter months when the heaters are actually used, and 2) there was a desire to maintain temperatures in the CRG which would facilitate testing procedures and personnel comfort. As a minimum, at least 50% of the heater rods were expected to be on under any condition in the high heat mode.

The results of the samplings showed that no acrolein, cyanide or hydrogen chloride was present in the air in the CRG shelter. All samples were below the detection limit of the sampling methods. Traces of formaldehyde were found both inside and outside the CRG shelter, but the levels found were so low that they did not constitute any hazard. An unknown compound which interfered with the analysis for amines was present in the ambient air at Ft.

Bliss. Carbon dioxide and carbon monoxide levels inside the CRG shelter were not significantly different from the levels found in the ambient air outside the shelter. The charcoal tube test for semi-volatile organics and aromatics did not detect any contaminants at hazardous levels. These quantities of volatile organic and aromatic compounds were found in the Porapak N sampling tubes, but were well below levels considered to be hazardous.

Post-test inspections of both air conditioners revealed no significant changes to either unit. For further detailed information on data collection during these tests, refer to Appendix K.

2.8.4 VSE test. After the inspection and subsequent testing of air conditioner S/N 81013, the unit was shipped back to VSE for further investigation. The overtemperature switches in the unit were tested to establish that they opened at reasonable settings to protect the system.

The CRG shelter, at the time of the incident at the Raytheon plant, was located outdoors in very cold weather with the air conditioner operating in the high heat mode. The fresh air intake duct is mounted on the right (curb) side of the air conditioner on this shelter (refer to Fig. 2, Appendix L). With this configuration, if the return air is severly restricted, a large quantity of cold, fresh air is introduced into the air conditioner, bathing the overtemperature switches in cold air and preventing them from sensing the true temperature in the inner evaporator compartment. Therefore, they will not turn the heaters off and cannot protect the heaters or evaporator compartment materials under this abnormal operating condition.

A test was run at VSE on 8 October 1982 on air conditioner S/N 801185 which was identical to S/N 81013. The test objectives were to determine critical internal air conditioner unit temperatures with the return air inlet block, and to investigate 'quick fix' possibilities to minimize the hazards under adverse operating conditions. Dry ice was maintained in a fabricated cooling box at the fresh air makeup to keep the intake air cool enough so that over-temperature switches did not trip during testing. Figure 3 of Appendix L illustrates the completed test set-up. Temperatures were independently monitored by thermocouples placed throughout the unit.

The first test was run in the low heat mode, with the fresh air intake duct on the right (curb side) of the air conditioner unit and the return air duct blocked various amounts from wide open to completely closed. The condensate drain tube temperature reached 322°F. The same test under the high heating mode yielded a maximum drain tube temperature of 386°F before the heaters were manually turned off because of a burned rubber odor coming from the unit. The test data indicated that unless the return air duct opening is restricted more than 90%, no excessive temperatures are evident in the evaporator compartment. Tests indicated a repeatable drain tube temperature of approximately 385°F with the return air completely restricted, and the fresh air intake duct on the right side. That was a direct result of the observation, during operation, that the overtemperature switches generally would not trip with outside air temperatures below about 68°F. The Tygon

tubing used for the condensate drain had a normal maximum working temperature of approximately 180°F. Under the same conditions, but with the fresh air intake on the left side, the overtemperature switches repeatedly tripped, limiting the right drain tube to about 307°F. With the exception of the heater elements that drain tube, with the fresh air intake in either configuration, appeared to be the hottest component within the evaporator compartment under very restricted return air conditions. In addition, the lower right rear wall reflective metal reached about 340°F under the same condition. This metal was cemented directly to a synthetic foam insulation material, which could also be adversely affected by temperatures in that high temperature range.

Disassembly and inspection of the unit following these tests revealed that the right side plastic drain tube had melted and burned exactly like the one found when S/N 81013 was inspected 23 August 82 at Fort Bliss.

A couple of "quick fixes" were attempted to keep the outside air from affecting the over-temperature switches and to reduce temperatures at or near the right plastic drain hose. One quick fix was a metal baffle to shield the right drain tube from heat radiation which originated at the heater elements, and which was reflected off of the reflective metal which protected the foam rubber wall insulation. Another test was run in the high heat mode with the return air intake closed. The results showed that the installation of a baffle reduced the drain tube temperature to a high of about 270°F with the fresh air intake on the right or curb side of the unit. With the intake on the left side, the high temperature of the tube was about 307°F.

The other quick fix tested was a small air deflector, in the right side fresh air opening, to deflect incoming air away from the overtemperature switches and downward toward the right drain tube (Refer to Fig. 4, Appendix L). The diverter, during test, deflected the cold air away from the over-temperature switches, and kept the right drain tube temperature from exceeding 160°F. However, the diverter was ineffective with air conditioner units configured with the fresh air intake duct on the left side. The drain hose attained about 307°F in that configuration before the overtemperature switches reduced the heat.

Therefore, it was apparent from the test results that neither "quick fix" offered adequate protection to internal materials of the evaporator section in both configuration of air conditioners. Of note at this time in the chronology of events is that Engineering Change Proposal number ECP 82HE0387 had been initiated during late October or early November 1981. This ECP was developed to correct an unnecessarily high heater element failure rate. It also had the ability to completely protect the unit, regardless of external blockage of the return air duct, by relocating the overtemperature switches to be more responsive to heater and internal temperatures, and less affected by the air supplied through the fresh air intake.

After the previously described testing at VSE 8-18 October 1982, the scenario of a return air duct completely blocked was agreed to as the cause of the irritant release incident in Massachusetts on 5 April 1982 (Reference Appendix M). Temperatures within the evaporator assembly were suspected of reaching values above the normal working temperatures of several materials located in that compartment when the return air duct is blocked in the high heat mode.

Outgassing experiments were performed on several suspect materials within the air conditioner, as was previously reported. The temperature at which these materials were heated to (280°F) was determined by the measurement of normal operating temperatures within the evaporator section under a high heat mode. An additional margin of 15% was added to arrive at 280°F. After the 23 August 1983 inspection of the previously overheated air conditioner at Fort Bliss, it was decided that the insulating foam and Tygon tubing be investigated at the elevated temperature of 340°F, which would have been typical under the over-temperature situation with the return air duct blocked. Still no significant out-gassing was detected at those temperatures (Reference Appendix M). The knowledge of that fact and the occurrence of several events around that point in time rekindled the exhaustive search for the cause of the irritant.

2.9 Second and third irritant exposure incidents. On 27 October 1982 another irritant exposure occurred at Fort Huachuca, Arizona in an ANTSC 109 System communication shelter using a 36,000 BTUH military unit. On 3 November 1982 a third irritant exposure occurred in a shelter similar to the PATRIOT shelter at Fort Bliss, in which VSE had done their sampling. However, the return air duct was reported to be unobstructed. It was reported that seven individuals had been exposed to some form of chemical irritation over a period of two weeks. The chemical exposures happened when the heaters were used, and significant damage to the Teflon grommets of both heaters in the shelter was observed. Coughing and dryness of throat were the most commonly reported effects first noted. Other symptoms of sleeplessness, severe headaches, and chest pains were also reported (see Appendix N).

Because the irritant source was still unconfirmed as a result of the aforementioned occurences, a new set of hypotheses had to be derived. There were general suspicions that the Teflon grommets, which were in direct contact with the heating rods, were not limited to 280°F under normal operating conditions. Also, the surface temperature of the rods at the alleged "cold" end had never been measured (see Appendix N).

An investigation was planned to determine the surface temperature of these heater rods near their cold ends. Also, surface tempertures on the cold ends of finned heating rods were looked at because ECP 82HE0387 would soon direct a change of the unfinned rod elements to the finned version to reduce heater failure.

2.10 Teflon (TFE) grommet tests

2.10.1 VSE test. Testing commenced on 5 November 1982 at VSE. Section drawings in Appendix M show that the electric wire element inside the finned heater stops considerably farther, approximately 2 inches, from the cold end of the rod as compared to the 0.63 inches of the unfinned heater. The results of temperature measurements taken during those tests showed that, at the Teflon grommet interface (.75 in from the cold end of the rod), the temperatures varied from 1228°F to 1000°F. At that same critical area, .75 inches from the cold end, for the finned heating rod no temperature greater than 400°F was recorded. Test results showed that the finned elements conducted heat away from the electrical wire element more readily than the unfinned rods, and therefore would significantly increase heater life. The lower radiant energy would result in lower temperatures in other materials, including the plastic and rubber materials within the evaporator compartment. The unfinned heater rod cold end surface temperature was found to greatly exceed the normal working temperature of Teflon by at least 600°F.

2.10.2 VERSAR tests. Concurrent with the testing at VSE, MERADCOM, on 5 November 1982, contacted VERSAR to ask that an appropriate investigation be undertaken. An industrial hygiene investigative team was dispatched to Fort Bliss. This team interviewed six of the seven individuals who had been exposed to some form of chemical irritation over a period of two weeks at Fort Bliss (See Appendix N). Based on their observations and discussions with AEHA, it was determined that the air would be monitored for hydrolyzable fluoride, chloride, sulfur dioxide, acrolein, and several other organics. The air conditioner units involved in the incident on 23 November 1982 at Fort Bliss would be tested at low heat and high heat, with and without grommets. The following sampling scheme was conducted with the Teflon (TFE) grommets in position on both heater units and operated as described below:

1) 1/2 hr sampling run with both units on high heat.
2) 1 hr sampling run with both units on high heat.
3) 1 hr sampling run with both units on low heat.
4) 1 hr sampling run outside shelter - referred to make-up air.

All TFE grommets were removed from both heaters and were submitted to VERSAR's laboratory for gravimetric analysis after the above sampling runs. A final sampling run, without the TFE grommets in position, was conducted under a one-hour sampling run with both units on high heat

An analysis of the sampling revealed the highest flouride levels occurred during the first 30 minutes of heating in the high heat mode (see Appendix N). Fluoride was not detectable in the air samples after the TFE grommets were removed. It was not detectable in the ambient air. There was no evidence of elevated sulfur dioxide, acrolein, volatile or semi-volatile organic compounds.

Each grommet removed from the air conditioners during the sampling was weighed, and the results compared to a new set of grommets obtained from the manufacturer of the units. The average weight of the used grommets was less

than the new. Since TFE is 76% fluorine, an estimate of fluorine lost from the grommets in both air conditioner units was 3.61 grams (see Appendix N). There were no officially accepted Threshold Limit Values (TLVs) for the decomposition products of TFE.

Based on the weight loss and obvious damage to TFE grommets in the units involved in the 3 November 1982 incident at Fort Bliss, MERADCOM decided to remove all TFE grommets from similar units. All enclosures in use at Fort Bliss and White Sands, New Mexico were subjected to the same test series as previously described. Field sampling was conducted on 22 November 1982 at Fort Bliss and on 23 November 1982 at White Sands Missile Range. Seven shelters were sampled while the heater/air conditioners on each shelter were operated in the high heat mode. During all tests all TFE grommets were removed from the heater rods. No fluoride was detected in the ambient samples, and little or no hydrolyzable fluoride was found in the seven shelters. No significant amounts of chloride, acrolein, or semi-volatile organic compounds were found in the samples taken.

In all the grommets that were removed from the heaters at Fort Bliss, a weight loss was observed in every set. A testing arrangement was set up at VERSAR to determine the major products of the decomposition of TFE grommets in contact with a heater rod from a PATRIOT Heater/Air Conditioner (see Appendix N). A grommet was placed 0.3 cm and 1.5 cm from the end of a single heating rod. It was bathed in a stream of purified air, which facilitated collection of the gases resulting from TFE decomposition.

The data showed that the amount of fluoride lost, estimated through weight measure, will consistently show up as hydrolyzable fluoride. Visual and quantitative results showed that most of the grommet in direct contact with the rod was vaporized within the first 30 minutes of the test.

No acrolein was detected during these experiments. The decomposing TFE grommets did not produce measureable amounts of acrolein. A fairly large amount of semi-volatile organic compounds were produced during the decomposition of TFE. Given the large air dilution that occurs when the PATRIOT Heater/Air Conditioners are running, the results would probably be below the detection limit in actual use. In contrast to this, the results for hydrolyzable fluoride were 2 million times greater than the detection limit (see Appendix M). A coating of fine white powder was observed on the inside of the test equipment. This vaporized TFE particulate matter accounts for the remainder of the grommet weight loss during decomposition.

Additional field sampling tests were conducted at VSE on 8 January 1983. A PATRIOT heater/air conditioner was outfitted with new TFE grommets and then operated in a "controlled" high heat mode. The results of that sampling demonstrated that fluoride concentration reached a maximum sometime after 10 to 20 minutes of operation. The concentration slowly fell off for the rest of the experiment. The grommets were then weighed after sampling. It was found that between 19.2% to 26.0% of the fluoride lost appeared as hydrolyzable fluoride.

On 20 January 1983, further testing was performed in an ICC shelter at Fort Bliss. The heater/air conditioner units were run with new grommets in them. Every sample collected contained hydrolyzable fluoride. The maximum concentration of hydrolyzable fluoride was always found during the first thirty minutes of operation. The maximum fluoride levels for the experiment ranged from 48 ug/m^3 to 448 ug/m^3. Other publications indicate that decomposing TFE may cause symptoms of Polymer Fume Fever when the concentrations of hydrolyzable fluoride are approximately 50 ug/m^3. This indicates that the hydrolyzable fluoride levels found in the ICC shelter were unacceptably high (Refer to Appendix N).

The results collected also showed that the conditions with the highest return air flow and the greatest percentage of return air also had the least weight loss and the lowest fluoride concentration. The return air in the PATRIOT Heater/Air Conditioners entered the units directly in front of the heating rods. As the return air flow increased, the heating rods were cooled and the TFE grommets were exposed to lower temperatures. When the return air flow decreased, the heating rods got hotter, and the TFE grommets were exposed to higher temperatures. The make-up air did not appear to affect the fluoride levels because it entered the units very close to the intake of the squirrel cage fans. The air probably did not pass over the heater rods, thus it had no effect on the temperatures that the TFE grommets are exposed to. The highest fluoride concentrations were found when both heater/air conditoners were running, and when the shelter cooling fans were on. This increased the total air flow through the shelter, and increased the dilution of the TFE decomposition products. However, it also decreased the return air flow, and therefore increased the amount of TFE decomposition, or weight loss, and the concentration of hydrolyzable fluoride. The cooling fans had the same effect as blocking the return air. The exit air temperature was raised and the TFE grommets underwent a more rapid decomposition.

3. CONCLUSIONS

Conclusions reached by this investigation were:

1) Persons who became ill while working in PATRIOT Missile System equipment shelters were exposed to the decomposition products of Teflon (TFE) heater rod grommets installed in shelter air conditioners.

2) Decomposition of TFE grommets occured when shelter air conditioners were being operated in their high heat mode.

3) Decomposing TFE grommets produced unacceptable levels of decomposition products, many of which were known to be of a hazardous nature. Of these, hydrolyzable fluoride was released in substantial quantities, and most likely produced the symptoms described by those persons who became ill (see Appendix M).

4) The amount of decomposition of TFE grommets was inversely proportional to the return air flow of the air conditioners.

5) Poor manufacturer's quality assurance allowed one air conditioner to be delivered without a piece of reflective aluminum protective material.

4. RECOMMENDATIONS

Recommendations made to prevent further outgassing of heater rod Teflon (TFE) grommets were:

1) Remove heater rod TFE grommets from all shelter air conditioners.

2) Replace TFE grommets with acceptable high-heat resistant materials.

3) Relocate the overtemperature switches.

4) Reform manufacturer's quality assurance procedures.

5. FOLLOW-ON ACTIVITY

5.1 PATRIOT air conditioner modifications

5.1.1 Engineering Change Proposal (ECP). ECP 82HE0387, discussed in paragraph 1.4, included two very important modifications to the PATRIOT air conditioner. These modifications were:

1) Change unfinned heater rods to finned heater rods.

2) Relocate heater overtemperature switches to make them less responsive to fresh air intake and more responsive to unit internal temperatures.

This ECP was applied to all new production air conditioners with 82--- and later serial numbers. The change to finned heater rods eliminated the earlier design which used TFE grommets with unfinned heater rods (see Appendix O).

5.1.2 VSE quick-fix. MERADCOM requested VSE to develop a quick-fix to remove TFE grommets from 80--- and 81--- serialed PATRIOT air conditioners. The unfinned heater rods were retained, but a new metal adapter was used to replace the TFE grommets (see Appendix P).

5.1.3 Modification status. According to MERADCOM records 473 PATRIOT air conditioners were produced. Of these, 234 with 80--- and 81--- serial numbers underwent the quick-fix modification, and the remainder were produced according to ECP 82HE0387. The air conditioner Technical Data Package (TDP) was updated, to include all known ECPs, by 1 January 1984.

5.2 Fourth irritant exposure investigation. On 29 June 1983 the PATRIOT air conditioners were operating in the high heat mode, under test condition, at the Raytheon, Andover, Massachusetts facility. Employees testing an equipment shelter reported that these two air conditioners produced objectionable odors. Both air conditioners had 82--- serial numbers and were therefore

produced with all ECP 82HE0387 changes incorporated into their design. MERADCOM requested VERSAR to assist in evaluating this new objectionable odor problem.

5.2.1 MERADCOM evaluation. MERADCOM, assisted by VERSAR, tested four 82--- serial numbered air conditioners at their Fort Belvoir facility. Of these four units two came from the New Cumberland Army Depot, one from Raytheon, and one from VSE. All units had finned heater rods. The VSE unit, a 82--- prototype, had heater rods manufactured by Company "A", whereas the other three unit's heating rods were manufactured by Company "B".

VERSAR sampled and analysed air outputs of the four units as they operated in the high heat mode. Test results showed that Company "B" finned heater rods produced the same objectionable odor, a "new paint" odor, as reported by Raytheon. The odor was traced to the heater rod paint coating used by Company "B". The odor was not toxic and not hazardous to humans. It was most intense when the heaters were first turned on, but diminished as the heaters were used. Different air conditioners produced varying amounts of this odor, probably due to production variations of the amount of paint applied to individual heating rods (see Appendix Q).

The final steps in this evaluation process consisted of MERADCOM personnel operating two air conditioners installed in a PATRIOT shelter at the Raytheon facility. After four hours of exposure to the heated air, produced by the heaters operating in their high and low heat modes, the MERADCOM personnel did not evidence any ill effects. The paint odor was present upon initial use of the heater, but became nondetectable within an hour after the heaters were turned on (see Appendix Q).

5.2.2 Investigation conclusions. Based upon their evaluation, MERADCOM concluded that the:

1) PATRIOT air conditioners with 82--- serial numbers pose no special hazard because of the use of the new painted heater elements.

2) Odor of "new paint" recurs each time the heaters are restarted over some undertermined length of operating time.

3) PATRIOT air conditioners with 82--- serial numbers are safe and usable in their heat modes (see Appendix Q).

5.2.3 Recommendations. MERADCOM's recommendation to the Project Manager, PATRIOT Missile System, DARCOM, was that the 82--- serial numbered air conditioners be released for use in the PATRIOT system (see Appendix Q).

NOTE: GFE PATRIOT air conditioners with 82--- and later serial numbers were released for use in the PATRIOT system. Changes to the PATRIOT manual were not deemed necessary, nor were any made with concern for these air conditioners.

APPENDIX A

Skinner and Sherman Technical Report

LTC R. ASPLUND

C. RG

PRELIMINARY

Raytheon memo forthcoming with interpretation of this report - [illegible]

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TECHNICAL REPORT
prepared for

RAYTHEON

CASE NO. 15518

[illegible] E. sherman laboratories inc.
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TECHNICAL REPORT

26 April 1982

CLIENT: Raytheon
Hartwell Road
Bedford, MA 01730

Attention: Mr. Andrew Granese

CASE NO: 15518

REFERENCE: Purchase Order No. 71-3880BD16508

PROJECT DESCRIPTION:

To identify volatile contaminants emanating from air-conditioning/heating units.

SAMPLE IDENTIFICATION:

The following samples were taken from the CRG #1 (4-8-82), located at Bedford:

Communications Relay Set
Guided Missile System Truck
Mounted-AN/MRC-137 (XO-1)
Part No. 188/6-11456855
Serial No. 580373
Contract No. DAAH01-80-C0001

Air-Conditioning/Heater Unit Serial No. 81013, 184.8 hours.

1 of 12 - Charcoal Tube A, Skinner & Sherman Pump 7898, 1.18 liters per minute, three hours - 212.4 liters - inside closed shelter.

2 of 12 - Charcoal Tube B, Skinner & Sherman Pump 7896, 1.18 liters per minute, three hours - 212.4 liters - inside closed shelter.

3 of 12 - Gas Sampler C, flow-through sample - five minute flush - taken after unit running for three hours.

4 of 12 - Charcoal Tube D, Skinner & Sherman Pump 7896, 1.18 liters per minute, 2 1/2 hours, 177 liters, AC/Heater removed - outside shelter.

[illegible]

CLIENT: Raytheon

CASE NO: 15518

5 of 12 - Charcoal Filter E, Skinner & Sherman Pump 7898, 1.18 liters per minute, 2 1/2 hours, 177 liters, AC/Heater removed - outside shelter.

Note: Diesel EP Unit less than three feet away from shelter during testing. The following sample was taken from the ICC #1 (4-9-82) located at Andover:

Air-Conditioning/Heater Unit
Part No. 97403ASSY1322E9120
Serial No. 81014
364.6 hours

6 of 12 - Charcoal Filter F, Skinner & Sherman Pump 7896, 1.18 liters per minute, three hours, 212.4 liters - inside open shelter, power shut off for approximately 5 1/2 minutes during test.

The following samples were taken from an Air-Conditioning/Heater Unit (4-14-82) located at Bedford:

Serial No. 801160, New Unit Zero Hours

7 of 12 - Gas Sampler G, flow-through sample - taken after unit running 1/2 hour.

8 of 12 - Charcoal Tube H, Skinner & Sherman Pump 7896, 1.18 liters per minute, one hour, 70.8 liters, AC/Heater outside shelter.

9 of 12 - Gas Sampler I, flow-through sample - taken after unit running 1 1/2 hours.

10 of 12 - Charcoal Tube J, Skinner & Sherman Pump 7897, 1.18 liters per minute, two hours, 141.6 liters, AC/Heater outside shelter.

11 of 12 - Gas Sampler K, flow-through sample taken after unit running 2 1/2 hours.

[illegible]

CLIENT: Raytheon

CASE NO: 15518

12 of 12 - Charcoal Tube L, Skinner & Sherman Pump 7898, 1.18 liters per minute, three hours, 212.4 liters, AC/Heater outside shelter.

Note: The above testing sequence started at 1:30 PM:

1:37 PM - power shut off.

1:47 PM - power turned on.

1:52 PM - diesel EP Unit turned on outside building.

1:57 PM - power shut off.

1:58 PM - power turned on.

1:59 PM - right side of unit blocked off.

Note: During the testing of the three units, the heater controls were set on warmer and high heat.

METHODS OF TESTS:

Charcoal Tubes

Each charcoal tube was transferred to a flask and the flask was attached to the mass spectrometer. Each sample was slowly heated from -190°C to +125°C at a vacuum of 10^{-7} torr. Mass spectra were measured from mass 1 to mass 500.

Gas Samplers

The mass spectrometer was pumped out to the gas cylinder inlet. A background spectrum was then recorded. The gas cylinder inlet was then opened and the mass spectrum was recorded at different sensitivities. The intensity of each substituent could then be converted to percent concentration from the sensitivity factor of each molecule.

[illegible]

TECHNICAL REPORT

26 April 1982

CLIENT: Raytheon

CASE NO: 15518

RESULTS:

AC/Heater Unit, Serial No. 81013 - 184.8 Hours

Concentration, parts per million, by volume

Chemical Contaminant	Charcoal Tube inside, 3 hours		Gas Sampler inside, 3 hours	Charcoal Tube outside, 3 hours	
	A	B	C	D	E
Chloroform	0.8	0.4	0.2	0.4	0.2
Benzene	0.3	0.1	---	---	---
Toluene	0.02	0.03	---	---	0.01
Acrolein	0.05	0.06	---	0.02	0.02

AC/Heater Unit, Serial No. 81014 - 364.6 Hours

Concentration, parts per million, by volume

Chemical Contaminant	Charcoal Tube inside, 3 hours
	F
Trichlorotrifluoroethane	3
Chlorotrifluoroethane	1.5
Trichloroethane	0.15

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TECHNICAL REPORT

26 April 1982

CLIENT: Raytheon

CASE NO: 15518

AC/Heater Unit, Serial No. 801160, Zero Hours

Concentration, parts per million by volume

Gas Samples

Chemical Contaminant	G, 1/2 hr.	I, 1 1/2 hr.	K, 2 1/2 hr.
Chloroform	3	4	3
Benzene	0.5	0.3	0.2
Toluene	2	2	3
Acrolein	1	1	2
Dichloromethane	10	5	25
Trichloroethane	2	3	5
Dichloroethylene	-	-	-
Carbon tetrachloride	-	-	-
Heptanol	-	-	-

Charcoal Tubes

	H, 0-1 hr.	J, 0-2 hr.	L, 0-3 hr.
Chloroform	0.7	0.4	0.09
Benzene	0.01	0.01	0.005
Toluene	0.5	0.01	0.01
Acrolein	0.04	0.07	0.04
Dichloromethane	1.3	3.7	19
Trichloroethane	0.4	0.4	2.6
Dichloroethylene	0.2	0.3	0.01
Carbon tetrachloride	0.04	0.1	0.2
Heptanol	-	3	-

Note: The sensitivity limit for chemical contaminants was 0.01 part per million by volume in the charcoal tubes and 0.1 part per million by volume in the gas samples.

[illegible]

TECHNICAL REPORT

26 April 1982

CLIENT: Raytheon

CASE NO: 15518

COMMENTS:

The air sampler analyses provide precise numbers (ppm) for each chemical contaminant. The sample is collected and then measured directly by mass spectroscopy. The disadvantage with the air sampler analysis is that it is an instantaneous reading.

The charcoal tube procedure technique is less precise. Problems can arise from trapping efficiency, volatilizing after collection and desorption efficiency upon analysis. The main advantage with this technique is the fact that the potential contaminants are evaluated continuously over a long time period.

The Threshold Limit Value for acrolein is 0.1 part per million by volume.

Note: The principal chemists assigned to this case were David O. Bell and Robert E. Sacher, Ph.D.

Respectfully submitted,

SKINNER & SHERMAN LABORATORIES, INC.

Ralph Berger, P.E.

Ralph Berger, P.E.
President

RB/ls

This report is rendered upon all of the following conditions. This report is not to be reproduced wholly or in part without special permission in writing. Total liability is limited to the [illegible] Skinner & Sherman, Inc., Skinner & Sherman Technology, Inc., and/or New England Laboratories [illegible] conjunction with the contents of this report in any advertising media. The results listed relate only to tested samples and applicable parameters. Product endorsement is [illegible] Samples are held for thirty days following issuance of report. Samples will be stored at client's expense, if authorized in writing.

APPENDIX B

VERSAR Analytical Report

Versar inc.

VERSAR ANALYTICAL REPORT NO. 773.3

TO VSE Corporation ON May 20, 1982

TO THE ATTENTION OF Mr. Ralph Adolph, Manager, Testing Engineering

CONCERNING Interim Preliminary Report of Day 3 Testing for Inorganics

SUMMARY OF RESULTS:

Analysis of impinger samples for cyanide, fluoride, and chloride has been completed for Day 3, May 18, 1982. Attached is the preliminary data report. No cyanide or chloride was detected. However, fluoride was detected in one morning sample and all three afternoon samples. Both field control samples were blank. The afternoon samples show the concentration of fluoride in the air intake sample (1F) is equivalent to the average of the heated air discharge samples (2F and 3F). This suggests that the air in the vicinity of the test area is being contaminated from another source and does not reflect changes due to the heater.

The fluoride levels detected are low (6-14 ng/l air). Permissible OSHA exposure for an average work day is a time weighted average of 2 mg/m^3 or 2,000 ng/l air. The level established for Imminent Danger to Life and Health (IDLH) for 30 minutes exposure is 13,000 ng/l air.

Susan Sonchik

PROJECT SUPERVISOR

Versar inc.

773 BATCH 3

Received May 19, 1982

SAMPLE NO.	LAB NO.	$[CN^-]$ (ng/ℓ_{air})	$[F^-]$ (ng/ℓ_{air})	$[Cl^-]$ (ng/ℓ_{air})
NaOH Control AM	1511	<4.2	<4.2	<42.
1E	1512	<4.2	<4.2	<42.
2E	1513	<4.2	6.7	<42.
3E	1514	<4.2	<4.2	<42.
NaOH Control PM	1515	<4.2	<4.2	<42.
1F	1516	<4.2	10.6	<42.
2F	1517	<4.2	6.1	<42.
3F	1518	<4.2	14.2	<42.
Method Decection Limit		4.2	4.2	42.

APPENDIX C

Proposed Test Plan

VSE CORPORATION
FORMERLY VALUE ENGINEERING COMPANY

2550 HUNTINGTON AVENUE
ALEXANDRIA, VIRGINIA 22303

May 21, 1982
0300.032

Commander
U. S. Army Mobility Equipment Research
and Development Command
DRDME-EPAT (F. Good)
Fort Belvoir, Virginia 22060

Subject: Contract DAAK70-81-D-0109, Task Order 032

Dear Sir:

In accordance with data item A006 of the subject task order please find attached the proposed test plan which will be observed in determining the PATRIOT Air Conditioner discharge air quality. Air conditioner operating conditions will be recorded on the attached sample data form.

If you have any questions, please feel free to call.

Very truly yours,

VSE CORPORATION

Ralph J. Adolph
Project Engineer

RJA/djm

Attachment

cc: DRDME-EME

(CAPITAL BELTWAY EXIT 2S, ROUTE 241 SOUTH, TELEGRAPH ROAD) (703) 960-1600, TWX 710-832-1155

16 April 1982

PATRIOT AIR CONDITIONER

TEST PLAN

I. Purpose. To identify the possible source(s) of an apparent health problem that has been blamed on the air conditioner and to gather information that can lead to reasonable corrective action. The objectives of the test should be:

a. Identify and quantify any substances given off by the air conditioner that could cause human physical irritation.

b. Learn whether the quantities of irritants change with time and in what way they change.

c. Identify, if possible, the sources of the irritants.

II. Procedure.

a. Select a new, unused unit from those presently in storage at the Newington, VA warehouse. Unit Serial Number 801191 has been selected.

b. Turn the unit over to VSE who will conduct and supervise all testing. Mr. Ralph Adolph will be in charge of the tests.

c. Perform a physical inspection of the air conditioner as received, especially the interior of the evaporator compartment. Note and record condition of materials and components before test, with special attention to:

(1) Insulation
(2) Wiring near heater elements
(3) Heater elements
(4) Heater gromments
(5) Any debris evident in compartment
(6) All other items particularly any non-metal parts.

d. Perform an operational check to be sure that the unit will run when tested.

e. Record all operation time. Keep a record of mode and conditions while operating. Operate as little as possible in the heat mode before air sampling is begun.

f. Instrument the air conditioner to measure, as a minimum:

(1) Air temperature entering evaporator compartment.

(2) Air temperature leaving compartment. (Use thermocouple grids for air temperature.)

(3) Insulation surface temperatures. (Measure about six locations that receive radiant heat from heater elements.)

(4) Temperature of some heater gromments.

(5) Power consumption data: volts, amps, watts.

g. Have air samples collected and analysed by a competent chemical laboratory. During air sampling tests run air conditioner in high heat mode. Record concurrent data from f. above during air sampling, at regualr intervals (perhaps 20 minutes periods). Take air samples in a manner that will indicate how the rate of contaminant production changes with time. (i.e. sample for "first X minutes," sample for "next x minutes", etc.) Continue sampling until rate stablizies or reduces to zero, but not longer than 40 operating hours.

h. The contaminants to look for should be any organic or inorganid substances that may be irritants. We suspects, for "openers":

(1) Chlorine based substances
(2) Fluorine based substances
(3) Acrolein
(4) Other aldehydes
(5) HCN or other cyanogen based
(6) HCL
(7) Paint, adhesive components.
(8) Plastic, insulation, elastomer components.

i. Take concurrent background air samples of air entering air conditioner to eliminate identifying things not coming from the air conditioner.

j. Repeat the physical inspection of c. above at the end of the testing or after any incident such as apparent component failure that may occur during the test.

III. Product of Test. Prepare a brief, informal report describing the methods of test, tabulating all results and giving whatever factual information is collected. Return air conditioner to storage when testing is completed.

1.0 SAMPLING AND ANALYSIS TEST PLAN

INTRODUCTION

Versar proposes the following sampling and analysis test plan to evaluate the MERADCOM Patriot Air Conditioner. The test plan is designed to identify and quantify using NIOSH methodology, inorganic and organic substances given off during operation of the air conditioner/heater. This technical proposal contains the Sampling and Analysis Test Plan, a brief description of the corporate facilities, and a summary of the Standard Versar Quality Assurance/Quality Control Program.

1.1 Sampling

Air samples will be collected for performance of a general GC/MS organic scan and of specific inorganic parameter analysis. Sampling will be conducted over a ten (10) day period with samples being collected on five non-consecutive sampling days. Sampling activities will be conducted starting on April 28, 1982. Versar recommends that results be reviewed on the afternoon of the 29th and if necessary revise the sampling approach. The results of the April 28th samples may result in a need to change the basic approach provided below.

Sampling methodology will use methods recommended by the National Institute for Occupational Safety and Health (NIOSH). Two types of sampling trains will be used. Air samples for the organic scan will be collected for four (4) hours each run, with a run in the morning and one in the afternoon using Tenax sorbent material. A sample will be collected at the intake of the heating system and two replicate samples at the outlet. Samples collected for specific inorganic parameters will be collected using midget impingers. One series of samples will be collected using 0.1 N NaOH solution for chloride, fluoride, and cyanide.

Use or disclosure of proprietary data is subject to the restrictions on the title page of this document

Samples collected for GC/MS analysis of the organic substances will be collected on Tenax sample tubes. A total of three Tenax samples plus one control, and three 0.1 N NaOH impinger solution will be collected during each four hour run. Runs of shorter duration are not recommended because they would result in lower detection limits than desired. Field controls will be collected to ensure procedures used for sampling do not introduce contaminants into the sorbent which may interfere with analytical detection limits. Air samples for the organics will be collected using a low-volume (0.2 liters per minute) pump and Tenax sorbent tubes. Impinger samples will be collected using a high-volume (1-4 liters per minute) pump with the appropriate impinger solution in an individual midget impinger.

Strict quality control procedures will be followed through all phases of equipment preparation, sampling, and preparation of samples provided to the laboratory for analytical analysis. Any safety precautions necessary will be followed during preparation and sampling activities.

Versar requests that a modification be performed to the existing outlet duct work. This modification, we feel will allow for a more representative sample to be collected. We would like an additional six foot extension to be placed onto the ducting on the outlet side. The dimensions of the new duct should be 5 1/2" x 30" x 6'. During sampling, a temporary barrier should be placed between the heater unit and the loading dock to protect the sampling area from wind that may offset the sampling activities.

Use or disclosure of proprietary data is subject to the restrictions on the title page of this document

1.2 Analysis for Inorganic and Organic Substances

1.2.1 Inorganic Substances

The inorganic substances will be determined from air samples collected in impinger solutions. These samples will be analyzed for the inorganic substances cyanide, fluoride, and chloride by NIOSH methodology. The methods are published in the NIOSH Manual of Analytical Methods, Volume I.

For cyanide in air, Method P&CAM 116, the samples are collected in impingers that contain 10 ml of 0.1 M NaOH. The samples are analyzed using an Orion cyanide ion specific electrode. The recommended range and sensitivity of the method is 0.113 - 13 mg/m^3 in air.

For hydrochloric acid determination, chloride air samples are collected following NIOSH Method P&CAM 115. Chloride compounds in air are collected in midget impingers containing acetate buffer (pH 5.0). For the purpose of this study, the impinger solution will be 0.1 M NaOH. The resulting solutions are analyzed using a Orion chloride ion specific electrode. The range of the method is 0.1 to 1750 mg/m^3 for a 200-liter air sample.

For hydrogen fluoride in air, Method P&CAM 117 specifies collection of the air samples in 10 ml of 0.1 M NaOH. The air sample impinger solution used for this analysis will be the same as that collected for cyanide. The impinger solution is diluted with Total Ionic Strength Adjustment Buffer (TISAB) and the diluted samples are analyzed using an Orion fluoride ion specific electrode. The analytical range of the method is 0.05 to 475 mg/m^3.

1.3 Organic Substances, GC/MS Analysis

The air samples collected on Tenax and charcoal will be analyzed by GC/MS for organic substances. A general organic scan will be performed.

Use or disclosure of proprietary data is subject to the restrictions on the title page of this document

Prior to analysis of samples, the GC/MS will be calibrated to FC-43 and the calibration checked by a direct injection of DFTPP. The sample tubes will then be analyzed by thermally adsorbing the trapped organics onto an SP 1000 gas chromatographic column with a flow of helium carrier gas. The sample will then be introduced into the mass spectrometer by temperature programming the column from 45°C to 250°C.

For comparison purposes, a sample will also be collected on charcoal during the first day of sampling. The sample tube will be desorbed with an organic solvent and analyzed by GC/MS using the same gas chromatographic conditions as above.

Use or disclosure of proprietary data is subject to the restrictions on the title page of this document

ITEM 18,000 BTU/HR Air Conditioner

MFGR KECO Industries Inc.

SERIAL NO. 801191

VSE CORPORATION
AIR QUALITY
ANALYSIS

DATE _____

SHEET ____ OF ____

PROJECT E.G _____

TIME	HOUR METER READ.	TEMPERATURE													SAMPLE	
		AIR			INSULATION						GROMMET		VOLTS	WATTS	NO.	OBSERVER
		AMB	IN	OUT	P-1	P-2	P-3	P-4	P-5	P-6	NO. 1	NO. 2				
SWITCH POS.		1	2	3	4	5	6	7	8	9	10	11				

NOTES

APPENDIX D

Minutes of Coordination Meeting

DEPARTMENT OF THE ARMY
US ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA 22060

JUN 16 1982

DRDME-EPAT

SUBJECT: PATRIOT Air Conditioner Testing for Toxic Gases

Project Manager
PATRIOT Missile System, DARCOM
ATTN: DRCPM-MD-T-C (Mr. Huie)
Redstone Arsenal, AL 35898

Attached (Incl 1) for your information are the minutes for the meeting held on 8 June 1982 to discuss subject item. The POC for the effort at MERADCOM is George Sams, AV 354-5871 or Comm. (703) 664-5871.

FOR THE COMMANDER:

1 Incl
as

JOHN E. WADDICK
A/Development Project Officer
PATRIOT Support Project Office

CF:
VSE (Mr. Adolph, Mr. Caldwell, Mr. Sherfy)
US AEHA (Mr. Valis, Mr. Esposito)
MERADCOM Safety Ofc (Mr. Longe)
Skinner & Sherman (Mr. Dalzell, Mr. Berger)
PATRIOT Prog Ofc, Raytheon (Mr. Arsevault)
Raytheon, Bedford (Mr. Granese)
VERSAR (Mr. Richards, Mr. Ronan, Mr. Powers)
MERADCOM (Mr. Waddick, Mr. Brantly, Mr. Larson, Mr. Sams, Mr. Good)

DRDME-EPAT 11 June 1982

SUBJECT: Minutes, Coordinating Meeting on Testing of PATRIOT Air Conditioner, VSE Corporation, 8 June 1982

1. Short Concise Synopsis of Meeting: The purpose of the meeting was to obtain an agreement on a coordinated test plan, test instrumentation and analysis procedures for follow-on testing of PATRIOT Air Conditioners.

2. Personnel Present: See attached list.

3. Discussion: Outgassing tests conducted by Raytheon/Skinner and Sherman Labs and MERADCOM (VSE/VERSAR) on the PATRIOT 18,000 BTUH Air Conditioner and the Army Environmental Hygiene Agency (AEHA) on an Army Standard Horizontal 18,000 BTUH Air Conditioner provided entirely different data as to the content of the gases present in the air flow of the air conditioner. It should be noted that both of the above air conditioners were manufactured by KECO. As a result of this wide difference in test data, the PATRIOT Office requested MERADCOM to take the lead in coordinating and finalizing a plan of test as well as to initiate testing of new production air conditioners.

Prior to the meeting, MERADCOM forwarded to Raytheon and AEHA a proposed draft test plan.

MERADCOM (PATRIOT DPO) reviewed the purpose of the meeting to be assured that everyone was aware of the urgency of this test program and the necessity of arriving at an agreed upon test plan including test and analysis of data by one company. This was later changed to have AEHA and Skinner and Sherman Labs do duplicate analysis for greater creditability in the results.

There was considerable discussion of the effort performed by VSE/VERSAR on a production PATRIOT air conditioner, on the effort of AEHA on the standard air conditioner, the problems that Raytheon has experienced at their plant and the ensuing effort by Skinner and Sherman. This discussion was considered essential to establishing a

coordinated test program. Since Raytheon/Skinner-Sherman found the large quantities of constituents in their tests, it was agreed that a test plan should be generated around the verification of the existence of those constituents in the air flow from the air conditioner.

The following plan was drafted and agreed to:

CONSTITUENTS	SAMPLING METHOD	ANALYSIS
Acrolein	Tenax (cooled)	HRGC/MS
Aromatics	Tenax (cooled)	HRGC/MS
Phalates-Universal (others)	Charcoal	HRGC/MS
Formaldehide	Std-NIOSH-bisielfides	Standard
Hydrogen Cyomide	Std-NIOSH-OLIN NAOH	Standard

VERSAR agreed to draft the sampling plan, coordinate it with AEHA and Raytheon/Skinner-Sherman and have a final plan to MERADCOM by 11 June 1982. The sampling plan will include the testing of four new production air conditioners for a period of three hours. During those three hours of operation, there will be three one-hour samples taken. The plan will indicate that VERSAR will perform analysis on 100% of samples, Raytheon/Skinner-Sherman on 25% of samples and AEHA on 25% of samples.

The test will begin on or about 28 June 1982 and be completed by 16 July 1982. The draft test report is due out by 23 July 1982.

4. Conclusions: The coordination meeting is considered a success for the following reasons:

a. A test plan was formulated and agreed to by MERADCOM, Raytheon and AEHA for the purpose of determining the existance of certain constituents in the air flow from the PATRIOT air conditioner.

D-3

DRDME-EPAT 11 June 1982

SUBJECT: Minutes, Coordinating Meeting on Testing of PATRIOT Air Conditioner, VSE Corporation, 8 June 1982

b. A working relationship was established between the government, Raytheon and the commercial laboratories in an attempt to resolve this potential problem.

c. The test program is a very ambitious one and every effort will be made to complete it at the earliest date.

5. Action: The following actions were agreed to:

a. VERSAR will draft the sampling plan and coordinate it with AEHA and Raytheon/Skinner-Sherman on 9 June 1982. The final coordinated plan will be forwarded to MERADCOM by 11 June 1982.

b. Tests will begin on/about 28 June 1982 at VSE Corporation on four units as outlined in the above plan, including the sampling plan. However, this date is dependent on awarding a new Task Order to VSE to cover the effort on that date.

1 Incl
as

8 June 1982

LIST OF ATTENDEES

COORDINATION MEETING ON TESTING OF

PATRIOT AIR CONDITIONER

NAME	ORGANIZATION	PHONE NO.
Ralph Adolph	VSE	703-960-4600
Robert Valis	US AEHA	301-671-2208
George Esposito	US AEHA	301-671-2208
Bryan Longe	MERADCOM Safety	703-664-2681
Robert McKechnie	MERADCOM PATRIOT Office	703-664-5871
Hal Dalzell	Skinner & Sherman	617-890-7200
Ernest Arsevault	PATRIOT Prog Ofc, Raytheon	617-475-5000
Ralph Berger	Skinner & Sherman	617-890-7200
George Sams	MERADCOM PATRIOT Office	703-664-5871
Andy Granese	Raytheon - Bedford	617-274-7100
John Richards	Versar Inc	703-750-3000
Richard Ronan	Versar Inc	703-750-3000
Scott Powers	Versar Inc	703-750-3000
Robert Caldwell	VSE, Program Manager	703-960-4600
Robert Sherfy	VSE	703-960-4600

Incl 1

APPENDIX E

Finalized Test Plan

DEPARTMENT OF THE ARMY

U. S. ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND

FORT BELVOIR, VIRGINIA 22060

DRDME-EPAT

JUN 18 1982

SUBJECT: Test Plan for Follow-On Outgassing Tests on PATRIOT Air Conditioner

Project Manager
PATRIOT Missile System, DARCOM
ATTN: DRCPM-MD-T-C (Mr. Huie)
Redstone Arsenal, AL 35898

1. Reference is made to the Coordination Meeting held on 8 June 1982 between representatives of MERADCOM, Raytheon, Army Environmental Hygiene Agency (AEHA), VSE, VERSAR, and Skinner & Sherman to finalize the subject test plan.

2. Inclosed is a copy of the test plan that has been concurred by the three laboratories (AEHA, Skinner & Sherman, and VERSAR) who will be involved in the effort.

3. Plans are to initiate the preliminary validation study by VSE/VERSAR during the week of 21 June 1982 and the testing of the four (4) PATRIOT Air Conditioners beginning 28 June 1982. The final draft report is due NLT 28 July 1982.

FOR THE COMMANDER:

SIGNED

1 Incl
as

ROBERT M. McKECHNIE
Development Project Officer
PATRIOT Support Project Office

CF:
Army Environmental Hygiene Agency
Raytheon Company
DARCOM, DRCSG (LTC Vorpahl)
COMDT, USAADS, ATTN: ATSA-TSM-P, Ft. Bliss, TX 79916

PATRIOT AIR CONDITIONER

I. Purpose. To identify the possible source(s) of an apparent health problem that has been blamed on the air conditioner and to gather information that can lead to reasonable corrective action. The objectives of the test should be:

a. Identify and quantify any substances given off by the air conditioner that could cause human physical irritation.

b. Learn whether the quantities of irritants change with time and in what way they change.

c. Identify, if possible, the sources of the irritants.

II. Procedure.

a. Select new, unused production units from those presently in storage Newington, VA warehouse.

b. Turn the units over to VSE who will conduct and supervise all testing.

c. Perform a physical inspection of each air conditioner as received, especi the interior of the evaporator compartment. Note and record condition of materi and components before tests, with special attention to:

(1) Insulation
(2) Wiring near heater elements
(3) Heater elements
(4) Heater gromments
(5) Any debris evident in compartment
(6) All other items particularly any non-metal parts.

d. Perform an operational check to be sure that each unit will run when tes

e. Record all operation time. Keep a record of mode and conditions while operating. Operate as little as possible in the heat mode before air sampling is begun.

f. Instrument the air conditioners to measure, as a minimum:

(1) Air temperature entering evaporator compartment.

(2) Air temperature leaving compartment. (Use thermocouple grids for air temperature).

Inclosure 1.

(3) Insulation surface temperature. Measure about six locations that have radiant heat from heater elements).

(4) Temperature of some heater grommments.

(5) Power consumption data: volts, amps, watts.

g. Each air conditioner shall be provided with a discharge duct to direct conditioned air away from the units return air intake. To simulate the effect of ductwork on the air conditioner the return air intake shall be partially blocked to produce a negative pressure in the heater compartment. Similarly the discharge duct shall be partially blocked to produce positive discharge pressure. Combined negative and positive pressures shall not exceed 0.5" water gage. (i.e., minus 0.3" wg and positive 0.2" wg). The outside air intake shall be used, with filter, during the test operation.

h. Have air samples collected and analyzed by VERSAR as outlined in their Addendum, "Analytical Method References" dated 28 May 1982. During air sampling tests run air conditioner in high heat mode. Record concurrent data from f. above during air sampling, at regular intervals (perhaps 20 minut periods). Take air samples in a manner that will indicate how the rate of contaminant production change with time. (i.e., sample for "first X minutes", sample for "next X minutes", etc). Continue sampling until rate stabilizies or reduces to zero, but not longer than 40 operating hours.

i. The contaminants to look for should be any organic or inorganic substances that my be irritants. Possible contaminants are:

(1) Chlorine based substances
(2) Fluorine based substances
(3) Acrolein
(4) Other aldehydes
(5) HCN or other cyanogen based
(6) HCL
(7) Paint, adhesive components
(8) Plastic, insulation, elastomer components

j. Take concurrent background air samples of air entering air conditioner to eleminate identifying substances not coming from the air conditioner.

k. Repeat the physical inspection of c. above at the end of the testing or after any incident such as apparent component failure that may occur during the test.

III. Product of Test. Prepare a report describing the methods of test, tabulating all results and giving whatever factual information is collected including an analysis of the data. The analysis should include a table that depicts measured values vs acceptable tolerance levels. Return air conditioner to storage when testing is completed.

ITEM [illegible]

KECO Industries Inc.

MFCR ____________________

SERIAL NO. ____________________

AIR QUALITY ANALYSIS

DATE ____

SHEET ____ OF

PROJECT ENG ________

TIME	HOUR	TEMPERATURE											VOLTS	WATTS	SAMPLE	OBSI
	METER	AIR			INSULATION						GROMMET				NO.	
	READ.	AMB	IN	OUT	P-1	P-2	P-3	P-4	P-5	P-6	NO. 1	NO. 2				
SWITCH POS.		1	2	3	4	5	6	7	8	9	10	11				

NOTES

STATEMENT OF WORK AND SERVICES

The Contractor shall provide engineering evaluation, documentation, and testing services in support of the PATRIOT Program. Specifically, the Contractor shall test and evaluate four PATRIOT Air Conditioners for irritant emissions with the purpose of identifying, if possible, the source(s) of an apparent health problem that may be caused by these air conditioners. This work is to be performed in accordance with the requirements of Section C., paragraph C.1 and B.1 of the basic contract. The Contractor shall also identify, quantify, and document any substance given off by the air conditioner that could cause physical irritation and identify sources of the irritants, in accordance with B.1 and B.6 of the contract.

A copy of MERADCOM Test Plan is inclosed for revision and testing purposes.

Deliverables: Data, CLIN 0002, in accordance with Exhibit A, DD 1423, Sequence Items A005, A00H and A00K, apply.

Mr. John Waddick, 664-5871, is the Contracting Officer's Representative for this Task Order.

The Completion Date is: 30 July 1982.

ATCH NR _____ TO EXHIBIT A

TO CONTRACT/PR _____

CONTRACT DATA REQUIREMENTS LIST

CATEGORY _____

SYSTEM/ITEM _____

CONTRACTOR _____

1. SEQUENCE NUMBER	2. TITLE OR DESCRIPTION OF DATA	6. TECHNICAL OFFICE	10. FREQUENCY	12. DATE OF 1ST SUBMISSION	14. DISTRIBUTION AND ADDRESSEES	
4. AUTHORITY (Data Item Number)	5. CONTRACT REFERENCE	7.	11. AS OF DATE	13. DATE OF SUBSEQUENT SUBM/EVENT		
A001	2. Test Plan	6. DRDME-EPAT	10. 0/Time	12. Blk 16	14. DRDME-EPAT	1/0
4. DI-T-5204	5.	7. DD 8. A 9.	11. End of TechEffort	13. Blk 16	DRDME-EME	1/1
16. REMARKS Test Plan to be submitted 10 days after award of task order.						15. TOTAL 2/1
1. A00K	2. Test & Demonstration Reports	6. DRDME-EPAT	10. 0/Time	12. Blk 16	14. DRDME-EPAT	1/0
4. DI-T-1906	5.	7. LT 8. A 9.	11. End of TechEffort	13. Blk 16	DRDME-EME	1/1
16. REMARKS Draft shall be submitted NLT 30 days after test. Allow 10 days for government approval. Final Report shall be submitted NLT 20 days after government approval.						15. TOTAL 2/1
1. A005	2. Performance and Cost Report w/addendum dtd	6. DRDME-EPAT	10. Monthly	12. Blk 16	14. DRDME-PE	1/0
4. DI-F-1208A 5 Dec 80	5.	7. LT 8. A 9.	11.	13. Blk 16	DRDME-EME	1/1
16. REMARKS Report shall be submitted monthly for each open task. Required reporting date 15 days EOM.					DRDME-EPAT	1/0
						15. TOTAL 3/1
1.	2.	6.	10.	12.	14.	
4.	5.	7. 8. 9.	11.	13.		
16. REMARKS						15. TOTAL

APPENDIX F

Extract from VERSAR Report "Results of Sampling and Analysis Conducted on Four PATRIOT Heater/Air Conditioners at the VSE Corporation Facility: Alexandria, Virgina".

2.0 SAMPLING

2.1 Introduction

Versar was contracted by VSE Corporation to sample the exhaust air of four MERADCOM PATRIOT Heater/Air conditioners for selected inorganic and organic compounds as described in the Test Plan dated June 11, 1982 (see Appendix I). The intake air of each unit was sampled to determine baseline ambient conditions. The sampling of the PATRIOT units was conducted at VSE's facility in Alexandria, Virginia on June 30 and July 2, 1982. The project was performed with each Heater/Air conditioner operating continuously during sampling in the high heat mode, in an attempt to verify the existence of potentially hazardous compounds generated in the unit. Sampling techniques were used which would allow the detection of the target parameters acrolein, aromatics (less then 120 molecular weight), a broad range of organic compounds, formaldehyde and hydrogen cyanide.

2.2 Facility Description

As each of the four MERADCOM PATRIOT Heater/Air conditioners was to be tested, it was positioned on a table near an overhead bay door in the shop area. Intake and exhaust ducts were then connected to the unit. The ten-inch diameter intake duct terminated at a point along the exterior wall of the building approximately three feet from the edge of the overhead bay door frame. Thus, intake air originated from an area away from the unit's exhaust.

The rectangular exhaust duct extended approximately two feet from the face of the unit. The duct was partially closed at the end, leaving a 2.5 inch x 29.5 inch opening, to create a static pressure of approximately 0.4 inches of water inside the heater to simulate actual operation in a field application. Venicular traffic was restricted in the immediate area of the intake during testing.

The ductwork described above was used for each of the four units. As the tests for each unit were completed, that unit was removed and replaced with the next unit. The ductwork was then connected to the new unit.

2.3 Summary of Monitoring Operation

Testing of the PATRIOT units was conducted by Versar personnel on two non-consecutive days. Two units were tested each day on June 30 and July 2, 1982. Three one-hour tests were conducted on each unit. The total number of samples collected is summarized in Table 3. During Versar's sampling activities, VSE Corporation personnel recorded ambient, unit intake, and unit exhaust temperatures at 15-minute intervals as well as voltage, wattage, Hobbs hours meter recordings, and static pressure created by unit operation.

2.4 Sample Collection Equipment and Methods

The following list represents the equipment used to collect the first-hour set of samples from each of the four units:

9 Tenax tubes (3 tubes were field blanks)
9 Charcoal tubes (3 tubes were field blanks)
2 Midget impingers, standard
8 Midget impingers, fritted
6 Liquid traps
6 Bendix pumps
2 Electric vacuum pumps
2 Six-tube manifolds
10 Sample bottles
1 Liter 0.1 M sodium hydroxide (NaOH) stock solution
1 Liter 1% sodium bisulfite ($NaHSO_3$) stock solution
Ice packs
Tygon tubing

Before collecting samples, impingers were cleaned according to the following procedure:

a) Wash with mild detergent
b) Rinse with water
c) Rinse with 1:1 nitric acid
d) Rinse six times with deionized water
e) Shake out excess water.

TABLE 3

SUMMARY OF TOTAL SAMPLES COLLECTED FOR PATRIOT HEATER/ AIR CONDITIONER PER UNIT AND PER FOUR UNITS

	Exhaust	Intake	Blanks Field	Blanks Lab	Recovery Spike	Unit Summary	4 Unit Summary
Hour 1							
Recovery Spike	--	--	--	--	3*	3	3*
Tenax Tubes	3**	3**	3**	3**	--	12	48
Charcoal Tubes	3**	3**	3**	3**	--	12	48
0.1M NaOH	1	1	1	--	--	3	12
1% $NaHSO_3$	2+	2+	2+	--	--	6	24
Hour 2							
Tenax Tubes	3**	3**	--	--	--	6	24
Charcoal Tubes	3**	3**	--	--	--	6	24
0.1M NaOH	1	1	--	--	--	2	8
1% $NaHSO_3$	2+	1	--	--	--	3	12
Hour 3							
Tenax Tubes	3**	3**	1	1	--	8	32
Charcoal Tubes	3**	3**	1	1	--	8	32
0.1M NaOH	1	1	--	--	--	2	8
1% $NaHSO_3$	2+	1	--	--	--	3	12
						74	287

* A recovery spike on Tenax was prepared by Versar and submitted to U.S. AEHA and Raytheon/Skinner & Sherman as well as Versar for analytical analysis during the first unit's operation.

** Duplicate Tenax and charcoal samples, and blanks were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman for analysis.

\+ Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks were collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

In the field, the impingers were cleaned between sampling sets by first rinsing with deionized water and then rinsing with the particular impinger solution to be used in the impinger.

The sampling lines for the impinger traps and the glass sorbent trap tubes were inserted directly into the ducts at the points indicated in Figure 1. The intake locations were on the cowl that joined the round intake duct to the face of the air conditioner, approximately 18 inches in front of the face of the unit. The exhaust locations were approximately 15 inches from the face of the exhaust side of the unit.

2.4.1 Day One - June 30

On Day One, June 30, two PATRIOT Heater/Air conditioner units were tested. These units were designated as unit A (serial #801193) and unit B (serial #801198). Each unit was subjected to three 1-hour tests and operated continuously in the high heat mode during testing.

During the first hour, samples were collected at the points indicated as 1 - 18 in Figure 1. The samples collected at points 1, 9, 17, and 18 were to be analyzed for acrolein and formaldehyde. These samples were collected by drawing air through 1% $NaHSO_3$ impinger solution. Each sampling train consisted of two fritted midget impingers connected in series, each containing 15 ml of impinger solution. Bendix high-flow pumps were used to draw air through the sampling train at a rate of 333 ml/min from points 9, 17, and 18 and 317 ml/min from point 1. A liquid trap was installed between the impingers and each pump to prevent impinger solution from accidently being drawn into the pump.

For the collection of each impinger sample for acrolein and formaldehyde, one end of a flexible Tygon tube was placed at the desired sampling location and the other end connected to the sampling train. The pump was then started and allowed to run for one hour. Afterward, the solution from the two impingers was combined and poured into a labeled sample bottle and placed into a portable cooler at 4°C.

SAMPLING POINTS

1% $NaHSO_3$	1, 17 & 9, 18
0.1 M NaOH	2 & 10
Tenax Traps	3, 4, 5 & 11, 12, 13
Charcoal Traps	6, 7, 8 & 14, 15, 16

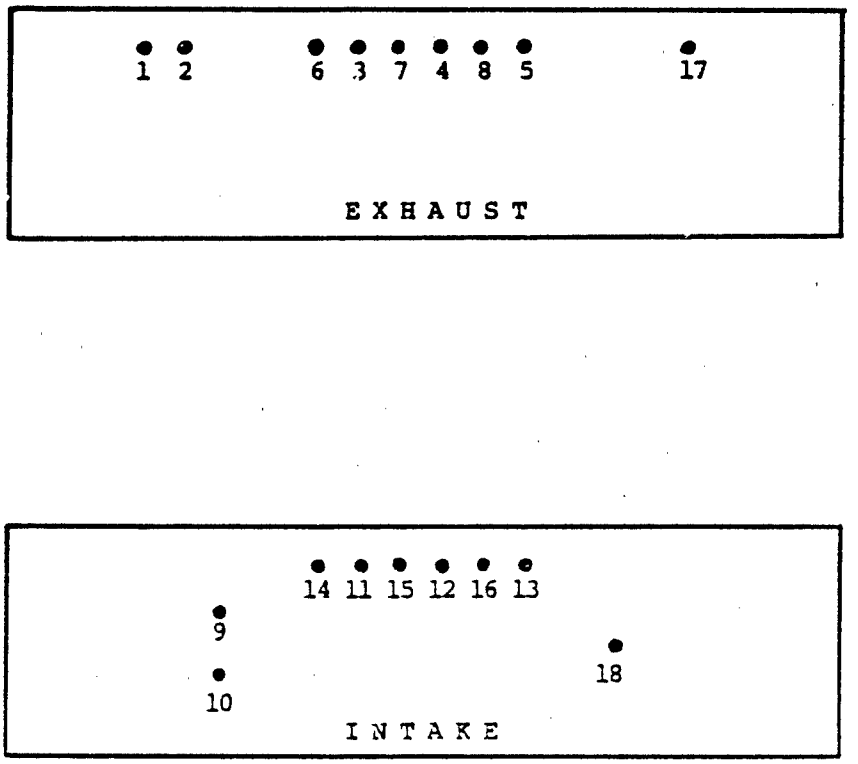

FIGURE 1 LOCATION OF SAMPLING POINTS

The samples collected at points 2 and 10 were to be analyzed for hydrogen cyanide. These samples were collected by drawing air through a 0.1 M NaOH impinger solution. Each sampling train consisted of one standard midget impinger, containing 15 ml of impinger solution, followed by a liquid trap. Bendix high-flow pumps were used to draw air through the sampling trains at a rate of 1,000 ml/min.

For the collection of each hydrogen cyanide sample, one end of a flexible Tygon tube was placed at the desired sampling location and the other end connected to the sampling train. The pump was then started and allowed to run for one hour. Afterward, the impinger solution was poured into a labeled sample bottle and placed in a portable cooler at 4°C.

The samples collected at points 3, 4, 5, 11, 12, and 13 were to be analyzed for acrolein. These samples were collected by drawing air through traps made of 18 cm x 6 mm OD glass tubes packed with 6 cm of Tenax GC. Before sampling, the traps were pre-conditioned for 12 hours at 250°C with a helium flow rate of 5 ml/min. A manifold was constructed which allowed one pump to draw air through all six of the Tenax traps. The pump was adjusted to pull 100 ml/min of air through each of the tubes.

Holes were drilled in the duct walls to allow the traps to be inserted directly into the duct at the appropriate points. Styrofoam holders were constructed to secure the traps in a vertical position. Each holder also accommodated three ice packs which were used to cool the traps to a temperature of 50° - 60°F. For sample collection, the tubes were connected to the manifold and inserted, between the ice packs, into the duct (three at the intake, three at the exhaust). Flexible Tygon tubing was used to connect the manifold to the vacuum pump. The pump was started and allowed to run for one hour. Immediately afterward, the tubes were removed from the manifold, capped, and labeled.

The samples collected at points 6, 7, 8, 14, 15, and 16 were to be analyzed for aromatics and general organic compounds. These samples were collected by drawing air through two-section charcoal tubes (400 mg

front section; 200 mg break-through section) purchased from SKC Inc. (catalogue number 226-09). Sample collection procedures for the charcoal traps were identical to those described for the Tenax traps.

In addition to samples 1 - 18, the first-hour sample set contained the following field blanks:

3 Tenax traps
3 Charcoal traps
1 0.1 M NaOH impinger solution
2 1% $NaHSO_3$ impinger solution

The Tenax and charcoal blanks were prepared by opening the ends of the tubes inserting into the manifold, and then resealing them with appropriate caps. The NaOH and $NaHSO_3$ impinger solution blanks were prepared by pouring 15 ml of the appropriate solution into a clean impinger and then into a labeled sample bottle and placed in a cooler a 4°C for transportation to the analytical labs.

During the second hour of testing, samples were collected from points 1 - 17. The collection procedures for each of these samples were identical to those of the first hour. As scheduled in the Test Plan, no field blanks were prepared during the second hour.

During the third hour of testing, samples were again collected from 1 - 17 in the same manner as described for the first hour. Also, the following field blanks were prepared:

1 Tenax trap
1 Charcoal trap

These blanks were prepared according to the same procedures as those described for the first-hour blanks.

2.4.2 Day Two - July 2

On the second day of sampling, two additional PATRIOT heater/air conditioners were tested. These units were designated as unit C (serial #801188) and unit D (serial #801185). Each unit was subjected

to three one-hour tests, which were similar to those described in Section 2.4.1 except for the following changes:

1. Ice packs were used to cool the 1% $NaHSO_3$ impingers (sampling points 1, 9, 17, and 18). Also, the air flow rate through these impingers was increased to 1000 ml/min. Finally, after each sampling run, the solutions from the two in-line impingers were poured into two separate sample bottles.

2. The volume of solution in the 0.1 M NaOH impingers (sampling points 2 and 10) was decreased from 15 to 10 ml. Also, the air flow rate through these impingers was increased to 1235 ml/min from 1000 ml/min.

Field blanks were prepared according to the same schedule and procedures as described for the day one tests, except that the 0.1 M NaOH blanks were reduced in volume to 10 ml.

2.5 Sample Handling

Immediately after each one-hour sampling run, all samples were appropriately sealed and placed, with ice packs, in coolers. They were maintained in this refrigerated condition until returned to the laboratory. There, the appropriate samples were either turned over to Versar's laboratory or prepared for shipment to Skinner & Sherman and U.S. AEHA. The latter were packed in ice (blue ice) and shipped via Federal Express and delivered the next day. A completed chain-of-custody record (see Appendix III) accompanied the samples for each laboratory. The chain-of-custody records also contained sampling duration and sampled volume data.

2.6 Air Volume Data Calculations

The volume of air sampled at each point, as reported on the chain-of-custody record, was determined from the known sampling duration and the calibrated flow rates of the sampling pumps. This volume was calculated as:

$$\text{Sampled Volume} = \text{Sampling Duration (time)} \times \text{Flow Rate } \frac{\text{volume}}{\text{time}}$$

Prior to each sampling day, the pumps were calibrated with the appropriate sampling train in place. A soap-film bubble flowmeter was used for these calibrations and the pump flow rates were assumed to be constant throughout the sampling period.

3.0 ANALYSIS

The following sections will describe the method summary for the target parameters and analtical methodologies for all samples analyzed. A discussion of the analytical results for the tests conducted on the four PATRIOT Heater/Air Conditioner units is provided and conclusions of the results discussed.

3.1 Method Summary For Target Parameters

Target parameters were determined as described in the Test Plan dated June 11, 1982. The following section will provide a summary of the methods used for analytical analysis.

3.1.1 Acrolein

Air samples for acrolein were collected on Tenax traps, charcoal traps and in a 1% sodium bisulfite impinger solution. Tenax was conditioned for 12 hours at 250°C with a flow of 5 ml/min 99.999% Matneson grade helium, then capped until sampling activities were conducted. Sampling was conducted by drawing 100 ml/minute of air through a Tenax trap cooled to 50° - 60°F. After sampling, the traps were cooled to 4°C until they were analyzed. Analyses and quantification were performed by HRGC/MS and GC/MS. The charcoal was activated by SKC Inc. prior to sealing both ends of the tube. Sample air was drawn through the charcoal trap cooled to 50° - 60°F at a rate of 100 ml/min. Upon completion of sampling, the charcoal tubes were sealed with polyethylene caps and cooled to 4°C until extraction procedures were performed using carbon disulfide. Analysis was performed by GC/FID. Identification and quantification of specific mass peaks was performed on GC/MS. The 1% sodium bisulfite impinger solution is described below in Section 3.1.3

3.1.2 Aromatics and General Organics

General organic samples were collected on NIOSH charcoal tubes purchased from SKC Inc. and Tenax tubes prepared by Versar. The sampling method was equivalent to that discussed for acrolein in Section 3.1.1 above.

3.1.3 Formaldehyde

Samples for formaldehyde and acrolein were collected using the NIOSH methods P&CAM 125 and 211. The sampling train consisted of two fritted-midget impingers with 15 ml of 1% sodium bisulfite ($NaHSO_3$) solution in each. The impingers were connected in series, cooled to 4°C, and air drawn through the solution at a rate slightly greater than one liter per minute using a high-volume personnel sampler. Upon completion of sample collection, samples were stored overnight at 4°C in a cooler and analyzed the next day. Samples were prepared according to the NIOSH analytical method, analyzed using a spectrophotometer and absorbance was compared against prepared standard curves to determine sample concentrations. The detection limit of the method is one part per million.

3.1.4 Cyanide

Cyanide as hydrogen cyanide was collected using NIOSH method P&CAM 116. This method required the use of a single standard midget impinger attached to a high-volume personnel sampler. Air was drawn through 10 - 15 ml of 0.1 M sodium hydroxide (NaOH) solution at a rate of one liter per minute for 60 minutes. Upon completion of sample collection, samples were stored overnight at 4°C in a cooler and analyzed the next day. Analysis was performed using a specific electrode method which has a detection limit of approximately 0.02 ppm.

3.2 Tenax and Charcoal Trapped Organics

The primary objective of the use of sorbent traps (Tenax and charcoal) was to collect samples of acrolein and the other organics as observed in the analysis conducted by Skinner & Sherman. It was determined by the consensus team listed in Table 1 that the best compromise among all possible trapping choices were Tenax and charcoal. The Tenax was believed to be the best choice and the charcoal was added to extend organic sorbtivity and also to provide an extract for

subsequent confirmatory analysis. The discharged air of the PATRIOT Heater/Air conditioner system in the high heat mode approaches 125°F. This temperature is beyond the useful temperature range of both Tenax and charcoal and it was decided to cool the tubes during sample collection.

3.2.1 Preliminary Study

A preliminary study was performed on spiked Tenax to determine recovery of acrolein, benzene and toluene. In addition, thermal measurements were made during this test to determine the extent to which the sorbent could be cooled in the 125°F discharge air. This study was done on June 25, 1982. Six Tenax tubes were spiked with acrolein (420 ng) benzene (440 ng) and toluene (435 ng). Three tubes were mounted in the exhaust and three tubes mounted in the intake of the PATRIOT Heater/Air conditioner and the system was operated for one hour in the high heat mode. Commercial ice packs were placed in contact with approximately one-inch of each sorption tube. The resultant final temperature was 80° - 90°F. The test was completed in this mode. Review of the temperature results caused the Versar staff to believe that increased cold contact of each tube would be advantageous so the spike recovery test was redone on July 1, 1982 exposing approximately 50% of the sorbent within the tubes to the cold packs. The resultant temperature inside the sorbent tubes was 50° - 60°F.

The results of these two preliminary studies is presented in the following subsections.

3.2.2 Tenax Method Summary

The GC/MS Tenax method used was developed from EPA methodologies adapted to the evaluation of acrolein, aromatics and other potential solvent contaminants in the discharge of the tested Heating/Air conditioning units tested. The three methods used as guidelines were EPA Method 602, Purgeable Aromatics; EPA Method 603, Acrolein and Acrylonitrile; and EPA Method 624, Purgeables, published in the Federal

Register, Vol 44, No. 233, Monday, December 3, 1979 entitled "Guidelines Establishing Test Procedures for the Analysis of Pollutants, Proposed Regulations". These methods provided the guidelines for gas chromatographic and mass spectrometric condition selection. The conditions used for the analysis are listed in Table 4. Some minor changes of the method proposed by the consensus team were required, as the proposed capillary column could not be adapted to the analysis without major changes in instrumentation. An EPA-approved column was substituted for the purpose of this analysis

The Tenax method for acrolein and aromatics consists of removing the end caps (Swagelok with teflon ferrules) of the sample Tenax trap, and spiking an internal standard onto the adsorbent material. The sample Tenax trap is then connected to the desorb unit. The GC column carrier gas is diverted through the trap while it is flash heated to 170°C for 5 minutes. The effluent of the trap is injected onto the head of a 6 foot x 2mm ID glass Chromosorb 101 GC column with a carrier flow rate of Helium at 30 ml/min. Following desorption into the column, the GC column is temperature programmed to 240°C at 12°C/min and the materials are chromatographically separated and introduced into the mass spectrometer via the glass jet separator interface.

The retention times for acrolein, benzene and toluene were 13 min, 18.3 min and 21.6 min, respectively. These retention times allowed baseline separation of the three materials and sufficient resolution for the required sensitivity. Detection limits were in the order of 0.01 mg/m^3 for acrolein, benzene and toluene, as well as the other solvent materials listed in Table 5. These detection limits are defined only as the sensitivity of the GC/MS to the materials spiked onto the Tenax traps and recovered through analysis. No detection limits are available or can be derived for the total method.

TABLE 4

GAS CHROMATOGRAPHIC CONDITIONS

Desorbtion Sample Injection:	5 minutes at 170°C
Carrier Gas:	Helium (99.999%)
Carrier Gas Flow Rate:	30 ml/minute
Initial Column Trapping Temperature:	80°C for 4 minutes
Column Configuration:	6' x 2mm ID glass Chromosorb 101 (80/100 mesh)
Solvent/Air/Divert:	6 minutes
Column Temperature Ramp Rate:	12°C/minute
Final Column Temperature:	240°C for 30 minutes

MASS SPECTROMETER CONDITIONS

Mass Scan Rate:	2 sec/scan
Mass Scan Range:	20 - 505 amu
Calibration:	FC-43/BFB
Vacuum Conditions:	2×10^{-7} torr
EM Voltage:	2200V
Ionizer Mode:	Electron impact positive ion
Minimum Peak Width:	3 scans
Minimum Peak Area:	100
Baseline:	0
A/D Threshold:	1
Minimum Fragment Width %:	81

TABLE 5

VOLATILE ORGANICS DETERMINED BY THE APPROVED EPA METHODOLOGY METHOD 624 AND THEIR CORRESPONDING TIME WEIGHTED AVERAGES (TWA[1]) AND DETECTABLE AMOUNTS

Volatile Organics	TLV-TWA[2]	Cons. (ppm) air
Chloromethane	100	<0.01
Bromomethane	20	<0.01
Vinyl Chloride	1.0	<0.01
Chloroethane	1000	<0.01
Methylene Chloride	500	<0.01
Acrolein	0.1	<0.01
Trichlorofluoromethane	1000	<0.01
Acrylonitrile	2.0	<0.01
1,1-Dichloroethylene	—	<0.01
1,1-Dichloroethane	100	<0.01
Trans-1,2-dichloroethylene	200	<0.01
Chloroform	10	<0.01
1,2-Dichloroethane	50	<0.01
1,1,1-Trichloroethane	350	<0.01
Carbon Tetrachloride	10	<0.01
Bromodichloromethane	—	<0.01
1,2-Dichloropropane	75	<0.01
Trans-1,3-Dichloropropene	—	<0.01
Trichloroethylene	100	<0.01
Benzene	1.0	<0.01
1,1,2-Trichloroethane	10	<0.01
Cis-1,3-Dichloropropene	—	<0.01
Dibromochloromethane	—	<0.01
Bromoform	0.5	<0.01
Tetrachloroethylene	100	<0.01
1,1,2,2-Tetrachloroethane	5.0	<0.01
Toluene	200	<0.01
Chlorobenzene	75	<0.01
Ethylbenzene	100	<0.01
2-Chloroethyl vinyl ether	—	<0.01

[1] TWA = Time Weighted Average.
(Level in ppm at which worker can be exposed for 8 hours without damage to health, as determined by OSHA.)

[2] NIOSH/OSHA Pocket Guide to Chemical Hazards, Sept. 1978, Reprinted August 1980.

Quality control for the method consisted of daily checking of the GC/MS calibration by directly injecting the calibration compound BFB, 3-point standard response factor calibration, numerous laboratory blanks, field blanks, spiked sample traps, preliminary method evaluation studies and internal standards monitoring.

Prior to analysis of samples, each day the mass spectrometer calibration was verified by a direct injection of bromoflurobenzene (BFB) and the ion criteria in Table 6 were verified. A standard mixture of acrolein, benzene, and toluene prepared in methanol was injected onto a blank Tenax trap and analyzed in the same manner as a sample. From the peak height response of the mass peaks (27 m/z for acrolein, 78 m/z for benzene, and 92 m/z for toluene) external standard response factors were calculated for each day's analysis.

Between samples it was found necessary to frequently run laboratory blanks to verify that no laboratory contamination was occurring. This was extremely important due to the high amount of water condensed onto each trap. This moisture was introduced into the system upon injection of samples and extensive baking of the lines was required between sample analysis to prevent carry over between samples, as well as degradation of analytical conditions. It was observed that the effect of water was decreased resolution of GC peaks, shifting retention times, and decreased sensitivity. These problems were prevented through the extensive trap bake out and laboratory blank analysis between samples. No laboratory contaminants were observed.

Field Tenax trap blanks were taken into the field and treated as sample traps. These traps were prepared in the same manner, handled in the field by the same procedures (except that no air was drawn through them), and analyzed by the same methods as samples. Field blanks coupled with laboratory blanks provide information necessary to determine sources of contamination. For this study it was determined that there were two potential sources of contamination. Field blanks revealed that methylene

TABLE 6

GC/MS PERFORMANCE STANDARD REQUIREMENTS
Bromofluorobenzene (BFB) 20 ng
Method 624

m/e	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% relative abundance
173	less than 1% of mass 95
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 50% of mass 95
177	5-9% of mass 176

chloride, acetone and hexane contamination was introduced to the Tenax tubes in cold storage as the seals became loose when refrigerated. This problem has been solved by increased tightening of the Swagelok fittings and storage of the samples in an isolated environment. Further contamination has been identified as ambient levels of benzene, toluene and trichloroethene found in intake and discharge samples from the VSE testing facility as they were not found in field or laboratory blanks.

Prior to collection of the actual test samples, two preliminary method studies were implemented to test the sampling and analytical method. The first test consisted of spiking Tenax traps with known amounts of acrolein, benzene, and toluene and collecting samples of air from the V1 unit heater (the second test was conducted on the VB unit heater). These traps were then analyzed to determine whether the acrolein, benzene, and toluene were recovered after collection of samples. The results of the method study are listed in Table 7.

Acrolein was not recovered in either method study. Benzene and toluene were recovered in both studies. The following information was obtained from the method studies. Acrolein may not be trapped by Tenax under the condition of sampling. The spiking level was too low for all materials and a ten-to one hundred-fold increase in the spike level is required to provide meaningful data. Acrolein was spiked at close to the actual method detection limit level. The benzene and toluene concentrations on the spike were also too low, since ambient concentrations of benzene and toluene were possibly present during testing, as revealed by testing of the other units. From these initial tests the appropriate spiking levels for a comprehensive method detection limit determination can be established, should it become necessary to further develop and validate the method.

Spiked Tenax sample traps (recovery spikes) were taken into the field. The purpose of the spiked recovery traps was to verify that the materials acrolein, benzene and toluene would not be lost during handling and storage of the traps. All materials were quantitatively recovered as follows. Acrolein, 86%; benzene, 100%; toluene, 123%.

TABLE 7

PRELIMINARY METHOD STUDY RESULTS

METHOD STUDY #1

	Spike Level	Intake % Recovery	Discharge % Recovery
Acrolein	420ng	0	0
Benzene	440ng	33	11
Toluene	435ng	110	66

METHOD STUDY #2

Acrolein	420ng	0	0
Benzene	440ng	56	27
Toluene	435ng	69	32

Additionally, each sample trap was spiked with a surrogate deuterated compound, benzene d6 as an internal standard to monitor analytical recovery. The mean recovery of the spike for samples was 102% with a standard deviation of 13.5.

As was noted earlier, a method change was necessary in order to complete the analysis satisfactorily. This change was agreed upon by all members of the initial analytical test plan team. A packed column was substituted for the capillary column designated at the planning meeting by the consensus team. This change was necessary for two reasons. First, the Carbowax 20M capillary column was found to perform inadequately with the Tenax desorption unit as configured in the Versar laboratory. Also, the column would have been destroyed by the water trapped by the Tenax tubes as the system does not provide any means for venting the moisture from the system. The amount of moisture collected was not anticipated when the plan was developed, nor had such a problem been indicated by previous sampling excursions. Additional interfacing would have been required to adapt the method to the existing instrumentation, which was not feasible during the time available. A change was implemented and a 6-foot 2mm ID glass column packed with Chromosorb 101, 80/100 mesh was substituted for the 60-meter capillary column. This column is the EPA required column by Method 603, for the analysis of acrolein. The Chromosorb column methodology was developed by EPA specifically to handle large amounts of moisture in the analytical system.

3.2.3 Charcoal Method Summary

General organic analysis was performed on the air samples collected on charcoal using EPA and NIOSH methodologies adapted to the testing of the PATRIOT Heater/Air conditioner units for determination of possible organic irritants. The methodologies are, NIOSH Method P&CAM 127 "Organic Solvents in Air" and EPA Method 625 Base Neutrals/Acids and Pesticides. In addition the fused silica capillary conditions were

selected from the EPA document entitled "Quality Control Protocol for the Fused Silica Capillary Column Gas Chromatography/Mass Spectrometry Determination of Semi Volatile Priority Pollutants", U.S. EPA, EMSL, Las Vegas, September, 1981.

Charcoal tube samples were broken open and the front and back portion of the sample tube transferred to serum cap vials and desorbed with carbon disulfide prior to analysis. Desorbtion was performed with shaking at least 30 minutes prior to analysis. All extracted samples were analyzed by NIOSH Method P&CAM 127 using GC/FID prior to GC/MS analysis. No organics were detected by GC/FID. Detection limits are on the order of 0.1 mg/m^3. Selected extracted exhaust air samples were then analyzed by HRGC/MS to confirm the results of analysis.

GC/FID analysis was performed using a 20-foot 1/8" stainless steel column packed with 10% SP-1000 on 80/100 mesh Supelcoport. The oven was programmed to hold at 100°C for two minutes following injection and was then programmed to 270°C at 8°C per minute. The elevated final temperature was used to chromatograph the phthalate esters which were targeted by the analysis.

The HRGC/MS analysis was performed by injecting, Grob style, 1 ul of the extract on a 60-meter SE54 fused silica capillary column. The sample was injected onto the head of the column at 45°C and then programmed to 275°C at 10°C/min. The conditions for analysis are listed in Table 8.

Prior to analysis of samples, the calibration of the GC/MS was verified by the direct injection of DFTPP, and the ion abundance criteria in Table 9 verified. The standard response factors for the 3-point standardization were checked and linearity verified. Samples and blanks were then analyzed. Results are reported in mg/m^3. No organic materials were observed in any of the sample extracts.

TABLE 3

GAS CHROMATOGRAPHIC CONDITIONS

Sample Injection:	1 ul GROB injection
Carrier Gas:	Helium (99.999%)
Carrier Gas Flow Rate:	1 ml/minute
Initial Column Temperature:	45°C for 4 minutes
Column Configuration:	60 meter SE54 fused silica capillary
Column Temperature Ramp Rate:	10°C/minute
Final Column Temperature:	275°C for 30 minutes

MASS SPECTROMETER CONDITIONS

Mass Scan Rate:	0.75 sec/scan
Mass Scan Range:	20 - 505 amu
Calibration:	FC-43/DFTPP
Vacuum Conditions:	2×10^{-6} torr
EM Voltage:	1800V
Ionizer Mode:	Electron impact positive ion
Minimum Peak Width:	2 scans
Minimum Peak Area:	50
Baseline:	0
A/D Threshold	1
Minimum Fragment Width %:	81

TABLE 9

DECAFLUOROTRIPHENYL PHOSPHINE (DFTPP) 50 ng
Method 625

m/e	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	<1% of mass 198
441	less than mass 443
442	greater than 40% of mass 198
443	17-23% of mass 442

3.3 Impinger Solutions Inorganic/Organic

Cyanide, formaldehyde, and acrolein were determined from impinger solutions. These samples were analyzed using NIOSH methodologies adapted to the study of the MERADCOM PATRIOT Heater/Air Conditioner system. A summary of each method is given in Section 3.1 and the detailed method is presented in Appendix IV.

3.3.1 Sodium Hydroxide for Cyanide

Cyanide in air analysis was performed according to NIOSH Method No. P&CAM 116. Atmospheric samples were taken using midget impingers containing 10 - 15 ml of 0.1 M NaOH. Sample volumes of 60 to 74 liters of air were collected. Blank impingers were handled similarly to the other samples except that air was not drawn through the impinger train. The determination of cyanide was accomplished using a cyanide ion specific electrode and a single junction reference electrode. Millivolt readings from a series of cyanide standards prepared in 0.1 M NaOH were recorded and used to prepare a calibration curve. The millivolt readings were plotted vs. the cyanide ion concentrations of the standards on semi-log paper. The cyanide ion concentration is ug/ml was plotted on the log axis. The millivolt reading from the analysis of a sample was converted to ug CN/ml of impinger solution using the calibration curve. The ug content of the sample was multiplied by the sample impinger volume to obtain the total ug CN in the sample. The concentration of cyanide in the air sample is expressed in ppm (volume) CN using the following equation:

$$\text{ppm (volume) CN} = (0.94) \text{ conc. } \frac{mg}{m3} \; CN^-$$

The range of NIOSH Method No. P&CAM 116 is 0.02 - 19 ppm (volume) CN in air. Spike recoveries of sample dosed at 1.6 ppm CN and 1.3 ppm CN were 94% and 90% respectively. The results for all samples are listed in Section 3.4.

3.3.2 Sodium Bisulfite For Formaldehyde

Formaldehyde in air was determined using NIOSH Method No. P&CAM 125. Air samples of 20 to 60 liters were drawn through two impingers connected in series each containing 15 ml 1% sodium bisulfite ($NaHSO_3$) solution. Blank impinger solutions were handled like other samples except that no air was drawn through them. A spectrophotometric determination of formaldehyde standards was performed to prepare a calibration curve. Formaldehyde reacts with chromotropic acid-sulfuric acid to form a purple chromogen. The absorbance of the colored solution is determined in a spectrophotometer at 580 nm and is proportional to the quantity of formaldehyde in the solution. The absorbance is plotted against micrograms of formaldehyde. The formaldehyde content of the sample impinger solutions was determined. Where two impinger solutions collected in series were analyzed the formaldehyde content of solution A was added to that determined in solution B to give the total amount in the sampled atmosphere by the impingers in series.

The concentration of formaldehyde in the sampled atmosphere was calculated by using the following equation:

$$\text{ppm formaldehyde (volume)} = (0.81)\ \text{conc.}\ \frac{mg}{m3}\ \text{formaldehyde}$$

The range of NIOSH Method No1 P&CAM 125 is 0.1 - 2.0 ppm (volume) formaldehyde. Spike recoveries of samples dosed at 0.4 ppm, 0.2 ppm and 0.4 ppm were 60%, 80% and 60% respectively.

Intake sample B-2-9 developed a purple-red color after reagent addition instead of the normal purple chromogen formed when formaldehyde is present. Wavelength scans of intake sample B-2-9 and a 0.5 ppm formaldehyde standard were performed to compare absorbance peaks. Figure 2 shows that similar absorbance characteristics in the range of 540 to 640 nm are apparent suggesting that formaldehyde is present in the sample. In the range of 440 to 520 nm the absorbance patterns are

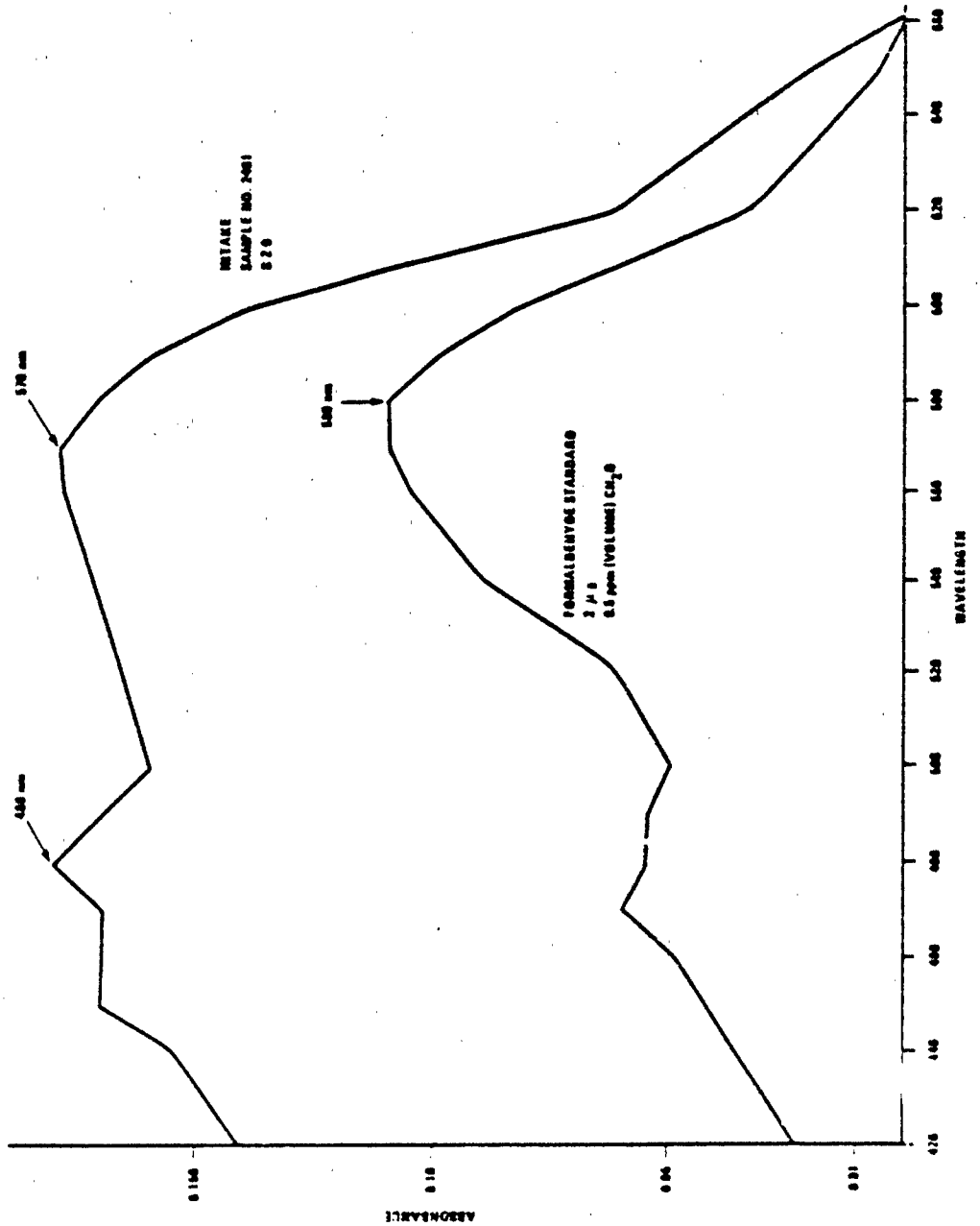

FIGURE 2 FORMALDEHYDE ABSORBANCE VS WAVELENGTH

different, indicating the presence of another compound of unknown identity in intake sample B-2-9. A summary of results is given in Section 3.4.

3.3.3 Sodium Bisulfite For Acrolein

Acrolein in air was determined using NIOSH Method No. P&CAM 211. Air samples of 20 to 60 liters were drawn through two midget impingers connected in series each containing 15 ml of 1% sodium bisulfite solution. Blank impinger solutions were handled similarly to the samples except that no air was drawn through them. A calibration curve was prepared using acrolein standards in the range of 0.06 to 1.8 ppm (volume) acrolein. The reaction of acrolein with 4-hexylresorcinol in an alcoholic trichloroacetic acid solvent medium in the presence of mercuric chloride results in a blue colored product whose absorbance is read at 605 nm in a spectrophotometer. The absorbance values were plotted against micrograms of acrolein in the color developed standards. Each sample impinger was analyzed separately in the case where impinger solutions connected in series were not mixed together in the field. The acrolein content of the sample solutions were determined after color developed, measurement in a spectrophotometer, and comparison to the curve previously prepared from the standard acrolein solutions.

The concentration of acrolein in the sampled atmosphere was calculated using the following equation:

$$\text{ppm (volume) acrolein} = 0.44\left(\text{conc. } \frac{\text{mg}}{\text{m3}} \text{ acrolein}\right)$$

Spike recoveries of samples dosed at 1.0 ppm and 0.3 ppm acrolein were 107% and 100% respectively. A summary of results is given in Section 3.4

3.4 Results and Conclusions For Target Parameters

The net results and conclusions of the analysis of effluent air from PATRIOT Heater/Air conditioner are discussed in this section. For a detailed discussion of quality assurance spikes, field blanks, laboratory blanks, reagent blanks, intake samples and other measures of performance, see Sections 3.1, 3.2, 3.3 and 3.5

3.4.1 Acrolein

3.4.1.1 Tenax Traps

No recovery of acrolein in either of the preliminary performance tests indicates that Tenax is unable to provide any useful results concerning the presence or absence of this chemical. The acrolein added to Tenax traps for the preliminary performance test and then subjected to a cooled environment during sampling combined with high humidity was lost. This loss would have come about by retention on Tenax during subsequent laboratory desorption, or possibly as a result of contact with the hot discharge air, or a reaction with the humid air during the preliminary performance tests or any combination of the above conditions.

3.4.1.2 Charcoal Tubes

No performance test of acrolein were performed on charcoal but it is reasonable to conclude, on the basis of Tenax results, that no useful acrolein conclusions either positive or negative could be extrapolated from the results of charcoal tube analysis.

3.4.1.3 Impinger Solution - 1% Sodium Bisulfite

No acrolein was detected from any unit using the standard NIOSH method. Detection limits varied with volume of air sampled and impinger solution from 0.375 mg/m^3 for units A and B to 0.06 mg/m^3 for all other analysis.

3.4.1.4 Conclusion Acrolein

The TLV-TWA for acrolein is 0.25 mg/m^3 and no acrolein was observed in units C and D at a detection level eight times below this level. In units A and B a slightly higher detection limit should pose no significant concern since the detection limit is trictly a function of sample taken and only slightly higher then the TWA and four times lower than reported in the one case of positive acrolein identified in unit R3 (serial No. 801160) by Skinner & Sherman in April 1982.

Acrolein is not produced by or from any units tested in this report.

3.4.2 Aromatic Organic Compounds

3.4.2.1 Tenax Traps

Benzene and toluene were observed in all intake and exhaust samples at very low levels (10 to 20 ug/m^3 for benzene with a TLV-TWA of 30,000 ug/m^3 and 10 to 200 ug/m^3 for toluene with a TLV-TWA of 750,000 ug/m^3).

3.4.2.2 Charcoal Traps

No benzene or toluene was observed even at extremely low levels any in extract tested.

3.4.2.3 Conclusion - Aromatic Organic Compounds

Benzene and toluene were observed at extremely low levels and appear to be contaminants in the area where sampling was conducted on the PATRIOT units. No other aromatic organic compounds were observed.

Aromatic organic compounds are not produced by or from any units tested in this report.

3.4.3 General Organics

3.4.3.1 Tenax and Charcoal Traps - Conclusion

With the exceptions of the laboratory/field contaminations discussed in Section 3.2, no organics were found in discharged air at any substantial levels. Trichloroethelene and ethylbenzene was found in most intake and exhaust samples at trace levels. The levels of trichloroetheylene were all <0.01 mg/m^3 and always slightly higher in exhaust than intake.

3.4.4 Formaldehyde

3.4.4.1 Impinger Solution - 1% Sodium Bisulfite

No formaldehyde was detected from any unit using the standard NIOSH method (P&CAM 125). Detection limits were at least a ten-fold factor lower then the TLV-TWA limit of 3 mg/m^3 (and in most cases a factor of 50).

3.4.4.2 Conclusion - Formaldehyde

Formaldehyde is not produced by or from any unit tested in this report.

3.4.5 Hydrogen Cyanide

3.4.5.1 Impinger Solution

No hydrogen cyanide was detected from any unit using the standard NIOSH method (P&CAM 116). Detection limit of 0.02 mg/m^3 is 550 times lower than the TLV-TWA of 11 mg/m^3.

3.4.5.2 Conclusion - Hydrogen Cyanide

Hydrogen cyanide is not produced by or from any units tested in this report.

3.5 Summary of Results by Units

In the following section a listing of all data by unit is covered by this report. The following units will be covered:

Unit SN	Date Manufactured
1. 801193	12/81
2. 801198	1/82
3. 801188	11/81
4. 801185	11/81

Analytical results of the above units are presented in Tables 10 through 13.

3.6 Comparison of Versar and Skinner & Sherman Results

Triplicate samples were taken during the first hour of operation of each unit following exactly the June 11, 1982 plan. These samples were sent to U.S. AEHA, Skinner & Sherman and Versar for analysis. In addition, Skinner & Sherman requested and Versar provided 1% sodium bisulfite solution for the same analysis. Skinner & Sherman has provided their report (see Appendix III). The U.S. AEHA results will be presented at the July 21, 1982 meeting.

No differences exist between the Versar and Skinner & Sherman report that would in any way alter the general conclusions concerning target parameters discussed in Section 3.4. Although the Skinner & Sherman report lists acrolein found in the first hour of unit A (SN 801193). The GC/FID quantification level for acrolein is a 0.0025 mg/m^3. This number reflects three major uncertainties:

1. The GC/FID method alone can not uniquely identify acrolein.
2. The level reported is less than a factor of ten above the reported detection limit.

TABLE 10

RESULTS FOR UNIT 801193 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	<0.01	0.01	0.01
	Toluene	Intake	0.14	--	--
		Exhaust	0.11	0.08	0.05
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	--	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.025	<0.025	<0.025
		Exhaust	<0.025	<0.025	<0.025
1% $NaHSO_3$	Acrolein	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375
1% $NaHSO_3$	Formaldehyde	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

TABLE 11

RESULTS FOR UNIT 801198 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	<0.01	--	--
		Exhaust	<0.01	0.02	<0.01
	Toluene	Intake	0.01	--	--
		Exhaust	0.01	0.03	0.03
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.025	<0.025	<0.025
		Exhaust	<0.025	<0.025	<0.025
1% $NaHSO_3$	Acrolein	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375
1% $NaHSO_3$	Formaldehyde	Intake	<0.375	1.60***	<0.375
		Exhaust	<0.375	<0.375	<0.375

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
***Suspect chemical interference.
tr = trace
ND = Not detected

TABLE 12

RESULTS FOR UNIT 801188 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	0.01	0.02	0.01
	Toluene	Intake	0.04	--	--
		Exhaust	0.08	0.03	0.04
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	tr
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060
1% $NaHSO_3$	Formaldehyde	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

TABLE 13

RESULTS FOR UNIT 801185 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	0.01	0.01	<0.01
	Toluene	Intake	0.02	--	--
		Exhaust	0.03	--	--
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	tr
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060
1% $NaHSO_3$	Formaldehyde	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

3. The TLV-TWA for acrolein is 0.1 mg/m^3 and the reported value is only 1/40 of the eight hour exposure level.

Taken together the factors make the reported value extremely uncertain.

APPENDIX G

VERSAR Supplemental Report for Sampling and Analysis of Fifth Air Conditioner

Versar inc.

SUPPLEMENT TO JULY 16, 1982 REPORT RESULTS OF SAMPLING AND ANALYSIS CONDUCTED ON FOUR PATRIOT HEATER/AIR CONDITIONERS AT THE VSE CORPORATION FACILITY: ALEXANDRIA, VIRGINIA

Submitted to:

VSE Corporation
2550 Huntington Avenue
Alexandria, Virginia 22303
(703) 664 5871

Attention: Mr. R. Caldwell

Versar Project No. 783

Prepared by:

VERSAR INC.
6621 Electronic Drive
Springfield, Virginia 22151
(703) 750-3000

July 19, 1982

G-1

Versar inc.

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1.0 INTRODUCTION

This report is a supplement to the detailed account (July 16, 1982) of sampling and analysis of four MERADCOM PATRIOT Heater/Air Conditioners and covers one additional unit (SN 801160). This unit had been previously tested by Skinner & Sherman for Raytheon and shown to emit acrolein at the 2.5 to 5 mg/m^3 level. MERADCOM decided to test this unit with the same methods (June 11, 1982 Test Plan) applied to the intensive study of four new units.

2.0 SAMPLING

Sampling activities were conducted on July 15, 1982 at the VSE facility in Alexandria, Virginia for selected inorganic and organic compounds as described in the Test Plan dated June 11, 1982. The PATRIOT Heater/Air Conditioner unit sampled was designated as Unit R3. During sampling, the PATRIOT unit was operated continuously in the high heat mode. Sampling techniques were identical to those used previously on June 30 and July 2, 1982. Sampling techniques were used which would allow the detection of the target parameters acrolein, aromatics (less than 120 molecular weight), a broad range of organic compounds, formaldehyde and hydrogen cyanide.

The MERADCOM PATRIOT Heater/Air Conditioner was positioned near the overhead bay door for sampling activities. A ten-inch diameter intake duct was placed into position at a point along the exterior wall of the building approximately three feet from the edge of the overhead bay door frame. Thus, intake air originated from a area away from the units exhaust. To adequately separate the exhaust from the intake, the area in which the unit was located was completely sealed-off from the intake using a sheet of polyethylene and placing it in position so it effectively sealed the air-conditioned warehouse area from the outside environment. All other ductwork was unaltered from the original testing. There was no vehicular traffic in the area of the intake during the three hour sampling period.

The monitoring operation was conducted the same as previously described in the summary of results submitted July 16, 1982. During sampling activities, VSE Corporation personnel recorded ambient, unit intake, and unit exhaust temperature at 15-minute intervals as well as voltage, wattage, Hobbs hours meter recordings, and static pressure created by unit operation. Summary of total samples collected is presented in Table 1.

TABLE 1

SUMMARY OF TOTAL SAMPLES COLLECTED FOR PATRIOT HEATER/AIR CONDITIONER DESIGNATED AS R3

	Intake	Exhaust	Blanks Field	Blanks Lab	Unit Summary
Hour 1					
Tenax Tubes	3*	3*	3*	3*	12
Charcoal Tubes	3*	3*	3*	3*	12
0.1M NaOH	1	1	1	--	3
1% $NaHSO_3$	2**	2**	2**	--	6
Hour 2					
Tenax Tubes	3**	3**	--	--	6
Charcoal Tubes	3**	3**	--	--	6
0.1M NaOH	1	1	--	--	2
1% $NaHSO_3$	2**	1	--	--	3
Hour 3					
Tenax Tubes	3**	3**	1	1	8
Charcoal Tubes	3**	3**	1	1	8
0.1M NaOH	1	1	--	--	2
1% $NaHSO_3$	2**	1	--	--	3
					71

* Duplicate Tenax and charcoal samples, and blanks were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman for analysis.

** Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks were collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

Immediately after each one-hour sampling run, all samples were appropriately sealed and placed, with ice packs, in coolers. They were maintained in this refrigerated condition until returned to the laboratory. There, the appropriate samples were either turned over to Versar's laboratory or prepared for shipment to Skinner & Sherman and U.S. AEHA. The latter were packed in ice (blue ice) and shipped via Federal Express and delivered the next day. A completed chain-of-custody record (see Appendix I) accompanied the samples for each laboratory. The chain-of-custody records also contained sampling duration and sampled volume data.

The volume of air sampled at each point, as reported on the chain-of-custody record, was determined from the known sampling duration and the calibrated flow rates of the sampling pumps. This volume was calculated as:

$$\text{Sampled Volume} = \text{Sampling Duration (time)} \times \text{Flow Rate} \left(\frac{\text{volume}}{\text{time}}\right)$$

Prior to each sampling day, the pumps were calibrated with the appropriate sampling train in place. A soap-film bubble flowmeter was used for these calibrations and the pump flow rates were assumed to be constant throughout the sampling period.

3.0 ANALYSIS

3.1 Summary

All methods and reference procedures can be found in the July 16, 1982 report. Laboratory sampling, handling and control was charged to isolate the impinger tubes for any contact with normal laboratory air. No laboratory contamination in either Tenax or charcoal traps was observed.

3.2 Results and Conclusions

A summary of the results for this unit is given in Table 2. The results continue to show a real contamination of intake air by toluene. As was the general trend with the other four units, the exhaust toluene was somewhat higher indicating possible generation by units. But like the other four units the level observed is 0.04 mg/m^3 and therefore not likely a problem.

The analysis by target parameter are summarized below:

1. Acrolein - Tenax - not useful
   Charcoal - not useful
   1% $NaHSO_3$ - not found (d.l. 0.06 mg/m^3)

2. Aromatics - Tenax - none found
   Charcoal - none found

3. General Organics - Tenax - none found
   Charcoal - none found

4. Formaldehyde - 1% $NaHSO_3$ - none found

5. HCN - Cyanide - 0.1M NaOH - none found

The PATRIOT Heater/Air Conditioner (SN 801160) did not produce any of the target parameters at significant levels in the sampling configuration tested.

TABLE 2

RESULTS FOR UNIT 801160 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	<0.01	--	--
		Exhaust	<0.01	<0.01	<0.01
	Toluene	Intake	0.02	--	--
		Exhaust	0.04	--	--
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	--	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.06	<0.06	<0.06
		Exhaust	<0.06	<0.06	<0.06
1% $NaHSO_3$	Formaldehyde	Intake	<0.06	<0.06	<0.06
		Exhaust	<0.06	<0.06	<0.06

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

APPENDIX I

CHAIN-OF-CUSTODY FORMS

6621 ELECTRONIC DRIVE
SPRINGFIELD, VIRGINIA 22151

SAMPLES TO VEPORK

CHAIN OF CUSTODY RECORD

PROJ NO: 783
PROJECT NAME: VOE Analysis III
SAMPLERS (Signature): Dave Tagney, Ron Pitzgerald

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Sampling Duration (hr)	Sampled Volume (L/hr)	MATRIX				REMARKS
R3-1-5	7/5/82	11:55	✓		Fans - discharge	1	1	6	Air				
R3-1-13		11:55	✓		Fans - intake	1	1	6					
R3-1-8		11:55	✓		Charcoal - discharge	1	1	6					
R3-1-16		11:55	✓		Charcoal - intake	1	1	6					
R3-1-17		11:55	✓		$NaHSO_3$ - discharge	2	1	60					impingers a & b
R3-1-18		11:55	✓		$NaHSO_3$ - intake	2	1	60					impingers a & b
R3-1-2		11:55	✓		NaOH - discharge	1	1	24					
R3-1-10		11:55	✓		NaOH - intake	1	1	24					
R3-2-5		13:07	✓		Fans - discharge	1	1	6					
R3-2-13		13:07	✓		Fans - intake	1	1	6					
R3-2-8		13:07	✓		Charcoal - discharge	1	1	6					
R3-2-16		13:07	✓		Charcoal - intake	1	1	6					
R3-2-17		13:07	✓		$NaHSO_3$ - discharge	2	1	60					impingers a & b
R3-2-9		13:07	✓		$NaHSO_3$ - intake	2	1	60					impingers a & b
R3-2-10		13:07	✓		NaOH - intake	1	1	24					

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SPRINGFIELD, VIRGINIA 22151

CHAIN OF CUSTODY RECORD

PROJ NO: 783

PROJECT NAME: VSE Analysis III

SAMPLERS (Signature): D. Tagg

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Sampling Duration (hr)	Sampled Volume (L/hr)	Matrix				REMARKS
R3-2-2	7/15/82	13:07	✓		NaOH - discharge	1	1	24	NR				
R3-3-5		14:20	✓		Teox - discharge	1	1	6					
R3-3-13		14:20	✓		Teox - intake	1	1	6					
R3-3-8		14:20	✓		Chinox - discharge	1	1	6					
R3-3-17		14:20	✓		$NaHSO_3$ - discharge	2	1	60					Impingers on ice
R3-3-16		14:20	✓		Chinox - intake	1	1	6					
R3-3-9		14:20	✓		$NaHSO_3$ - intake	2	1	60					Impingers on ice
R3-3-2		14:20	✓		NaOH - discharge	1	1	24					
R3-3-12		14:20	✓		NaOH - intake	1	1	24					
Un-R3		11:55			Teox blank field - Hr 1	1	0	0	–				
Un-R3		11:55			Teox blank lab - Hr 1	1	0	0	–				
Un-R3		11:55			Chinox blank field - Hr 1	1	0	0	–				
Un-R3		11:55			Chinox blank lab - Hr 1	1	0	0	–				
Un-R3		11:55			NaOH blank field - Hr 1	1	0	0	–				
Un-R3		11:55			$NaHSO_3$ blank field - Hr 1	1	0	0	–				

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SPRINGFIELD, VIRGINIA 22151

CHAIN OF CUSTODY RECORD

SAMPLES TO VERSAR

PROJ NO: 783

PROJECT NAME: VSE Analysis III

SAMPLERS (Signature): D. Topping

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Sampling Duration (hr)	Sampled Volume (liters)	MAIPIX				REMARKS
Unit B	7/15/82	14:20	✓		Tenax blank, field - Hr 3	1	0	0	-				
Unit B	↓	14:20			Tenax blank, lab - Hr 3	1	0	0	-				
Unit B	↓	14:20			Charcoal blank, field - Hr 3	1	0	0	-				
Unit B	↓	14:20			Charcoal blank, lab - Hr 3	1	0	0	-				

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6621 ELECTRONIC DRIVE
SPRINGFIELD, VIRGINIA 22151

CHAIN OF CUSTODY RECORD

SKINNER & SHERMAN

PROJ NO: 783
PROJECT NAME: VOE Analysis III

SAMPLERS (Signature): Dave Tagney, John Richards, Mathew Sparks, John Pelsulo, Mathew Shaw

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Analysis Duration (hr)	Sampled Volume (L/hr)	MATRIX				REMARKS
B3-1-3	7/15/82	11:55	✓		Tenax - discharge	1	1	6	AIR				
B3-1-11	7/15/82	11:55	✓		Tenax - intake	1	1	6					
B3-1-6	7/15/82	11:55	✓		Charcoal - discharge	1	1	6					
B3-1-14	7/15/82	11:55	✓		Charcoal - intake	1	1	6					
B3-1-1	7/15/82	11:55	✓		$KHSO_3$ - discharge	2	1	60					a: 1st impinger ; b: 2nd
B3-1-9	7/15/82	11:55	✓		$KHSO_3$ - intake	2	1	60					a: 1st impinger; b: 2nd
B3-2-3	7/15/82	13:07	✓		Tenax - discharge	1	1	6					
B3-2-11	7/15/82	13:07	✓		Tenax - intake	1	1	6					
B3-2-6	7/15/82	13:07	✓		Charcoal - discharge	1	1	6					
B3-2-14	7/15/82	13:07	✓		Charcoal - intake	1	1	6					
B3-2-1	7/15/82	13:07	✓		$KHSO_3$ - discharge	2	1	60					a: 1st impinger; b: 2nd
B3-3-3	7/15/82	14:20	✓		Tenax - discharge	1	1	6					
B3-3-11	7/15/82	14:20	✓		Tenax - intake	1	1	6					
B3-3-6	7/15/82	14:20	✓		Charcoal - discharge	1	1	6					
B3-3-14	7/15/82	14:20	✓		Charcoal - intake	1	1	6					

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
[signature]	7/15/82 15:30				
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

G-13

9-0620

versar
6621 ELECTRONIC DRIVE
SPRINGFIELD, VIRGINIA 22151

SAMPLES TO SKINNER & SHERMAN

CHAIN OF CUSTODY RECORD

PROJ NO: 783
PROJECT NAME: VSE Analysis III

SAMPLERS (Signature): Dave Topping, John Richards, Nathan Graves, [illegible], John Ridall, Nathan Graves

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Sampling Duration (hr)	Sampled Volume (liters)	MATRIX				REMARKS
R3-3-1	7/15/82	14:20			NaHSO3 - discharge	2	1	60	air				a = 1st impinger; b = 2nd
Un-R3	7/15/82	11:55			Tenax blank, field	1	–	–	–				
Un-R3	7/15/82	11:55			Tenax blank, lab	1	–	–	–				
Un-R3	7/15/82	11:55			Charcoal blank, field	1	–	–	–				
Un-R3	7/15/82	11:55			Charcoal blank, lab	1	–	–	–				
Un-R3	7/15/82	11:55			NaHSO3 blank, field	1	–	–	–				

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
[signature]	7/15/82 16:30				
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

G-14

9 0620

6621 ELECTRONIC DRIVE
SPRINGFIELD, VIRGINIA 22151

SAMPLES TO
U.S. AEHA

CHAIN OF CUSTODY RECORD

PROJ NO: 7313
PROJECT NAME: VSE Air [illegible]

SAMPLERS (Signature): Dave Tagg, Mark Gray, Neal Drew

STA NO	DATE	TIME	COMP	GRAB	STATION LOCATION	NO. OF CONTAINERS	Sample Number (hr)	Sample Volume (L-hr)	MATRIX				REMARKS
B3-1-4	7/15/82	11:55	✓		Tenax - discharge	1	1	6	AIR				
B3-1-12	7/15/82	11:55	✓		Tenax - intake	1	1	6					
B3-1-7	7/15/82	11:55	✓		Charcoal - discharge	1	1	6					
B3-1-15	7/15/82	11:55	✓		Charcoal - intake	1	1	6					
B3-2-4	7/15/82	13:07	✓		Tenax - discharge	1	1	6					
B3-2-12	7/15/82	13:07	✓		Tenax - intake	1	1	6					
B3-2-7	7/15/82	13:07	✓		Charcoal - discharge	1	1	6					
B3-2-15	7/15/82	13:07	✓		Charcoal - intake	1	1	6					
B3-3-4	7/15/82	14:20	✓		Tenax - discharge	1	1	6					
B3-3-12	7/15/82	14:20	✓		Tenax - intake	1	1	6					
B3-3-7	7/15/82	14:20	✓		Charcoal - discharge	1	1	6					
B3-3-15	7/15/82	14:20	✓		Charcoal - intake	1	1	6	↓				
In-B3	7/15/82	11:55			Tenax blank [illegible]	1	–	–	–				
In-B3	7/15/82	11:55			Tenax blank [illegible]	1	–	–	–				
In-B3	7/15/82	11:55			Charcoal blank [illegible]	1	–	–	–				

Relinquished by (Signature)	Date / Time	Received by: (Signature)	Relinquished by (Signature)	Date / Time	Received by: (Signature)
[illegible]	7/15/82 15:35				
Relinquished by (Signature)	Date / Time	Received by: (Signature)	Relinquished by (Signature)	Date / Time	Received by (Signature)
Relinquished by (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment. Copy to Coordinator Field Files

9-0620

[illegible] INC
6621 ELECTRONIC DRIVE
SPRINGFIELD, VIRGINIA 22151

SAMPLES TO U.S. AEHA

CHAIN OF CUSTODY RECORD

PROJ. NO.: 7-3

PROJECT NAME: V&E Analysis III

SAMPLERS: (Signature) [illegible]

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	REMARKS
1/a-13	7-15-92	11:55			[illegible]	1	-	-	-				

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
[illegible]	7/15/92 11:35				
Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
Relinquished by: (Signature)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	

Distribution: Original Accompanies Shipment, Copy to Coordinator Field Files

G-16

9-1620

APPENDIX H

Results of Sampling and Analysis Conducted on Five Heater/Air Conditioners

Versar Inc.

RESULTS OF SAMPLING AND ANALYSIS CONDUCTED ON FIVE PATRIOT HEATER/AIR CONDITIONERS AT THE VSE CORPORATION FACILITY: ALEXANDRIA, VIRGINIA

Prepared by:

VERSAR INC.
6621 Electronic Drive
Springfield, Virginia 22151
(703) 750-3000

July 21, 1982

H-1

TABLE 1

PATRIOT HEATER/AIR CONDITIONER
TEST PLAN DEVELOPMENT COORDINATION TEAM

MERADCOM PATRIOT Office

R. McKechnie

U.S. AEHA

R. Bongiovanni
G. Esposito*
D. Dogeniero
R. Valis*

MERADCOM Safety

B. Longe

Raytheon

E. Ersevault
A. Granese*

VSE

G. Sams*
R. Caldwell*
R. Adolph*
R. Sherfy

Skinner/Sherman

R. Berger*
H. Dalzell*

Versar Inc.

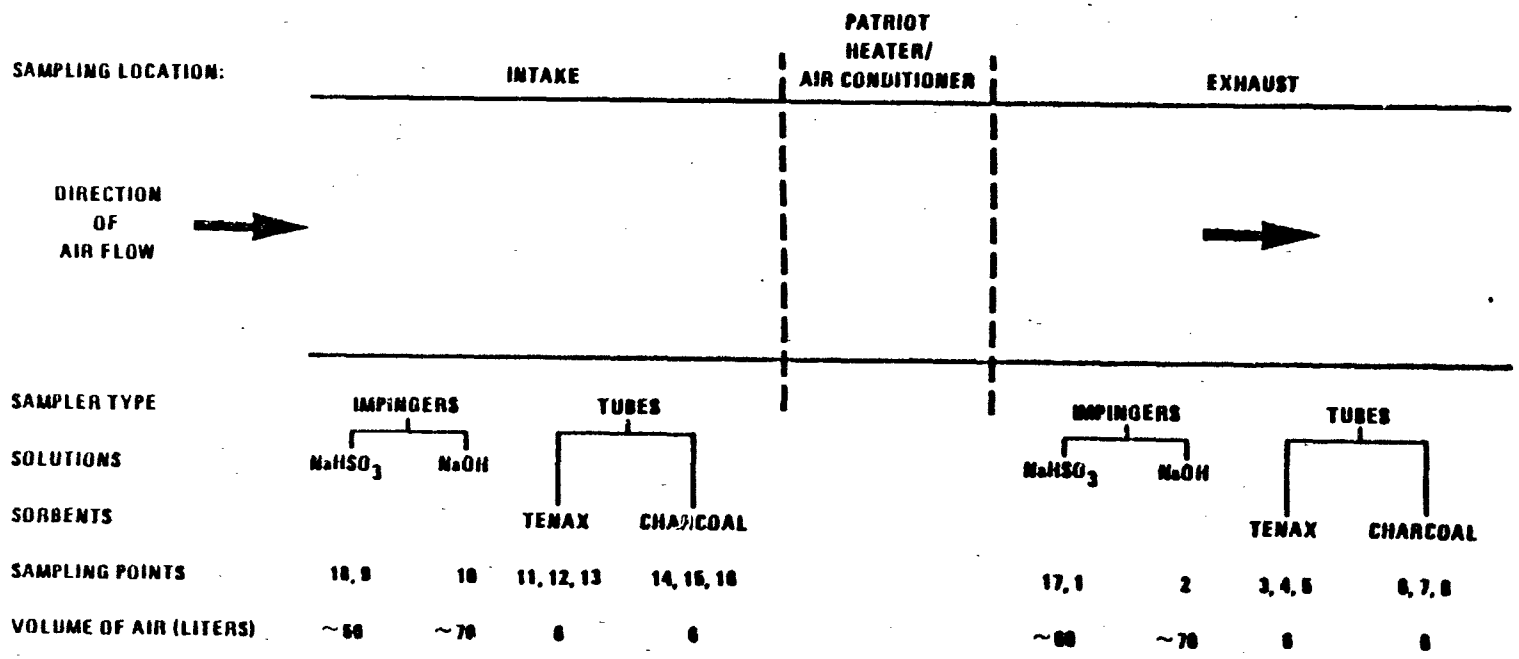
J. Richards*
R. Ronan*
S. Powers*
N. Jurinski*

*Consensus team who participated in the development of the June 11, 1982 test plan.

TABLE 2

PATRIOT HEATER/AIR CONDITIONER PLAN
(June 11, 1982)

TARGET PARAMETER	METHOD OF TRAPPING
1. Acrolein	a) Tenax (cooled) b) NIOSH - $NaHSO_3$ Impinger (cooled)
2. Aromatics (benzene, toluene, etc)	a) Tenax (cooled) b) Charcoal (cooled)
3. General Organics (phthalates, etc)	a) Charcoal (cooled) b) Tenax (cooled)
4. Formaldehyde	a) NIOSH - $NaHSO_3$ Impinger (cooled)
5. HCN - Cyanide	a) NIOSH - NaOH Impinger



SCHEMATIC OF PATRIOT HEATER/AIR CONDITIONER

TABLE 3

SUMMARY OF TOTAL SAMPLES COLLECTED FOR PATRIOT HEATER/ AIR CONDITIONER PER UNIT AND PER FOUR UNITS

	Exhaust	Intake	Blanks Field	Blanks Lab	Recovery Spike	Unit Summary	4 Unit Summary
Hour 1							
Recovery Spike	--	--	--	--	3*	3	3*
Tenax Tubes	3**	3**	3**	3**	--	12	48
Charcoal Tubes	3**	3**	3**	3**	--	12	48
0.1M NaOH	1	1	1	--	--	3	12
1% $NaHSO_3$	2+	2+	2+	--	--	6	24
Hour 2							
Tenax Tubes	3**	3**	--	--	--	6	24
Charcoal Tubes	3**	3**	--	--	--	6	24
0.1M NaOH	1	1	--	--	--	2	8
1% $NaHSO_3$	2+	1	--	--	--	3	12
Hour 3							
Tenax Tubes	3**	3**	1	1	--	8	32
Charcoal Tubes	3**	3**	1	1	--	8	32
0.1M NaOH	1	1	--	--	--	2	8
1% $NaHSO_3$	2+	1	--	--	--	3	12
						74	287

* A recovery spike on Tenax was prepared by Versar and submitted to U.S. AEHA and Raytheon/Skinner & Sherman as well as Versar for analytical analysis during the first unit's operation.

** Duplicate Tenax and charcoal samples, and blanks were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman for analysis.

\+ Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks were collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

TABLE 1

SUMMARY OF TOTAL SAMPLES COLLECTED FOR PATRIOT HEATER/AIR CONDITIONER DESIGNATED AS R3

	Intake	Exhaust	Blanks Field	Blanks Lab	Unic Summary
Hour 1					
Tenax Tubes	3*	3*	3*	3*	12
Charcoal Tubes	3*	3*	3*	3*	12
0.1M NaOH	1	1	1	--	3
1% $NaHSO_3$	2**	2**	2**	--	6
Hour 2					
Tenax Tubes	3**	3**	--	--	6
Charcoal Tubes	3**	3**	--	--	6
0.1M NaOH	1	1	--	--	2
1% $NaHSO_3$	2**	1	--	--	3
Hour 3					
Tenax Tubes	3**	3**	1	1	8
Charcoal Tubes	3**	3**	1	1	8
0.1M NaOH	1	1	--	--	2
1% $NaHSO_3$	2**	1	--	--	3
					71

* Duplicate Tenax and charcoal samples, and blanks were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman for analysis.

** Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks were collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

TABLE 10

RESULTS FOR UNIT 801193 ($\mu g/m^3$)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	<0.01	0.01	0.01
	Toluene	Intake	0.14	--	--
		Exhaust	0.11	0.08	0.05
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	--	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.025	<0.025	<0.025
		Exhaust	<0.025	<0.025	<0.025
1% $NaHSO_3$	Acrolein	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375
1% $NaHSO_3$	Formaldehyde	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

TABLE 11

RESULTS FOR UNIT 801196 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	<0.01	--	--
		Exhaust	<0.01	0.02	<0.01
	Toluene	Intake	0.01	--	--
		Exhaust	0.01	0.03	0.03
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.025	<0.025	<0.025
		Exhaust	<0.025	<0.025	<0.025
1% $NaHSO_3$	Acrolein	Intake	<0.375	<0.375	<0.375
		Exhaust	<0.375	<0.375	<0.375
1% $NaHSO_3$	Formaldehyde	Intake	<0.375	1.60***	<0.375
		Exhaust	<0.375	<0.375	<0.375

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
***Suspect chemical interference.
tr = trace
ND = Not detected

TABLE 12

RESULTS FOR UNIT 801188 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	0.01	0.02	0.01
	Toluene	Intake	0.04	--	--
		Exhaust	0.08	0.03	0.04
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	tr
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060
1% $NaHSO_3$	Formaldehyde	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

TABLE 13

RESULTS FOR UNIT 801185 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	0.01	--	--
		Exhaust	0.01	0.01	<0.01
	Toluene	Intake	0.02	--	--
		Exhaust	0.03	--	--
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	tr	tr
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060
1% $NaHSO_3$	Formaldehyde	Intake	<0.060	<0.060	<0.060
		Exhaust	<0.060	<0.060	<0.060

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

TABLE 2

RESULTS FOR UNIT 801160 (mg/m^3)

	PARAMETER	LOCATION	Hour 1	Hour 2	Hour 3
Tenax* Tubes	Benzene	Intake	<0.01	--	--
		Exhaust	<0.01	<0.01	<0.01
	Toluene	Intake	0.02	--	--
		Exhaust	0.04	--	--
	Trichloroethlene	Intake	tr	--	--
		Exhaust	tr	--	--
Charcoal** Tubes	General	Intake	ND	ND	ND
		Exhaust	ND	ND	ND
0.1 NaOH	HCN	Intake	<0.020	<0.020	<0.020
		Exhaust	<0.020	<0.020	<0.020
1% $NaHSO_3$	Acrolein	Intake	<0.06	<0.06	<0.06
		Exhaust	<0.06	<0.06	<0.06
1% $NaHSO_3$	Formaldehyde	Intake	<0.06	<0.06	<0.06
		Exhaust	<0.06	<0.06	<0.06

* Primarily GC/MS
** Primarily GC/FID (supported GC/MS).
tr = trace
ND = Not detected

Versar inc.

RESULTS AND CONCLUSIONS
FOR
TARGET PARAMETERS
FOR
801193/801198/801188/801185/801160

Target Parameter	Result	Conclusion
Acrolein	None Found	*
Aromatics	Traces Benzene Traces Toulene Traces Trichloroethylene Traces Ethylbenzene	*
General Organics	None Found	*
Formaldehyde	None Found	*
Hydrogen Cyanide	None Found	*

*None of the target parameters are present in the high heat mode discharge air in the sampling configuration tested.

Versar inc.

	R1	R2	R3	V1	VA	VB	BC	VD	VR3
Materials Above TWA	No	No	ACROLEIN	No	No	No	No	No	No
Organics Found Below TWA	YES	YES	YES	YES	YES	YES	YES	YES	YES
Inorganic Found Below TWA	No	No	No	No	No	No	No	No	No

TABLE 5

VOLATILE ORGANICS DETERMINED BY THE APPROVED EPA METHODOLOGY METHOD 624 AND THEIR CORRESPONDING TIME WEIGHTED AVERAGES (TWA[1]) AND DETECTABLE AMOUNTS

Volatile Organics	TLV-TWA[2]	Cons. (ppm) air
Chloromethane	100	<0.01
Bromomethane	20	<0.01
Vinyl Chloride	1.0	<0.01
Chloroethane	1000	<0.01
Methylene Chloride	500	<0.01
Acrolein	0.1	<0.01
Trichlorofluoromethane	1000	<0.01
Acrylonitrile	2.0	<0.01
1,1-Dichloroethylene	—	<0.01
1,1-Dichloroethane	100	<0.01
Trans-1,2-dichloroethylene	200	<0.01
Chloroform	10	<0.01
1,2-Dichloroethane	50	<0.01
1,1,1-Trichloroethane	350	<0.01
Carbon Tetrachloride	10	<0.01
Bromodichloromethane	—	<0.01
1,2-Dichloropropane	75	<0.01
Trans-1,3-Dichloropropene	—	<0.01
Trichloroethylene	100	<0.01
Benzene	1.0	<0.01
1,1,2-Trichloroethane	10	<0.01
Cis-1,3-Dichloropropene	—	<0.01
Dibromochloromethane	—	<0.01
Bromoform	0.5	<0.01
Tetrachloroethylene	100	<0.01
1,1,2,2-Tetrachloroethane	5.0	<0.01
Toluene	200	<0.01
Chlorobenzene	75	<0.01
Ethylbenzene	100	<0.01
2-Chloroethyl vinyl ether	—	<0.01

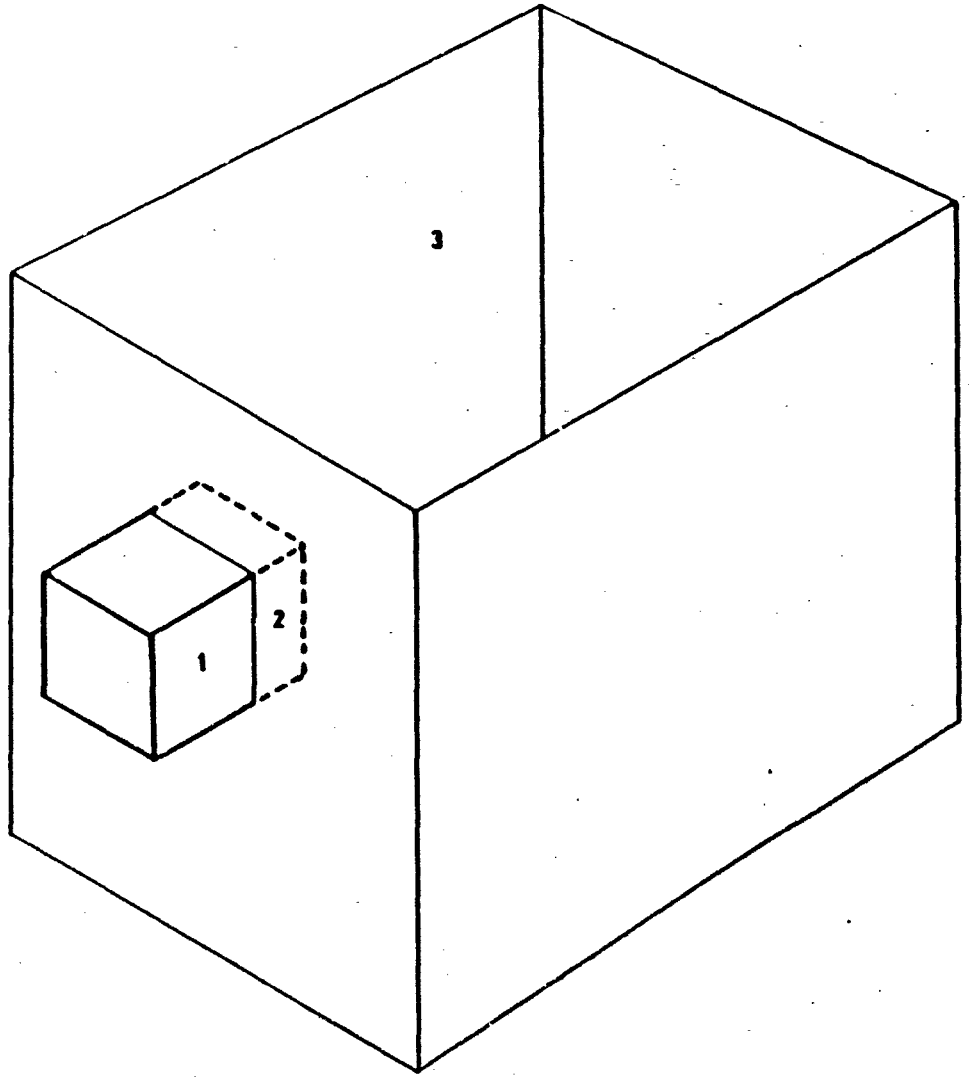
[1] TWA = Time Weighted Average.
(Level in ppm at which worker can be exposed for 8 hours without damage to health, as determined by OSHA.)

[2] NIOSH/OSHA Pocket Guide to Chemical Hazards, Sept. 1978, Reprinted August 1980.

Versar inc.

PATRIOT PARAMETER'S INVESTIGATED

	Inorganic	Organic
R1	No	100's
R2	No	100's
R3	No	100's
V1	HCN, HF, HCl	100's
VA	HCN	100's + Acrolein/Formaldehyde
VB	HCN	100's + Acrolein/Formaldehyde
VC	HCN	100's + Acrolein/Formaldehyde
VD	HCN	100's + Acrolein/Formaldehyde
VR3	HCN	100's + Acrolein/Formaldehyde



H-16

PATRIOT Heater/Air Conditioner
MODEL F-18114-2

	APRIL 1982		MAY 1982	JUNE/JULY 1982					
	R1	R2	R3	V1	VA	VB	VC	VD	VR3
	81013	81014	801160	801191	801193	801198	801188	801185	801160
Odor	?	?	?	YES	No	No	No	No	No
Date			7/81	12/81	12/81	1/82	11/81	11/81	7/81
Run	(184.8hr)	(364.6hr)	?	(9.4hr)	(8.4hr)	(9.0hr)	(9.0hr)	(10.0hr)	(14.2hr)
Tested	3/1	3	1	2	2	2	2	2	2
Personnel Complaints	YES	?	No	YES	No	No	No	No	No
Charcoal Tubes	Yes(3/s)	Yes(s/s)	Yes(s/s)	Yes(v)	Yes(all)	Yes(all)	Yes(all)	Yes(all)	Yes(all)
Tenax Tubes	No	No	No	Yes(v)	Yes(all)	Yes(all)	Yes(all)	Yes(all)	Yes(all)
Cold Traps	Yes(s/s)	No	Yes(s/s)	No	No	No	No	No	No
NaOH	No	No	No	Yes(v)	Yes(v)	Yes(v)	Yes(v)	Yes(v)	Yes(v)
$NaHSO_3$	No	No	No	No	Yes(v/ss)	Yes(v/ss)	Yes(v/ss)	Yes(v/ss)	Yes(v/ss)
Significant Irritant Found	No	No	YES	No	No	No	No	No	No

Versar inc.

RECOMMENDATIONS

1. PATRIOT Unit disassembled by an investigative team (mechanical engineer and environmental scientist)

   —Verify mechanical specifications

   —Find suspect materials that could add irritants to discharge air

   —Test suspect materials over observed operational temperature range

2. Test entire enclosure of the type that caused original incident

   —Develop plan with Raytheon/Skinner & Sherman/U.S. AEHA

   —Improve S&A technique as required

   —Control input air

APPENDIX I

Minutes of Meeting on 21 July 1982

Mr Sherfy
VSE

DEPARTMENT OF THE ARMY
US ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA 22060

AUG 13 1982

DRDME-EPAT

SUBJECT: PATRIOT Air Conditioner Testing for Toxic Gases

Project Manager
PATRIOT Missile System, DARCOM
ATTN: DRCPM-MD-T-C (Mr. Huie)
Redstone Arsenal, AL 35898

1. Attached (Incl 1) for your information are the minutes for the meeting held on 21 July 1982 to discuss the results of Irritant testing of five (5) production PATRIOT Air Conditioners conducted during the period 30 June - 2 July 1982.

2. It should be noted that final reports covering the Irritant testing of these five (5) PATRIOT Air Conditioners were distributed at the meeting.

FOR THE COMMANDER:

Robert M. McKechnie

ROBERT M. McKECHNIE
Development Project Officer
PATRIOT Support Project Office

1 Incl
as

CF:
AEHA (Mr. Doganiero, Cpt Critz, Mr. Valis)
DARCOM, DRCSG (LTC Vorpahl, Mr. Svalina)
Raytheon Co (Mr. Somes)
Comdt, USAADS, ATTN: ATSA-TSM-P, Ft. Bliss, TX 79916
ASD-SE, WPAFB (Mr. Price, Dayton, OH 45433
VSE (Mr. Sherfy, Mr. Adolph)
VERSAR (Dr. Ronan, Mr. Richards)
Skinner & Sherman (Mr. Dalzell)
DRDME-ZS, Safety Office
-UE (Mrs. Gutmann)
-EM (Good)

DEPARTMENT OF THE ARMY
US ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA 22060

DRDME- EPAT

AUG 13 1982

MEMORANDUM FOR RECORD

SUBJECT: Minutes, Meeting to Review Results of Irritant Testing of PATRIOT Air Conditioner, VSE Corporation, 21 July 1982

1. Short concise synopsis of meeting: The results of the irritant testing of five (5) new production PATRIOT Air Conditioners were discussed. Air samples were taken by VSE/VERSAR and the analysis was performed by the Army Environmental Hygiene Agency (AEHA), VERSAR, and Skinner & Sherman. It was concluded that none of the target parameters were present in the air flow from the Air Conditioners when they were operating in the high heat mode and tested to the agreed sampling configuration. The target parameter included acrolein, aromatics (benzene, toluene, etc), general organics (phthalates, etc), formaldehyde and HCN-Cyanide. A follow-on test program was proposed.

2. Personnel Present. See attached list.

3. Background:

a. In a meeting on 8 June 1982 between representatives of MERADCOM, AEHA, VSE, VERSAR, Raytheon, and Skinner & Sherman, a draft test plan was initiated. This was later finalized into a coordinated test plan which included a summary of the proposed sampling program, summary of samples to be collected and anlayzed by the three laboratories and the analytical methodologies to be used for analyses of the agreed on parameters.

b. Tests on four (4) production PATRIOT Air Conditioners began at VSE Corp. facility on 30 June 1982 and was completed on 2 July 1982. Tests were accomplished on the fifth (5) Air Conditioner on 15 July 1982. This fifth Air Conditioner (S/N 801160) had been tested in April 1982 by Skinner & Sherman and was found to exhibit a high level of acrolein when operated in the high heat mode.

4. Discussion:

a. VERSAR did a complete review of various methods and techniques that were used in obtaining samples of air in the testing of the five (5) PATRIOT air conditioners. They included explanations of the many precautions which they took to be assured that the gas samples taken were not contaminated and that the samples clearly represented the content of the air as it entered and exited from the PATRIOT air conditioner.

b. Considerable coordination was required between the three laboratories as they finalized and agreed on the test and sampling plan. This close coordination effort also was required during the analysis of the samples.

c. The result of the analysis performed by AEHA, VERSAR, and Skinner & Sherman indicated that none of the target parameters were produced by or from any of the five (5) PATRIOT air conditioners tested by VERSAR at the VSE Corp facility. These target parameters included acrolein, aromatic organic compounds, general organics, formaldehyde and hydrogen cyanide.

d. Complete reports on the results are on file in the PATRIOT Support Project Office.

5. Conclusion. The meeting concluded that:

a. Acrolein, hydrogen cyanide and the other target parameters were not produced by or from any of the PATRIOT Air conditioners tested.

b. Further effort should be expended in examining the various materials in the PATRIOT air conditioner to determine if there are any breakdowns in the material at the temperatures which the materials are exposed to within the air conditioner when it is operating in the high heat mode.

6. Actions: It was recommended that the following actions be initiated in an effort to resolve this potential problem of irritant gases from the air conditioner:

a. PATRIOT Air Conditioner:

(1) Temperature and air flow survey when unit is operating in high heat mode with the overtemperature device shorted out.

(2) Same as a(1) except that the right outlet port shall be blocked.

(3) Identify and analyze the various materials that could add irritants to the discharge air within the temperature range determined above.

(4) Review manufacturing process on foam to determine if acrolein or other irritant gases could be entraped in the material.

b. PATRIOT CRG Shelter: Conduct a sampling and analysis test on the CRG shelter with air conditioner (S/N 80113) to determine the existance of irritant gases.

Based on results of tests, make the necessary recommendation that would allow the air conditioners to be operated in the high heat mode.

DRDME-EPAT
MEMORANDUM FOR RECORD

George F. Sams

GEORGE F. SAMS
VSE Corporation

Robert M. McKechnie

ROBERT M. McKECHNIE
Development Project Officer
PATRIOT Support Project Office

I-4

July 21, 1982

DISCUSSION OF IRRITANT GAS TEST
ON PATRIOT AIR CONDITIONERS

ATTENDEES	REPRESENTING	PHONE NUMBER
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APPENDIX J

Test Plan for Task 1 and Task 2

2. TASK 1 - RECOMMENDATIONS 1 AND 2

2.1 Mechanical and Material Investigation of a PATRIOT Heater/Air Conditioner.

Based on all information at the July 21, 1982 Review, it was recommended that a detailed investigation of the design and material in the heater portion of a typical unit be carefully checked by a team of experts. Recommendations 1 and 2 (Table 2) cover all specific concerns mentioned. Task 1 will implement those recommendations. In this section of the Plan the makeup of the Investigative Team and the details of approach, materials choice and criteria, and analytical methods will be defined. The objective of this task is to define possible sources of chemical irritant production in a unit in the heating (or high heating) mode. The unit chosen for detailed review is the new unit tested by Raytheon/Skinner & Sherman and later by VSE/Versar Inc. and has SN 801160. The unit will be carefully reviewed by the investigative team and equivalent materials purchased and tested.

2.2 Development of Investigative Team.

The Investigative Team will be composed of experts who will be able to pinpoint sources of chemical irritants in the heated zones within Unit 801160. The team will be composed of engineer expertise provided by Raytheon and VSE; Chemical expertise (both material and toxological) will be provided by U.S. AEHA, Skinner & Sherman, and Versar. The following team makeup has been suggested:

Raytheon	- A. Granese
VSE	- R. Sherfy
U.S. AEHA	- G. Esposito, B. Valis
Skinner & Sherman	- H. Dalzell
Versar	- R. Ronan, J. Richards, C. Carter, S. Powers

Additional persons from all participating organizations might be added between now and the inspection date of August 9, 1982 as required.

2.3 Mechanical and Electrical Review

The major task in the mechanical and electrical review will be the disassembly of a unit by the investigative team. This is intended to pinpoint any problems with the design or construction of the units which could result in the release of irritants or toxicants. In order to do this the investigative team will verify adherence to the mechanical, electrical and material specifications as set forth in MIL-A-52963 (ME) and related documents. The investigative team will note any suspect materials (plastics, elastomers, insulation, paint) which may come in close proximity to the heating rods.

A preliminary inspection was done to begin the process of material collection. Bob Sherfy of VSE and Charles Carter of Versar conducted a preliminary inspection of a unit on July 28, 1982. This inspection identified a number of components present in the heater side of the PATRIOT units which contain organic polymers. The military specifications covering these components will be obtained and the materials in the components will be specified. This information will be supplied to the Investigative Team before the disassembly of a unit begins. Special attention will be paid to those materials which are in close proximity to the heating rods.

The unit which is used for nondestructive disassembly will also be used to study the temperatures attained at various locations (approximately 12 locations) in the unit under a number of operating conditions. The location and number of the points where thermocouples will be placed will be chosen by the investigative team performing the disassembly. The proposed operating conditions are:

1. normal high heat mode
2. normal high heat mode with 50% of the discharge air blocked
3. high heat mode with the safety temperature sensor bypassed.

The normal high heat mode is chosen because it will be a common operating situation during cold weather. During the preliminary inspection Bob Sherfy described a second condition that can cause the flow of discharge air to decrease if there is no place for air to escape from the CRG. In this case the abmient pressure inside the CRG increases to an extent where the net flow from the heating unit is reduced substantially. This could cause increased temperatures inside the unit and thus the second set of conditions have been chosen. Bob Sherfy also noted that 50% of the units have the air intake on the same side of the unit as the safety temperature sensor. This could cool down the temperature sensor, allowing the rest of the unit to reach higher temperatures than expected. The third set of conditons will simulate these conditions and all conditions used in tests to date.

The temperature sensing probes will be installed after the investigative team has disassembled the unit. This will assure that the investigative team is inspecting a unit which is representative of one as it would arrive directly drom the manufacturer. VSE will study the air flow characteristics of the unit in conjunction with the temperature study.

2.4 Material

Many organic based materials in the units were noted in the preliminary inspection done by Sherfy and Carter. Versar is currently obtaining the military specifications on these materials. The actual chemical identity of the materials will be obtained from the military specifications and from the manufacturers and/or suppliers of the materials. Other materials noted by the Investigative Team will be handled in an identical manner.

The most abundant organic material in the unit is the polyvinylchloride-acrylonitrile black insulating foam. Since this is present in large quantities, Versar will obtain detailed information concerning the materials and processes used in the manufacture of this material.

Once the chemical identities of the materials in the unit are known it will be possible to make preliminary determinations of the potential thermal degradation products of the materials. Literature sources will be consulted to determine the probable products.

2.5 Thermal Degradation Experiments

Two different types of thermal degradation experiments are planned. The first will determine the extent of outgassing and breakdown of various organic materials in the units at temperatures expected in the units. The second experiment will determine decomposition products at much higher temperatures than those expected during normal operation. This will simulate the accidental direct contact of one of these materials with the heating rods. Both experiments will be done at ambient air pressure.

2.5.1 Operating Temperature Experiment

The first experiment will simulate the behavior of the various materials during normal operation of the units. This experiment is intended to determine whether any irritants or toxicants will be released from the materials at the temperatures expected during normal operation. The experiment will be performed as described below.

A known amount of a sample will be placed inside an all glass container. The container will be closed so it is gas tight, and it will be heated in a water bath at ambient temperature and at 180°F (the exact higher temperature will be determined by the Investigative Team). These represent the likely extremes of temperature the unit may experience in

the heating mode. The sample will be held at the specified temperature for 4 hours. At the end of this period the reaction flask will be flushed with ultrapure helium into a trap containing Porapak R (80/100 mesh) or Porapak N (80/100 mesh) held at approximately -78°C. After the flushing is complete the trap will be heated and the compounds (ice-acetone bath) released will be analyzed by GC/MS. Porapak R is suggested because other authors have found it to have a superior efficiency for compounds such as hydrogen cyanide and acrolein than more commonly used sorbents such as Tanax GC.[1] Porapak N is the absorbent suggested by EPA for the analysis of acrolein and acrylonitrile.[2] The final choice of the analytical column will be based on preliminary tests. As many as ten unit materials will be tested by this headspace procedure at two temperatures each. Those which outgas or degrade significantly at the higher temperature will be studied at two intermediate temperatures also, probably 120°and 150°F. The results from this first set of experiments will determine which of the materials may under normal operating conditions release irritants or toxicants.

Special preparation steps will be taken in the case of certain materials. There are a number of adhesives and sealants in the heater/air conditioner unit which should be tested. These materials will be applied to the inside of the flask and will be allowed to dry. At the end of the drying period the epxeriment will be run as usual. While a number of volatile organic compounds will probably be released during the drying process, these are not relevant to the problem at hand. Any operational unit will have been allowed sufficient drying time during the assembly and shipping of the unit to remove these compounds. For some materials it may be necessary to measure the gasses in the headspace during the drying process.

Versar will determine the recoveries of some important compounds with the trapping and analysis system proposed here. A weighed amount of a compound of interest will be spiked into the reaction flask

in the absence of any other materials. The system will then be heated, purged and analyzed as usual. Comparison of the amount added with the amount recovered will indicate the effectiveness of the analytical system. Acrolein and acrylonitrile will definitely be subjected to this procedure. The review of the materials used in the unit may point out other compounds for which recoveries should be tested.

Every experiment will contain a isotopically labeled internal standard or surrogate compound. It is expected that the recoveries of these standards will be somewhat inconsistent because a portion of the internal standard will adsorb to the material being tested. The extent of sorption will depend on the nature of the material and the surface area of the material. Since these will not be the same for all of the materials, the recoveries will change. The presence of the internal standard will, however, detect any gross malfunctions in the analytical system and it will provide a retention time standard for the GC/MS analysis.

2.5.2 High Temperature Experiments

The high temperature experiment will simulate the accidental contact of one of the organic materials with the heating rods. In order to do this, the material will be placed in contact with a metal surface. The surface will then be heated up to a maximum temperature of 1200°F. Versar will construct a metal heating apparatus which is similar to the heating rods used and which can be heated in a reproducible fashion. During the heating ultrapure air at atmospheric pressure will be passed over the material. The air will be passed through a trap of Porapak R held at -78°C (using dry ice). Two chromatographic columns will be used for GC/MS analysis. For the very volatile compounds a column containing Porapak R or a suitable substitute will be used. For the less volatile compounds a fused silica capillary column coated with either OV-1 or SE-54. Other authors have successfully used similar trapping and

analytical conditions to study pyrolysis and combustion products of polymers.[1] Versar will run some preliminary tests to choose the analytical columns.

Approximately ten materials will be tested using this technique. The information obtained from the manufacturers and the military specifications will be used to choose the materials. Some materials that will likely be included are:

- acrylonitrile-vinyl chloride black foam
- tape sealant (sticky black material)
- heater grommet (teflon or silicone bushing on heating rods)
- electric motor paint
- plastic cover on motor harness (cable)
- plastic sleeve on air temperature sensor probe wire.

The configuration of the heating system is a critical variable in these experiments. It should conform as closely as possible to the conditions that may occur in an operating unit. The literature on pyrolysis of polymers shows that the products of pyrolysis will be dramatically different if oxygen is excluded from the system.[3] Another important variable is the length of time a compound spends in the hot zone. If the products of thermal degradation diffuse quickly from the hot surface to a cooler zone, any further reactions will be quenched. If, however, the compounds spend more than 0.5 seconds in the hot zone (1200°F in this case), extensive rearrangements can take place. This will favor the production of aromatic compounds. In the case of a mechanical failure or a manufacturing error in the units it is possible that both cases of the above conditions could apply. If a piece of material is in contact with a heating rod, the products from the section toward the edge of the point of contact would be exposed to oxygen and they could diffuse quickly away from the hot zone. It is likely, therefore, that different products will result from the center of the point of contact than from the edge of the point of contact. The experimental conditions will be chosen to produce both conditions in one experiment.

The available literature indicates that a number of irritants and toxicants will be produced during the pyrolysis and combustion of these materials.[1,4] The information obtained from the high temperature degradation study will reveal any materials which are particularly unsuitable for this application. The experiments will also provide fingerprints of the degradation products of the various polymers. The information obtained here may be helpful in interpreting the data collected from the sampling of the CRG (Task 2).

2.6 Schedule and Milestone Dates

Element	Date	Action/Comment
Plan Development	Friday, July 30, 1982, COB	- Send Draft of Plan
	Monday, Aug. 2, 1982, A.M.	- Plan Received by All Reviews
	Wednesday, Aug. 4, 1982, COB	- Verbal Summary of Comments to Versar (Ronan or Richards)
	Friday, Aug. 6, 1982, COB	- Written Summary of Comments to Versar cc to MERADCOM
	TASK 1	
Preliminary Chemical Review	Wednesday July 28, 1982, 8:30 A.M.	- Preliminary Chemical Investigation to Get Major Materials Ordered (Carter/Sherfy)
Information Collection	Thursday, July 29, 1982, 8:30 A.M.	- Collect Mil Specification and Begin to Order Major Materials - Begin Library Efforts - Begin Laboratory Preparation

Major Review	Monday, Aug. 9, 1982, 8:30 A.M.	- Investigation Team Begins Work at VSE of PATRIOT SN #8U1160 (Continues until Complete)
Lab Work Begins	Monday, Aug. 9, 1982	- Laboratory Thermal Studies Begin (Nominal Date-Work Effort to Begin ASAP)
Draft Report	Friday, Sept. 10, 1982 COB	- Draft Report from Versar Submitted to VSE
Comments	Wednesday, Sept. 15, 1982 COB	- All Comments Review Versar
Final Report	Friday, Sept. 17, 1982 COB	- Final Report Ready for Distribution
Review	Wednesday, Sept. 29, 1982, 8:30 A.M.	- Review Meeting VSE

3. TASK 2 - RECOMMENDATIONS 3, 4, and 5

3.1 Summary of Target Parameters

Versar along with the U.S. Army Environmental Hygiene Agency (U.S. AEHA) and Raytheon/Skinner & Sherman developed a test plan dated June 11, 1982 to monitor four PATRIOT Heater/Air Conditioners to monitor potential irritants released by the unit to the air during the high heat operational mode. This test plan presented target parameters along with sampling and analytical methodologies. The final approach to sampling and analysis received concurrence by all members of the Test Plan Development Coordination Team as assembled on June 11, 1982. The target parameters selected were:

- Acrolein
- Aromatics (less than 120 molecular weight)
- General Broad spectrum organic analysis
- Hydrogen cyanide
- Formaldehyde/acrolein

All testing conducted during late June and July on the PATRIOT Heater/ Air Conditioner units was performed for the target parameters above.

For the development of this Test Plan to collect air samples in the CRG shelter with PATRIOT Heater/Air Conditioner installed, the coordination team has reviewed the previous analytical results for the target parameters and have made several recommendations to be incorporated into the sampling and analysis test plan.

The first recommendation for the target parameter list was to collect samples for all of original target parameters. Modification in sampling and analytical methodologies may be made to further ensure representative samples are being collected.

The second recommendation was to include the general class of compounds called amines/polyamines as recommended target parameters. There was concern by members of the coordination team, that amines may be

present in components near the heater box area and may be out-gassed when exposed to heat. Therefore, sampling and analysis of this general class of compounds has been included in the new test plan.

The final recommendation by the coordination team to expand the target parameter list, was the addition of in situ monitoring for carbon monoxide and carbon dioxide gases. These gases will be monitoried during testing of other target parameters using EPA, APHA, and NIOSH approved methodologies. The concern for the inclusion of these target parameters is that previous incidents in similar type of shelters have shown that the resultant problems were probably caused by high levels of either carbon monoxide or carbon dioxide.

With the incorporation of these additional targets into this test plan for the CRG sampling, it is felt by the concensus team that all chemical parameters of concern will be sampled and found if present. The following sections present the sampling plan, and analytical methods for each target parameter as performed by Versar, Skinner & Sherman and U.S. AEHA. In addition, Versar's approach to perform the method validation study of NIOSH P&CAM 211 for acrolein, and schedule for accomplishing this plan. Taken together these actions cover Recommendations 3, 4 and 5 stated in Table 2.

3.2 Sampling

All sampling procedures will be either recommended or approved EPA, NIOSH, or APHA methods for the target parameters of interest. Air samples will be collected for the following chemical constituents and general groups:

- Acrolein
- Aromatics (less than 120 nolecular weight)
- General organics (broad spectrum analysis)
- Formaldehyde/acrolein
- Hydrogen Cyanide
- Armines and polyamines
- Carbon monoxide and carbon dioxide gas

During previous discussions for the planning of sampling activities to be conducted at VSE on the four PATRIOT Heater/Air Conditioners, agreement was reach among VSE, Versar, U.S. AEHA, Raytheon and Skinner & Sherman as to the most appropriate sampling media to collect the target parameters on originally identified in the June 11, 1982 test plan. The target parameters and sampling medium for each, as originally agreed upon are presented below:

- Acrolein - Tenax trap colled to 70°F
- Aromatics and General Organics - Activated charcoal trap cooled to 70°F.
- Hydrogen cyanide - 0.1M NaOH impinger solution.
- Formaldehyde/acrolein - 1% sodium bisulfite impinger solution.

In addition, the following paramters were recommended at the July 21, 1982 meeting by the various organizations involved in the development of this test plan. These new target parameters and their respective medium are :

- Amines and polyamines - acidified isopropanol mixture.
- Carbon monoxide - continuous direct measuring CO air monitor.
- Carbon dioxide - long-term dosimeter tube.

All of the above procedures will be reviewed by VSE, Versar, U.S. AEHA, Raytheon/Skinner & Sherman to ensure their applicability to efficiently collect the target parameters. If changes are recommended, they will be reviewed and considered for incorporation into the final test plan.

The sampling will be conducted on the CRG shelter in White Sands, New Mexico, during the week of August 23, 1982. The sampling excursion will be conducted in three phases over a 2-4 day period. Phase one will consist of a complete inspection of the CRG, the PATRIOT Heater/Air Conditioner, and a visual inspection of all components of the shelter. This complete inspection will document existing conditions before actual testing in the high heat mode. The second phase, will be testing for a 2- to 4-hour period to determine if irritants are present

shelter operating parameters (i.e., during the air conditioning mode). The third phase will be testing of the CRG shelter with the PATRIOT Heater/Air Conditioners in the high heat mode. These tests will be conducted over a 4-hour period. Each sample set will be of a one-hour duration.

Versar proposed to draw air through the various sampling media at the rates presented below:

- "Porapak" - 300 - 500 ml/minute; total sample 30-60 liters
- Tenax Traps - 300 - 500 ml/minute; total sample 30-60 liters
- Charcoal Traps - 500 - 1000 ml/minute; total sample 30-60 liters
- 0.1 M NaOH - 1000 ml/minute;total sample 60 liters
- 1% $NaHSO_3$ - 1000 ml/minute; total sample 60 liters
- Acidified isopropanol - 1000 ml/minute; total sample 60 liters

The sampling rates for the various media are thos recommended either by NIOSH, or agreed upon by all the test plan participants. The sampling design and summary of sample numbers are presented in Table 3. Triplicate samples will be taken for all Tenax, "Porapak" and charcoal traps for submission of a complete sample set to both U.S. AEHA and Skinner & Sherman for analysis as required. Duplicate acrolein samples collected in the 1% $NaHSO_3$ solution will be collected for analysis by Skinner & Sherman. The samples to be taken will completely characterize the exhaust air of the PATRIOT Heater/Air Conditioner, the air found in the CRG shelter during each hour of testing, and establish a baseline for ambient conditions in the CRG shelter. Samples to determine make-up air will be collected for acrolein and general organics only.

3.3 Analysis by Target Parameter - Versar

Organics analysis will be performed by GC/MS and GC/FID analysis. The following general requirements for the GC/MS or GC/FID calibration and quantitation are specified for all analysis to be performed. The guideline protocols to be used for these analyses are

TABLE 3

SAMPLING DESIGN FOR AIR SAMPLES COLLECTED IN THE CRG SHELTER EQUIPPED WITH THE PATRIOT HEATER/AIR CONDITIONER

	Shelter Air	Make-Up Air	Blanks Field	Blanks Lab	Recovery Spike	Hourly Summary	4-Hour Summary
Hours 1,2,3, & 4							
Recovery Spike	--	--	--	--	3*	3*	3
Tenax Tubes	3**	3**	3**	3**	--	12	48
"Porapak"	3**	3**	3**	3**	--	12	48
Charcoal Tubes	3**	3**	3**	3**	--	12	48
0.1 M NaOH	1	1	1	--	--	3	12
1% $NaHSO_3$	2+	2+	2+	--	--	6	24
Isopropanol	1	1	1	--	--	3	12
CO/CO_2++	1	--	--	--	--	1	4
				TOTAL SAMPLES		52	201

* A recovery spike on Tenax will be prepared by Versar and submitted to U.S. AEHA and Raytheon/Skinner & Sherman as well as Versar for analytical analysis.

** Duplicate samples and blank traps will be collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman.

\+ Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks will be collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

++ Carbon monoxide (CO) will be monitored continuously and carbon dioxide will be monitored using a dosimeter.

those established by NIOSH and EPA. The protocols are: EPA Methods 624 and 625 published in the Federal Register/Vol. 44, No. 233/Proposed Rules; and Method 127, "Organic Solvents", published in the NIOSH Manual of Analytical Methods, Second Edition, Vol. 1, April 1977. All Tenax and Porapak traps will be spiked with surrogate compound to assure and define accuracy of performance.

GC/MS calibration requirements will be those of EPA Method 624/625 and ion abundance criteria for either bromofluorobenzene (BFB) or decafluorotriphenyl phosphine (DFTPP) listed in Table 4. Quantitation will be performed from 3-point curve standard calibrations from standards spiked onto blank Tenax or charcoal traps and analyzed by the same technique as samples. The mass spectrometer will be set to scan from 20 amu to 450 amu at 0.75 second per scan.

3.3.1 Acrolein

3.3.1.1 1% $NaHSO_3$ Impinger Solutions

Acrolein samples will be collected following NIOSH Method No. P&CAM 211 using two midget impingers containing approximately 15 ul of solution which is cooled to 4°C (this is the same solution used for formaldehyde). The solution will be 1% $NaHSO_3$. This methodology will be validated and detections limits established as described in Section 6 of this plan. Analysis will be performed on site to assure no loss by remaining in the solution too long.

3.3.1.2 Sorption Studies

Because of the zero recovery of acrolein from both method studies in the July 16, 1982 PATRIOT Report, it has been decided to study the use of Porapak N or R, or Tenax/Ambesorb sorbent traps for acrolein analysis. A spike recovery study will be done in the laboratory under conditions which emulate the expected conditions in the CRG. Analysis will be performed by GC/MS using a 6 foot Chromosorb 101 GC column under

TABLE 4

GC/MS PERFORMANCE STANDARD REQUIREMENTS
Bromofluorobenzene (BFB) 20 ng
Method 624

m/e	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% relative abundance
173	less than 1% of mass 95
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 50% of mass 95
177	5-9% of mass 176

DECAFLUOROTRIPHENYL PHOSPHINE (DFTPP) 50 ng
Method 625

m/e	Ion Abundance Criteria
51	30-60% of mass 198
68	less than 2% of mass 69
70	less than 2% of mass 69
127	40-60% of mass 198
197	less than 1% of mass 198
198	base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	less than mass 198
442	greater than 40% of mass 198
443	17-23% of mass 442

instrumental conditions to be determined in the spiking studies defined above. The surrogate spikes to be used on the final tubes will be acrylonitrile D3.

3.3.2 Aromatics

Aromatics will be sorbed on Tenax traps, "Porapak" traps, and charcoal traps. The Tenax and "Porapak" traps will be prepared by Versar and blanks will be supplied to participating laboratories to validate background (12 hr at 250°C with 5 ml/min 99.999% He). The charcoal tubes will be on NIOSH standard commercial tubes supplied by SKC Inc. following collection at reduced temperatures they will be preserved at 4°C in individually sealed test tubes prior to analsysi.

Analysis of the Tenax and "Porapak" traps will be by flash heating each tube (170°C for 5 min for Tenax). The effluent of each trap is injected onto the head of a 6 foot x 2 mm ID glass Chromosorb 101 GC column with a carrier flow rate of Helium at 30 ml/min. These conditions as based on Tenax trap experience and similar conditions will be developed for the "Porapak" traps. Retention times and other instrumental specific information is defined in the July 16, 1982 PATRIOT Report. The surrogate spike to be used for aromatics is chlorobenzene D4.

Analysis of charcoal tubes will be by GC/FID (with GC/MS for all confirmation) analysis using a 20 foot 1/8" stainless steel column packed with 10% SP-1000 on 80/100 mesh Suplecoport. The oven will be prepared to hold 100°C for two minutes following injection and is programmed to 270°C at 8°C per minute. The elevated final temperatures is used to chromatograph the phthalate esters targeted for analysis. The GC/MS confirmation will be performed by injection onto a 60 meter SE 54 fused silica capillary column. The sample is injected onto the head of the column at 45°C and then programmed to 275°C at 10°C/min. The condition for analysis are presented in the July 16, 1982 PATRIOT Report.

3.3.3 General Organics

General organics will be determined simultaneously with the aromatics as this class of organics is trapped and desorbed from Tenax, "Porapak" and charcoal. The surrogate compounds to be used for general organic spiking are Naphthalene D8, Chyrsene D12.

3.3.4 Formaldehyde

Formaldehyde will be collected following NIOSH Method No. P&CAM 125. A total of 60 liters of air will be drawn through two midget impingers containing approximately 15 ml of 1% $NaHSO_3$ solution, cooled to 4°C. This solution is also used for acrolein. The standard colorimetric procedure will be followed.

3.3.5 Cyanide

Cyanide as hydrogen cyanide will be collected following NIOSH Method No. P&CAM 116 using midget impingers containing 10-15 ml of 0.1 M sodium hydroxide (NaOH). Air will be drawn through the impinger at a rate of 1 liter per minute for 60 minutes. The control and samples will be stored in a refrigerator overnight at 4°C and allowed to equilibrate to room temperature prior to analysis. The Orion meter will be calibrated to standard reference material using a cyanide specific electrode.

3.3.6 Amines in Air

Primary and secondary amines in air can be determined with APHA Method 124. Tentative method of Analysis for Primary and Secondary Amines in the Atmosphere (Ninhydrin Method). Amines in the atmosphere are collected in an impinger solution of acidified isopropanol. The absorbing solution is reacted with ninhydrin (1,2,3,-Triketohydrindene). Primary and secondary amines produce a purple complex whose absorbance is read at 575 nm and compared to a calibration curve prepared from

n-butylamine standards. The concentration of amine in the original air sample is expressed as mg/m^3 n-butylamine vapor when the amine identity is unknown. When using 10 ml of absorbing solution, a 30 liter air sample will provide a limit of detection equivalent to 1.3 mg/m^3 of butylamine vapor. The amine hydrochloride impinger solution is stable over a period of three weeks after collection. Some aminoacids are reported to interfere. Tertiary amines do not react with ninhydrin.

Primary Amine	$R\text{-}NH_2$	i.e.,	methylamine	CH_3NH_2
Secondary Amine	$R_2\text{-}NH$	i.e.,	dimethylamine	$(Ch_3)_2NH$
Tertiary Amine	$R_3\text{-}N$	i.e.,	trimethylamine	$(CH_3)_3N$

3.3.7 Carbon Monoxide - Carbon Dioxide

The carbon monoxide (CO) concentration in the CRG will be continuously monitored during sampling in situ, requiring no laboratory analysis. A Dasibi Model 3003 CO Portable Analyzer will be used to record CO concentrations in the CRG shelter during testing activities. This instrument employs the gas filter correlation technique (EPA Reference Designation No. RFCA-0381-051) to detect CO in the range of 0 to 50 ppm. The TLV is 50 ppm for CO, however, since the CO analyzer provides an instantaneous measurement levels of CO should not exceed the capability of the analyzer. The analog output of the analyzer will be recorded continuously on a strip chart recorder providing a permanent record.

The concentration of CO_2 will be evaluated by using long term dosimeter detection tubes (color detector tubes) over the 4-hour sampling period. These tubes are direct-reading method and will provide a result after 4-hours. This method will not quantify the CO_2 concentration with a high degree of accuracy, however, it will indicate whether the CO_2 concentration reaches a potentially hazardous level and is a NIOSH approved method to determine exposure levels.

3.4 Analysis by Target Parameters - Skinner & Sherman

Raytheon/Skinner & Sherman should list which parameters they plan to analyse and methods details similar to Section 3 above for inclusion in final plan.

3.5 Analysis by Target Parameters - U.S. AEHA

U.S. AEHA should list parameters they plan to analyse and method details similar to Section 3 above for inclusion in final report. The current work load of U.S. AEHA precludes major effort at this time only samples that show positive results are to be confirmed by U.S. AEHA.

3.6 Validation of NIOSH Method P&CAM 211 - Acrolein in Air

To determine the concentration of acrolein in an atmosphere the standard NIOSH Method P&CAM 211 is used. Air is drawn through two midget impingers containing 1% sodium bisulfite ($NaHSO_3$) which will trap the acrolein. Acrolein is determined colorimetrically after reaction with 4-hexylresorcinol in an alcoholic trichloroacetic acid solvent medium in the presence of mercury chloride. The absorbance of the blue colored product, having a strong absorption maximum at 605 nm, is read in a spectrophotometer. The performance of the NIOSH method with respect to detection limit and efficiency of sorption of acrolein will be investigated.

NIOSH reports that 0.01 ppm of acrolein can be determined in a 50 liter air sample. To establish the lowest concentration of acrolein which may be distinguished from zero, a series of measurements of a standard acrolein solution, the concentration of which is distinctly above, but close to the blank abosrbance, must be run. The detection limit will be defined as the concentration of acrolein which would yield an absorbance equal to twice the standard deviation of the measurements of the dilute acrolein standard solution. Absorbances from seven replicates of a 1 to 2 microgram standard acrolein solution is sufficient to calculate the detection limit.

Efficiency of collection of acrolein is reported to be approximately 95% when two impingers are used in series. The NIOSH procedure suggests an air sampling rate of 2 liters/min for a duration of one hours. To determine if acrolein is stripped from the 1% $NaHSO_3$ impinger solutions, 10 replicate solutions will be spiked with acrolein at 2.5x and 5x and 10x the detection limit. Five solutions at each spike level will be sparged with air for 60 minutes at a rate of 2 liters/min. The remaining five solutions at each spike level will not be sparged and will

serve as controls. Colorimetric analysis of each impinger solution will show if losses occured during sampling. A similar, but smaller, scheme will be performed to duplicate Versar's sampling technique where air is sampled at a rate of 1 liter/min for a duration of 60 minutes through two midget impingers.

By statistically determining the method detection limit and examining the stripping potential associated with the collection method. Statements concerning the validity of NIOSH Method P&CAM 211 - Acrolein in Air can be made.

3.7 Schedule and Milestone Dates

Element	Date	Action
Plan Development	Friday, July 30, 1982, COB	- Send Draft of Plan
	Monday, Aug. 2, 1982, A.M.	- Plan Received by All Reviews
Wednesday, Aug. 4, 1982, COB		- Verbal Summary of Comments to Versar (Ronan or Richards)
Friday, Aug. 6, 1982, COB		- Written Summary of Comments to Versar cc to MERADCOM
	TASK 2	
Order New Materials	Wednesday, July 28, 1982	- Review all Required Material and Order as Required
Methods Test	Monday, Aug. 2, 1982	- Begin NIOSH 211 Validation - Review and Prepare
	Other Methods as Required	
Begin CRG Testing	Tuesday, Aug. 24, 1982	- Implement Approved Plan - Do Field Analysis

Ship Samples	Thursday, Aug. 26, 1982	- Ship Samples to Laboratories
Begin Analysis	Monday, Aug. 30, 1982	- Begin Laboratory Analysis
Complete Draft Report	Friday, Sept. 17, 1982	- Draft Report from all Labs to VSE
Comments	Wednesday, Sept. 22, 1982, COB	- To Versar
Final Report	Friday, Sept. 24, 1982, COB	- Versar Compiles and Distributes
Review	Wednesday, Sept. 29, 1982, 8:30 A.M.	- Review Meeting VSE

APPENDIX K

Test Data - Task 1 and Task 2

2.0 TASK 1 - RECOMMENDATIONS 1 & 2 (Summary)

The Investigative Team inspected two heater/air conditioner units and noted design and manufacturing problems. The team also identified materials in the units which could conceivably release irritants or toxic materials when heated. One of the units inspected was missing a piece of reflective aluminum intended to protect the insulating foam from high heat. The investigative team concurred that this was a serious omission and that quality control procedures should be tightened so this can be prevented in the future.

The temperatures attained in various areas of the heater box were measured under a variety of conditions. The maximum temperature measured on any surface in the unit was 246°F.

A number of materials used in the units was heated and tested for the presence of outgassing products. At normal operating temperatures, only two materials released any compounds of concern. The adhesive released toluene, and the insulating foam released carbonyl sulfide, carbon disulfide and benzene. The quantities of products released will probably not be hazardous at normal operating temperatures.

Two materials (tubing and foam) were tested for outgassing products at temperatures significantly higher than the worst case temperature agreed to by the Investigative Team (i.e., 340°F rather than 280°F). These tests were untaken to simulate possible outgassing effects if major overheating occurred, as was apparent in the first units tested at Fort Bliss, Texas (see Section 2.3.4). The quantities of compound released from the foam at 340°F could pose a hazard to personnel in the CRG.

2.1 Results of Investigative Team

The members of the Investigative Team (Table 2-1) met at VSE Corp. on August 9, 1982 to inspect one of the PATRIOT Heater/Air Conditioners. Two units were non-destructively disassembled, and the

TABLE 2-1

INVESTIGATIVE TEAM FOR IRRITANT TESTING
OF PATRIOT HEATER/AIR CONDITIONERS

MEETING OF AUGUST 9, 1982

NAME	ORGANIZATION
F. Good	MERADCOM
R. Ronan	VERSAR
C. Carter	VERSAR
D. Topping, Jr.	VERSAR
S. Powers	VERSAR
A. Granese	RAYTHEON
H. Dalzell	SKINNER & SHERMAN
G. Esposito	AEHA
Maj. C. Moore	AEHA
G. Sams	VSE
R. Adolph	VSE
B. Caldwell	VSE

Investigative Team looked for design and manufacturing flaws. The team noted the materials inside the units which could conceivably release irritants or toxic compounds when heated.

2.1.1 Physical Review

A preliminary inspection of a Heater/Air Conditioner unit (SN 81015) by Bob Sherfy (VSE) and Charles Carter (Versar) on August 4, 1982 identified a number of organic based materials. A list of these materials was presented to the Investigative Team as an aid in the inspection. This list is presented in Table 2-2. After the inspection on August 9, 1982, the Investigative Team decided to narrow the materials tests to include only five materials which, due to the amounts used in the units and the proximity of the materials to the heating rods, seemed to warrant special concern. These five materials were:

1. Black insulating foam
2. Thermal bulb insulation tape
3. Adhesive for foam
4. Sealer for condensate trap
5. Tubing for condensate drain.

In the process of the inspection of the two Heater/Air Conditioner units the Investigative Team noted that a piece of reflective aluminum shielding was missing from unit SN 801160. This left the black insulating foam on the side of the heating rods uncovered. Since the aluminum is intended to protect the insulation from directly heating by the heating rods, this manufacturing flaw could result in the foam reaching unusually high temperatures.

A number of thermocouples were placed in unit SN 801160 to measure the temperatures attained at various locations in the unit under normal operating conditions. The first test was performed on August 9, 1982. Unfortunately the electrical connections were not made correctly so the heaters were not heating under full power, and the experiment was

TABLE 2-2

LIST OF PARTS AND COMPONENTS

Tubing, pn. 59
dn. 13218E0001-290
Type IV, clear, class 6, general use, MIL ZZ-T-831
Appears to be Tygon 3603

Terminal Quick Disconnect, pn. 11
dn. 13207-E5347-1
Mfg. pn. RA257, Thomas and Betts Corp., Raitan, N.J. 08869
Insulation Sleeve is PVC

Heater-Grommet, pn. 60
dn. 13219E2889
TFE MIL L-P-403, Type and class optional

Top Cover, pn. 17
dn. 13219E9481
Adhesive for insulation and gaskets meets MIL P-15280*
Adhesive sealant (silver polymer on corners) is Silicone RTV type I, MIL A-46106
Insulation, EMI gasketing and non-EMI gasketing, see below

Insulation, pn.
dn.
Form S, Plastic Material Unicellular sheet 1/2 or 1/4 inch. Exposed surface must have skin, inside surface may have skin. Material meets MIL P-15280
Rubatex Corp. R-1800-FS

Electromagnetic Interference (EMI) gasketing pn. 4,10,11,12
dn. 13219E9568-1
Silicone Sponge elastomer, no adhesive on back
Metex Corp., Edison, N.J. 08817

Non EMI gasketing pn. 5,6,8,9
dn. 13219E9528
PVC resin foam, high tack synthetic adhesive on one side,
Norton Co., Tape Division and Sealant Operation, Grainville, N.Y. 12832
Specifications state that it is stable to 180°F

Table 2-2 (Continued)

Heating Elements, pn. 57
dn. 13219E9554-1
Crimp type terminals meet MIL-T-7928
Specifications state that leads should be manganese nickel with asbestos insulation. Insulation on unit SN 81015 appeared to be plastic material
Electrical leads sealed with Silicon Seal, GE Dry Film 88 air drying varnish
Chromalox rods manufactured by Wiegand, E.L., Div of Emerson Electronics, Pittsburgh, PA 15208, (Rm 1041, 4 Allegheny Center 412-323-3900)
Specifications call for glass sleeving insulation

Motor, pn. 47
dn. 13221E9096
Bearings lubricated from -60 to +160°F
Finish is MIL Std 186, finish #50.3
Class H insulation defined per NEMA std. MG-1
Varnish on motor windings MIL V-173 containing copper 8-quinolate
IMC Magnetics Corp., Eastern Div., Westbury, Long Island, N.Y. 11591 516-334-7070, mfg pn. PN-BT-5315

Air Temperature Sensor Probe
dn.
Lead wire fiberglass insulated, lead wire guard is teflon
Fenwal Inc., Water Kidde and Co. Ashland, MA 01721
617-881-2000, mfg pn. 28-250706-304

Male disconnect splice
dn.
Vinyl sleeve, Thomas and Betts, Elizabeth, N.J.
mfg pn. RB-14-250

Housing, Evaporator Section
dn.
Sealer, pn. 62, dn 13211E3465
Adhesive, pn. 61, meets MIL P-15280*
Adhesive, pn. 60, Silicone RTV, meets MIL-A-46106

TABLE 2-2 (Continued)

Thermal Bulb Insulation, pn.
dn. 13219E9543
Insulation tape (gummy black material) Synthetic rubber-refined asphalt filled with virgin cork and inert fillers. Temp range from -20 to +158°F continuous, +200°F for one hour
Inmont Corp., 1218 Central Industrial, St. Louis, MO. 63166

Over Temperature Switch pn. 55
dn. 13216E6224
Plastic housing, Therm-O-Disc Inc., 1320 S. Main St., Mansfield, OH 44907, mfg pn. HLAS4947

Notes: pn. is part number from drawings of unit
dn. is the drawing number of the particular part
The manufacturers listed above are only the suggested sources, not necessarily the actual manufacturer for these units.
* This is apparently a typographical error in the drawings for the Heater/Air Conditioners. MIL P-15280 describes plastic materials, not adhesives. The adhesive used is Scotch Green Adhesive, 4518, according to George Sisk and David Groves of Keco Industries.

aborted. The experiment was successfully conducted on August 11, 1982 by C. Carter and D. Topping, Jr. (Versar), R. Sherfy and R. Adolf (VSE). This experiment is described below.

2.1.2 Thermal Experiments

On August 11, 1982 experiments were performed to determine the typical operating temperatures attained in various locations inside the PATRIOT Heater/Air Conditioners. Seventeen thermocouples were placed in one unit, and extensive measurements were taken under a variety of conditions. Following this experiment four thermocouples were placed in a second unit, and this unit was tested under two operating conditions.

First Unit

The serial number of this unit was SN 801185. The shipping date was November 1981. For the purposes of this discussion the front of the unit is that side which faces the front of the CRG truck when it is installed. The front bulkhead has a shield of reflective aluminum which faces the heating elements. If one is standing at the back of the unit the heating elements are situated on the back, toward the right side of the unit. On unit SN 801185 the fresh air intake was on the left side and the over-temperature switch was on the right side (closest to the heating elements). The locations of the seventeen thermocouples in unit SN 801185 are described below. The thermocouples were fastened to the unit with epoxy except where noted. This resulted in the measurement of an actual surface temperature as opposed to an air measurement very near the surface.

Placement of Thermocouples

1. ~~Ambient air~~. Placed six inches above the unit. No epoxy.
2. Intake air. Bank of four sensors placed across both intake ducts; three thermocouples in each. No epoxy.

3. Exit air. Bank of six sensors placed across both discharge ducts; three thermocouples in each. No epoxy.

4. Thermal bulb tape (insulation tape). Imbedded in the thermal bulb tape, a few inches to the left side of the heater. No epoxy.

5,6,7 & 8. Front bulkhead. Four thermocouples placed left to right across the front bulkhead, attached to the reflective aluminum, six to nine inches off the bottom of the unit, so they were toward the top of the heating elements. This location is farther away from the heater elements than the bottom of the front bulkhead.

9. Front bulkhead. Attached to front bulkhead, approximately two inches from the bottom of the unit, directly in front of the center of the heating elements.

10. Motor. Attached to the motor at the closest point to the heating elements.

11. Right wall front. Attached on the right side wall on the reflective aluminum, six to nine inches from the bottom of the unit, near the front corner.

12. Right wall. Attached on the right side wall on the reflective aluminum, directly to the right of the heating elements. Approximately two inches from the bottom of the unit.

13. Right wall front. Attached to the right side wall near the front corner. Approximately two inches from the bottom of the unit.

14. Front wall. On the front wall near the right corner on the cut out for the Riv nut. The cut out on this unit was extremely small, so the epoxy holding the thermocouple in place completely covered the insulation. In other units a substantial area of black insulation is exposed. Approximately two inches from the bottom of the unit.

15. Heating element. Attached to heating element which glowed the least during heating (all elements glowed visibly). Thermocouple was not attached with epoxy. Actual measurement is an air measurement very close to the surface. This is true for points 16 and 17 also.

16. Heating element. Attached to heating element which glowed typically during heating. See point 15.

17 of another first
18 " 1 hole

13-(16) ~~17.~~ Heating element. Attached to a heating element which glowed the most during heating. See point 15.

Three different heating configurations were tested. The first was the high heat mode with all controls bypassed. In this configuration all 15 heater elements in the unit were running at full power at all times. The second configuration was the normal high heat mode with the thermostat and the over-temperature switch operational. The thermostat was turned to the highest setting during this test. Neither the thermostat nor the over-temperature switch had any effect during this test, so the test was essentially identical to the first. In the third configuration the right side exit air duct was blocked. Within two minutes of the time when the exit air was blocked the over-temperature switch turned off a number of the heating elements (either 6 or 9). The heating elements which were turned off cooled down rapidly, while the remaining heating elements glowed brighter and apparently increased their temperature. The temperature at each of the 17 thermocouple locations was recorded for each test for about 30 minutes. The data are presented in Tables 2-3 and 2-4.

Second Unit

The serial number of the second unit was SN 801198, and the shipping date was January 1982. This unit was selected because it has a larger cut out around the Riv nut than the unit used for the first test. In unit SN 801198 (used for the second test) approximately 1/2 inches of black insulating foam was exposed around the cut out. This unit, like the unit used for the first test, had the fresh air intake on the left side, and the fresh air intake was open during the test. Four configurations were tested on this unit:

1. Normal high heat mode.
2. Normal high heat mode with 50% of the intake blocked with paper strips. The strips were placed vertically on the intake to evenly block the intake air across the unit.

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TABLE 2-3

THERMOCOUPLE TEMPERATURE vs. TIME
HIGH HEAT MODE, ALL CONTROLS BYPASSED, IN DEGREES FAHRENHEIT

CONFIGURATION I

UNIT SN 801185

Start: 1032 hours, 202 volts, 8650 watts throughout experiment

Time:	1040 Hr	1049 Hr	1103 Hr*	1117 Hr
Location:				
1.	77	78	76	79
2.	74	74	75	76
3.	110	111	112	113
4.	107	117	122	122
5.	155	157	156	157
6.	180	182	179	180
7.	194	197	193	194
8.	190	192	188	188
9.	215	217	214	216
10.	97	91	94	96
11.	176	177	173	172
12.	158	160	157	156
13.	195	197	191	189
14.	186	189	188	187
15.	744	744	739	738
16.	761	760	735	740
17.	850	850	824	817

* Tightened top.

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TABLE 2-4

THERMOCOUPLE TEMPERATURE vs. TIME

HIGH HEAT MODE, WITH NORMAL CONTROLS, IN DEGREES FAHRENHEIT
CONFIGURATIONS 2 & 3

UNIT SN 801185

Start, 1200 hours, 202 volts, 8650 watts

Time:	1210 Hr	1220 Hr	1230 Hr	1240 Hr	1258 Hr*	1310 Hr
Location:						
1.	78	79	78	77	77	75
2.	74	74	74	74	75	74
3.	111	112	112	112	109	108
4.	109	117	120	121	113	111
5.	153	154	155	155	134	133
6.	176	177	178	178	152	152
7.	189	190	191	191	162	162
8.	184	185	186	185	155	155
9.	210	211	212	211	173	174
10.	96	99	99	100	98	97
11.	171	172	172	172	145	146
12.	155	157	157	156	136	136
13.	189	190	191	191	155	155
14.	185	188	190	190	156	156
15.	735	738	738	737	851	855
16.	738	741	740	743	185	186
17.	833	831	829	825	163	164

* Air flow blocked in right duct at 1245 hours. Over-temperature switch kicked out at 1246 hours. Wattage dropped to 5700 and remained there for the rest of the experiment.

3. Normal high heat mode with the bottom half of the air intake blocked.

4. Normal high heat mode with the top half of the intake blocked.

The over-temperature switch did not turn off in any of these configurations. R. Sherfy (VSE) stated that blocking the intake would reduce the flow through the unit significantly.

The placement of the thermocouples was as follows. Four thermocouples were used in this test.

1. Front bulkhead. Approximately two inches from bottom, in front of the center of the heating elements.

9. Right side wall on reflective aluminum. Approximately two inches from bottom, near front corner right next to the cut out for the Riv nut.

16. Front bulkhead in cut out for Riv nut. Thermocouple was imbedded in the black insulating foam.

18. Front bulkhead. Approximately two inches from bottom, toward left side of heating elements.

Thermocouples 1, 9, and 18 were attached with duct tape. Thermocouple 16 was imbedded in the black insulating foam. The results of the experiment are presented in Table 2-5.

Summary

These experiments were intended to determine the likely maximum temperatures at various locations in the PATRIOT Heater/Air Conditioners. This information was used to choose maximum temperatures for conducting outgassing experiments. The Investigative Team suggested that the highest temperature used in the outgassing experiments should be 15% higher than the maximum observed in the thermal experiments.

The maximum temperature reached by the thermal bulb insulation was 122°F. The specifications for the material indicate that it should

TABLE 2-5

THERMOCOUPLE TEMPERATURE vs. TIME
HIGH HEAT MODE, IN DEGREES FAHRENHEIT

UNIT SN 801198

Start, 1420 hours, 202 volts, 8650 watts.

Time:	1423 Hr	1433	1441 Hr	1446 Hr*	1452 Hr	1458 Hr**
Location:						
1.	215	217	225	247	246	241
9.	194	209	211	206	206	213
16.	193	211	209	205	205	213
18.	175	183	185	193	194	190

Time:	1503 Hr	1508 Hr***	1514 Hr
Location:			
1.	244	211	210
9.	211	214	214
16.	211	208	208
18.	190	194	195

* Put paper strips over approximately 60% of intake at 1442 hours. One 8 1/2" x 11" sheet torn in five strips. Strips laid vertically over intake, evenly spaced.

** At 1453 hours the paper strips were moved to block the bottom half of the intake.

*** At 1504 hours the paper strips were moved to block the top half of the intake.

be stable indefinitely at 158°F and should be able to withstand temperatures of 200°F for one hour.

The motor was tested on unit SN 801185. The maximum temperature observed was 100°F at the surface of the motor.

The surface of the reflective aluminum was tested in a number of locations on unit SN 801185. The highest temperatures were observed at location number 9 directly in front of the center of the heaters. This temperature was 217°F. In the high heat mode with all of the heaters running the coolest point on the reflective aluminum was at point number 5, where the maximum temperature observed was 157°F. Most of the other points ranged between 170°F and 200°F.

The temperatures of the reflective aluminum were substantially higher in unit SN 801198, but this may be due largely to the placement of the thermocouples. The maximum temperature observed was 247°F, but this depended strongly on the air flow characteristics in the unit. This particular point (#1) was as low as 210°F when the air flow patterns were changed by partially blocking the return air intake.

The only direct measurement of the black foam was done on unit SN 801198. The temperature varied from 193°F to 213°F, again depending on the air flow characteristics.

Based on the observations of the temperatures on the reflective aluminum and the black foam, the maximum temperature used for the outgassing experiments was 280°F. Experiments were also performed at lower temperatures.

The tubing in the bottom of the unit toward the right side will be exposed to temperatures which will probably be similar to those measured at point 11 on unit SN 801185. The maximum temperature at this point was 177°F. The temperature in this area of the unit depended strongly on the air flow, so the tubing was tested at the same temperatures as the foam.

The adhesive for the foam and the sealer were also tested at the same temperatures as the foam. The adhesive holding the reflective aluminum to the foam will probably be exposed to these temperatures. The portions of the adhesive holding the foam to the body of the unit will be exposed to temperatures much less than this, probably closer to the external temperature of the unit. The test may therefore be too extreme.

The temperatures in the other areas of the unit will probably have a maximum temperature close to the temperature of the exit air. This varies between about 110°F and 140°F. It would be reasonable to test these materials at 160°F.

The sampling team noted that the tygon tubing had partially decomposed in unit SN 81013, due to excessive heat (see Section 3.2.2). We therefore tested some of the materials at much higher temperatures (340°F).

2.2 Material Acquisition

In the meeting of August 9, 1982 the Investigative Team decided that it would be desirable to obtain samples of the materials used in the air conditioners directly from the manufacturer. Versar contacted David Groves of Keco Industries in order to do this. Keco agreed to supply Versar with the materials which were requested. A list of the samples supplied is presented in Table 2-6. Five of these materials were singled out for special attention by the Investigative Team: the black foam (1), the thermal bulb insulation tape (2), the rubber adhesive which is used to attach the reflective aluminum to the foam (4), the sealer (5), and the tubing (10). A subsample of each of these materials was sent from Versar to Skinner and Sherman. Each lab was to perform outgassing experiments on the materials.

2.3 Outgassing Experiments

The outgassing experiments were run in the following fashion. A weighed sample was placed in a 10 ml Hypo-Vial (Pierce Chemical Co.,

TABLE 2-6

LIST OF SAMPLES SUPPLIED BY
KECO INDUSTRIES, INC.

	Part Number	Description
1.	13222E8984 13221E9113 13219E9481	- 1/2" Thick Plastic Unicellular Material - Surface Skin on one or both sides. - Per MIL-P-15280 - Supplier: Miami Valley Gasket Company Focke Rubber Products Division 113-15 East Third Street Dayton, Ohio 45402 Tel: (513) 228-0781
2.	13219E9543	- Thermal Bulb Insulation Tape. - Synthetic Rubber - Asphalt filled with Virgin Cork and Asbestos. - Supplier: Inmort Corporation Prestite Products 3738 Chouteau Avenue St. Louis, Missouri 63110
3.	N/A	- Adhesive Per MIL-A46106. - Silicon RTU - Silicon/Rubber - Aluminum Sealant - Supplier: Dow Corning.
4.	N/A	- Adhesive Rubber Per MMM-A1617 - Scotch Grip Contact Cement. - Green 4518 - Supplier: 3M Company Adhesives, Coatings, Sealers Division, 3720 South Venoy Road Wayne, Michigan 45184
5.	13211E3465	- Sealer. - Supplier: 3M Company 3M Center St. Paul, Minnesota 55101

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TABLE 2-6 (Continued)

LIST OF SAMPLES SUPPLIED BY
KECO INDUSTRIES, INC.

	Part Number	Description
6	13219E9554-1	- Heating Element. - Drawing enclosed. - Supplier: E. L. Weigand c/o Cromolox Sales 1132 West Kemper Road Cincinnati, Ohio 45240
7.	13219E9528	- Non-EMI Gasketing. - PUC Resin Foam. - Supplier: Norton Corporation Franville, New York 12832
8.	13219E9568-1	- EMI Gasketing. - Silicon Sponge Elastomer. - No Adhesive. - Supplier: ME Tex Corporation Eslison, New York 08817
9.	13219E2889	- Heater Grommet. - Supplier: Midwest Precision 11297 Grooms Road Blue Ash, Ohio 45242
10.	13218E0001-290	- Tubing. - Type IV, Clear, Class 6. - Per MIL-Z-Z-T-831. - Supplier: Read Plastics Address Unavailable.

Rockford, IL.). The vial was sealed with a teflon-lined silicone septum and an aluminum seal. The material inside the vial was therefore exposed to air during the course of the experiment. The sealed vial was placed inside an oven at a specified temperature for two hours. Immediately upon removal from the oven the vial was connected to the front of a gas chromatograph through a stainless steel fitting. The septum on the vial was punctured and the vial was purged with air for four minutes at 10 ml/min. This operation transferred the volatile compounds produced during thermal decomposition to the analytical column. The column (12' x 1/8" Chromosorb 101) was then programmed from 40°C to 200°C at 16°C/min with a nitrogen flow of 40 ml/min. Under these conditions acrolein eluted from the column in about 10.5 minutes and toluene eluted from the column in about 14.5 minutes. A number of the experiments were run in both the presence and absence of an acrolein internal standard to verify that the vial did not leak and lose volatile compounds during the two hour heating time.

The experiments were run first using flame ionization detection (FID). The FID screening identified those materials which produced a significant quantity of outgassing products. These were then tested using GC/MS. It was important to define what constitutes a "significant" quantity of outgassing products. The criteria used to do this is described in the next section.

The thermal destruction analysis of materials suggested in Recommendation 1 (f) were not done. During the August 9, 1982 meeting the Investigative Team determined that all materials would produce chemical irritants in this experiment and no useful results would be obtained. All agreed to drop these experiments.

2.3.1 Criteria for Screening Materials

The following assumptions were used to define what quantity of outgassing products was significant.

1. The internal volume of the CRG is 14.4 m^3.

2. All of the material in the heater/air conditioner unit was heated to the maximum experimental temperature.

3. All of the outgassing products are released at once, the first time the unit is turned on the heating mode in the CRG.

4. There is no air exchange between the CRG and the outside air. All outgassing products are diluted in only 14.4m^3.

Using these assumptions a predicted maximum air concentration can be calculated from the experimental data. For example, assume that the experiments show that material A releases 1 mg of a contaminant per gram of material A when it is heated to 280°F. If there are 100 grams of material A in the heater/air conditioner, the predicted maximum air concentration would be 6.9 mg/m^3.

$$\frac{(1\ mg/g \times 100\ g)}{14.4m^3} = 6.9\ mg/m^3$$

If the predicted maximum air concentration is greater than the Threshold Limit Value (TLV) published by NIOSH then the material deserves further consideration. If it is lower, the material will not cause any problem.

TLV's have been published by the American Conference of Governmental Industrial Hygienists. They state:

> "Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness."[1]

Table 2-7 presents the allowable release quantities for the different materials at various values for the TLV of the products. A few

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TABLE 2-7

ALLOWABLE RELEASE QUANTITIES (mg PRODUCT/G MATERIAL)

TLV (mg/m^3)	FOAM	TUBING	INSULATION TAPE	GROMMETS	ADHESIVE	SEALER
0.25	0.002	0.09	0.018	0.21	0.009	0.036
1.0	0.008	0.39	0.072	0.84	0.036	0.144
2.0	0.016	1.6	0.29	3.4	0.144	0.58
5.0	0.04	1.95	0.36	4.2	0.18	0.72
10.0	0.08	3.9	0.72	8.4	0.36	1.44
100.0	0.8	39.0	7.2	84.0	3.6	14.4
1000.0	8.0	390.0	72.0	840.0	36.0	144.0

ESTIMATE WEIGHT IN UNIT

FOAM	TUBING	INSULATION TAPE	GROMMETS	ADHESIVE	SEALER
1800 g	40 g	200 g	21 g	400 g	100 g

things should be noted from this table. First, the materials present in small quantities in the units (grommets) can release more contaminants and still pose no hazard than the materials present in large quantities (foam). Second, products with higher TLV's can be safely released in larger quantities than products with low TLV's. For example, if 0.016 mg/g of toluene (TLV = 820 mg/m^3) are released from the foam, there will be no cause for concern. If, however, the same quantity (0.016 mg/g) of acrolein (TLV = 0.25 mg/m^3) is released from the foam there will be substantial cause for concern.

The FID experiments estimated the release quantities at various temperatures for the materials chosen by the Investigative Team. Using the above assumptions, the estimated release quantities were used to predict maximum air concentrations. If the predicted maximum air concentration exceeded 0.25 mg/m^3 for any outgassing product, the experiment was repeated using GC/MS.

It should be noted that this procedure leaves some uncertainty concerning the actual amount of products. In the FID experiments it is not possible to identify the compounds produced. For this reason it was necessary to use the response factor for acrolein for all of the peaks observed in the chromatogram. Since different compounds have different response factors this will cause an error in the estimate of the quantity of products found. We have therefore included a safety factor of 3 in our FID screening. That is, if the quantity of products is within a factor of 3 of the level of concern, a GC/MS experiment was performed. In most cases the FID chromatograms indicated that there were no qualitative changes in the identity of the products obtained at different temperatures. When this was observed the GC/MS experiments were only run at the temperature which produced the most compounds.

The assumptions used here are strongly on the side of safety. The temperature measurements inside the operating units (Section 2.1.2)

show that the maximum temperature will not be attained in all areas of the units. Assumption #2 above is therefore certainly in error. Even at the points in the heater/air conditioners where the maximum temperatures are reached this is only true at the surface of the material. For example, the temperature of the foam will decrease from the inside temperature to the ambient outside temperature as one moves through the thickness of the foam. In the experiment, however, the foam was uniformly heated to the maximum temperature. In the units, the exposed surface area of any material is fairly small. In the experiments the materials were cut into small pieces, therefore increasing their surface area. It is likely that this will increase the amount of products found. This suggests that assumption #3 also overestimates the amount of contamination that could be produced. Assumption #4, that the CRG is air tight, is also probably in error. The errors in these assumptions indicate that this procedure will overestimate the quantity of products and will underestimate the volume in which the products are diluted. For these reasons we believe that the assumptions include a large safety factor.

2.3.2 Results of Outgassing Experiments

The normal operating temperature experiments were run in duplicate. One of the duplicates was run on a chromatographic column for low boiling compounds (Chromosorb 101). The second duplicate was run on a column appropriate for less volatile compounds (SP-2250). A number of the experiments with the low boiling compounds were also run after spiking the sample with an aqueous solution of acrolein. This was done to confirm that the vials were not seriously leaking during the heating time. If serious leaks had occurred, very low recoveries of the spike would be observed. The acrolein could not be recovered in the presence of the black foam, probably due to surface or gas phase reactions.

2.3.2.1 Low Boiling Compounds

The results of the thermal decomposition experiments for the low boiling compounds are presented in Table 2-8. The low boiling compounds are defined as those that elute from the chromatographic column before ethyl benzene under the analytical conditions used. The allowable release levels are those calculated in the previous section, expressed in ug/g. The experiments on the thermal bulb insulation tape and the heater grommets showed that the quantity of products found after heating was very small. Neither exceeded the criteria levels at the highest temperatures tested, so the experiments were not run using GC/MS.

Although the outgassing of the tubing was also below the criteria levels, the experiments were run using GC/MS. This was done because of the appearance of the tubing in unit SN 81013 during the inspection at Fort Bliss, Texas as discussed in Section 3.2.

The adhesive, the sealer and the insulating foam all exceeded the criteria levels at normal operating temperatures. Further work was done on these materials using GC/MS.

When interpreting the data from these experiments, it should be noted that the FID does not respond to all compounds. That is, some compounds such as hydrogen chloride, water and carbon disulfide do not cause the FID to respond, and they would therefore be missed in these experiments. Some typical chromatograms from these experiments are presented in Figures 2.1 through 2.7.

2.3.2.2 High Boiling Compounds

The outgassing experiments were run in an identical fashion for the high boiling compounds except that the vial containing the outgassing products was heated with a heat gun during the transfer of the products to the chromatography column. This was done to ensure that the compounds would not condense on the wall of the vial during the transfer

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TABLE 2-8

ESTIMATED QUANTITY OF THERMAL DECOMPOSITION PRODUCTS (ug/g)

Temperature / Allowable Release Quantity	Foam	Tubing	Adhesive	Sealer	Thermal Tape	Grommets
	2	90	9	36	18	171
280°F	60	6	++	77	NA	0.4
245°F	23	2	NA	NA	NA	NA
194°F	6	NA	4300	160	4	NA
158°F	NA	NA	2500	110	2	NA
70°F	NA	NA	75	16	0.5	NA

NA = Not analyzed.
++ = High levels, beyond linear range of detection.

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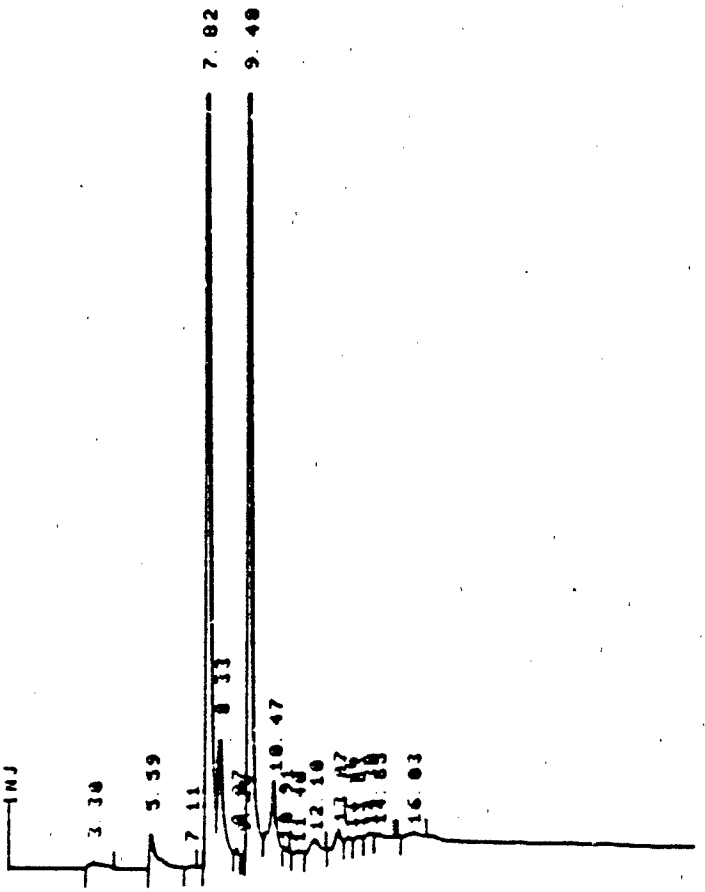

FIGURE 2.1
Foam, 280°F, Spiked

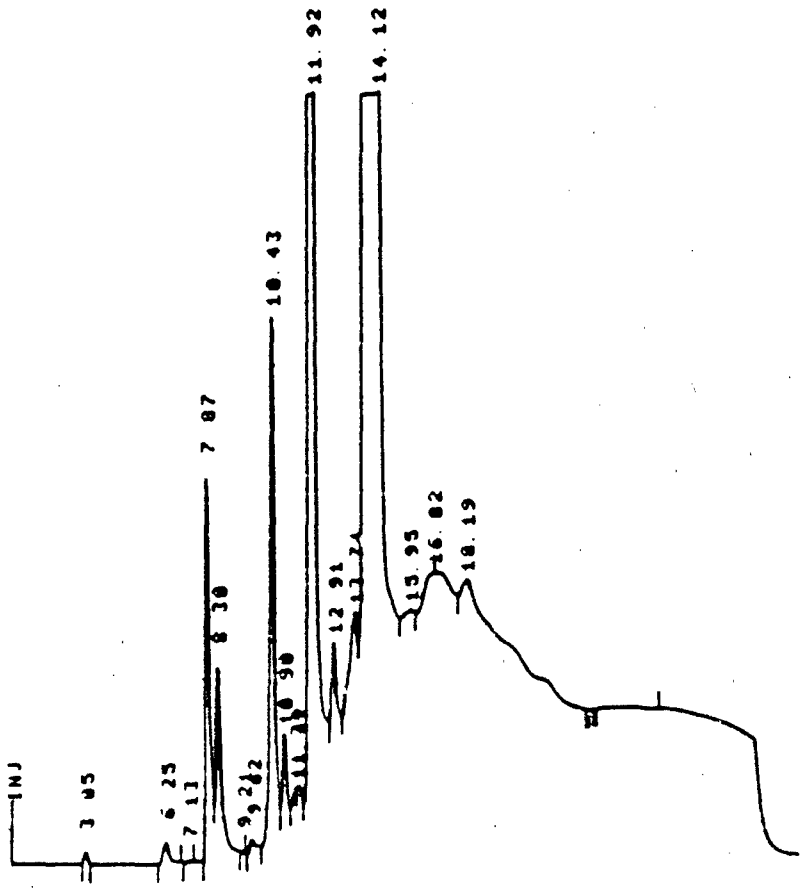

FIGURE 2.2
Sealer, 245°F

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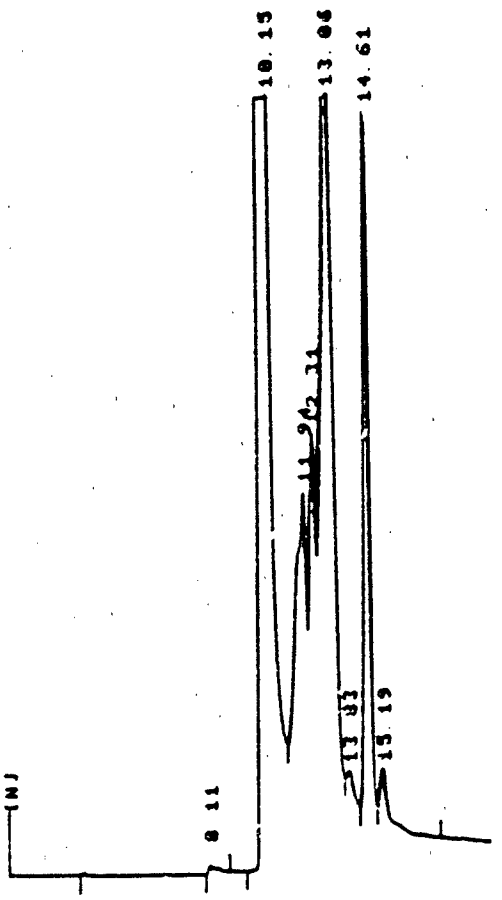

FIGURE 2.3
Adhesive, 160°F

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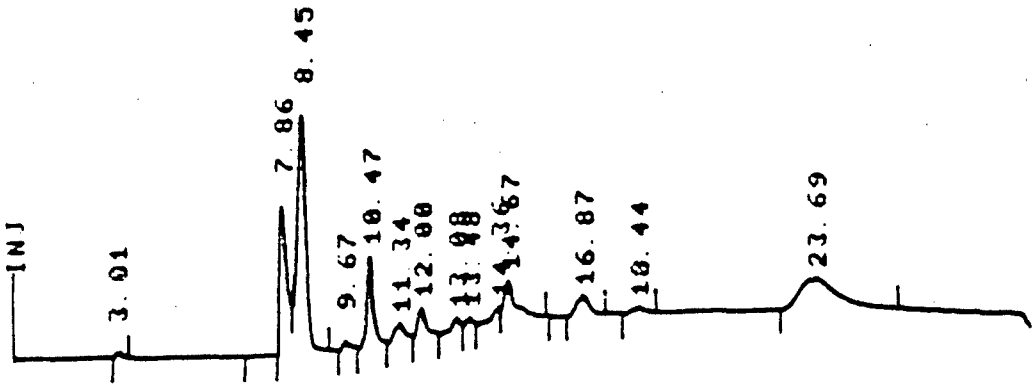

FIGURE 2.4
Tubing, 280°F

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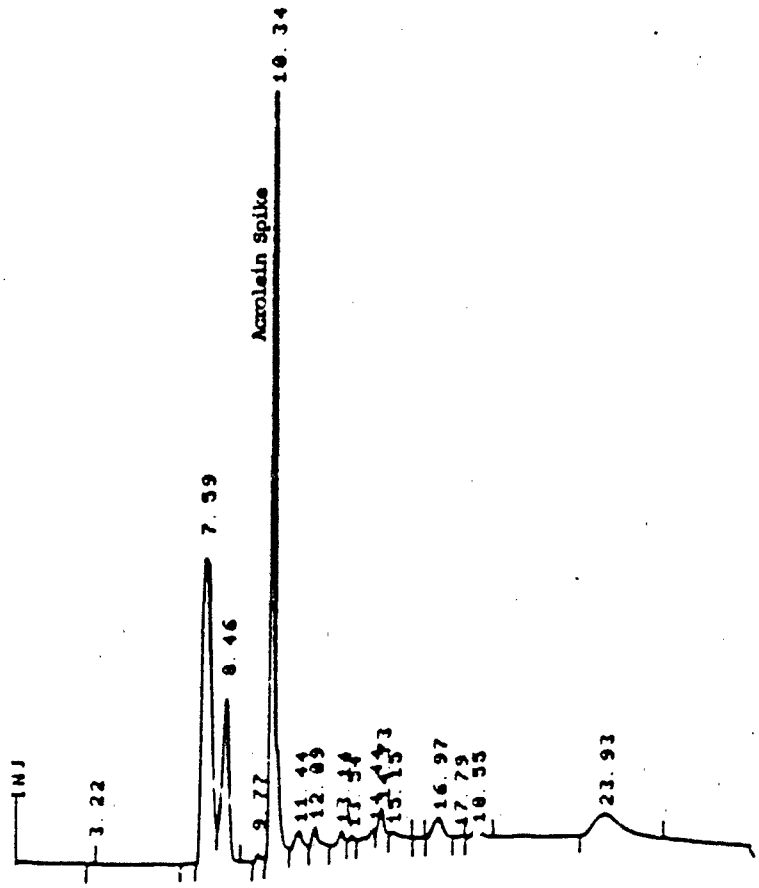

FIGURE 2.5
Tubing, Spiked, 280°F

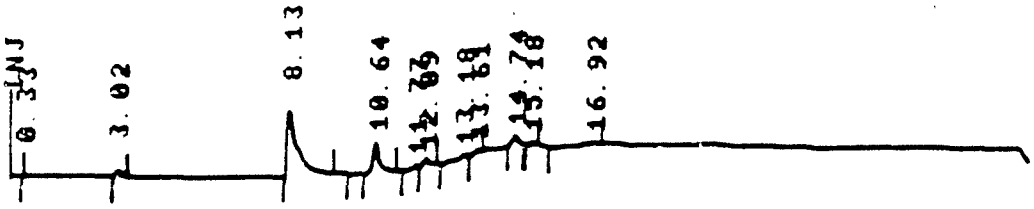

FIGURE 2.6
Grommet, 280°F

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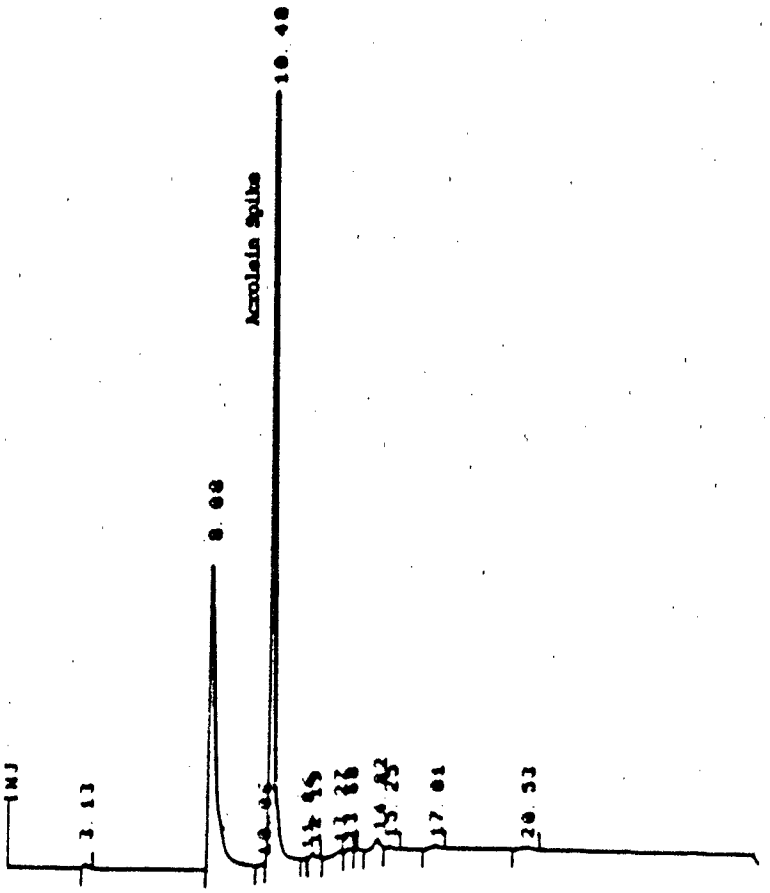

FIGURE 2.7
Grommet, Spiked, 280°F

operation. The chromatographic column was 3% SP-2250 on 100/120 mesh Supelcoport. A chromatogram containing xylene and benzo g,h,i, perylene was run before starting the experiments to confirm that the chromatographic system was operating properly. Two ug of xylene were spiked into each experimental vial before heating to confirm that the vials did not leak during the heating process. The xylene was recovered in all of the experiments.

The following materials were tested by this technique for the presence of high boiling outgassing products:

1. foam
2. adhesive
3. sealer
4. tubing

The materials were heated to 280°F for two hours before sweeping the products onto the chromatographic column.

None of the materials produced significant quantities of high boiling compounds at 280°F. Approximately 0.5 grams of material were used in all of the experiments. The highest intensity peaks in any of the chromatograms were less than 10% of the intensity of the xylene internal standard. These peaks were observed in the experiments on the adhesive. The maximum estimated release quantity for all of the materials is 0.4 ug/g at 280°F. Referring to Table 2-8, it is clear that the high boiling outgassing products are of no concern. Irrespective of their identity they will not reach hazardous concentrations.

2.3.3 Outgassing Experiments Using GC/MS

Due to the observations of the outgassing experiments using GC/FID, a number of materials were run using GC/MS as the analytical tool. The technique was similar to that described for the GC/FID experiments. The materials investigated using GC/MS were:

1. black insulating foam
2. tygon tubing
3. green adhesive
4. brown sealer

The materials were heated to 280°F for two hours before sweeping the volatile products into the instrument.

2.3.3.1 Insulating Foam

The black insulating foam produced six compounds in appreciable quantities. Some of the data is presented in Figure 2.8 through 2.11. The compounds are:

1. carbonyl sulfide
2. methanol
3. ethanol
4. acetone
5. carbon disulfide
6. benzene

Three of these compounds are of little concern. The Threshold Limit Values for acetone, ethanol and methanol are 2400 mg/m^3, 2050 mg/m^3 and 285 mg/m^3, respectively. The quantities of materials found in the FID experiments show that these compounds will not approach dangerous levels in the CRG. The three remaining materials have relatively low TLV's. The TLV for benzene is 30 mg/m^3 and the TLV for carbon disulfide is 30 mg/m^3. There is no TLV for carbonyl sulfide. However, the inhalation toxicity and the toxicity ratings presented in "Dangerous Properties of Industrial Materials"[2] are similar to those of carbon disulfide. It is probably reasonable therefore to assume that the hazard is about the same for both materials.

The data from the FID experiments were used to estimate the amount of benzene which may be produced by heating the foam. The largest peak eluting in the region of the FID chromatograms was used to calculate an approximate amount of benzene present in the experiments. This was

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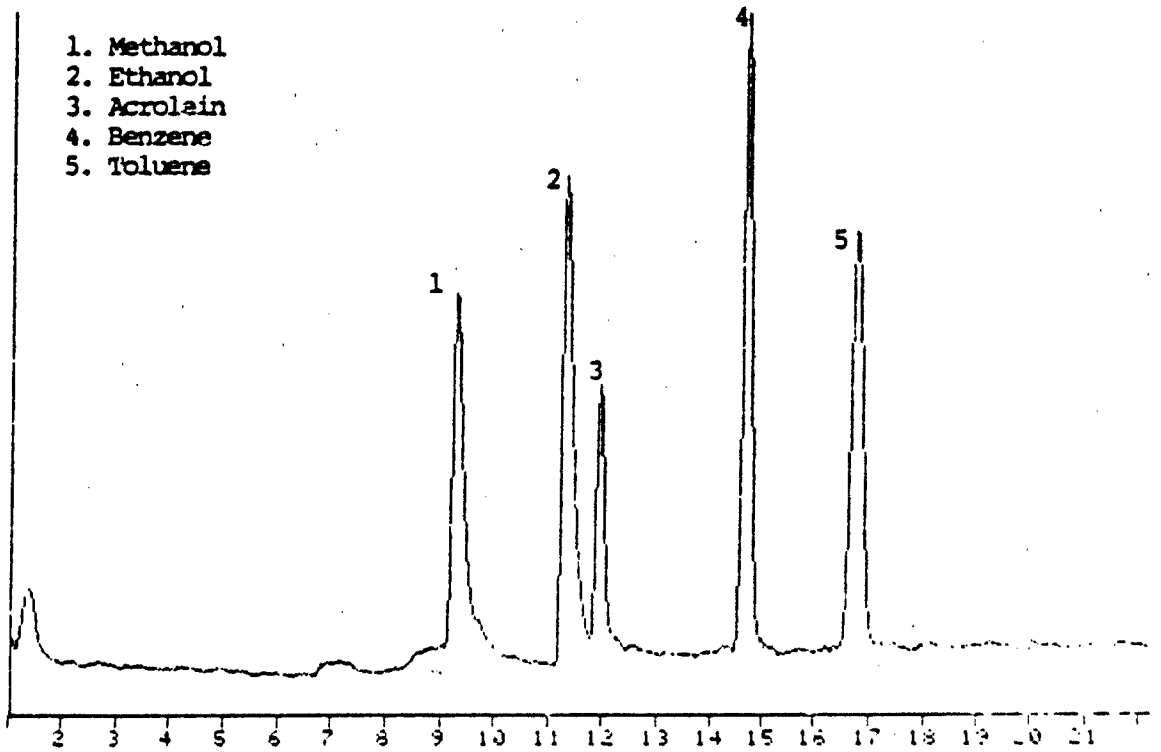

FIGURE 2.8
GC/MS Standards

K-34

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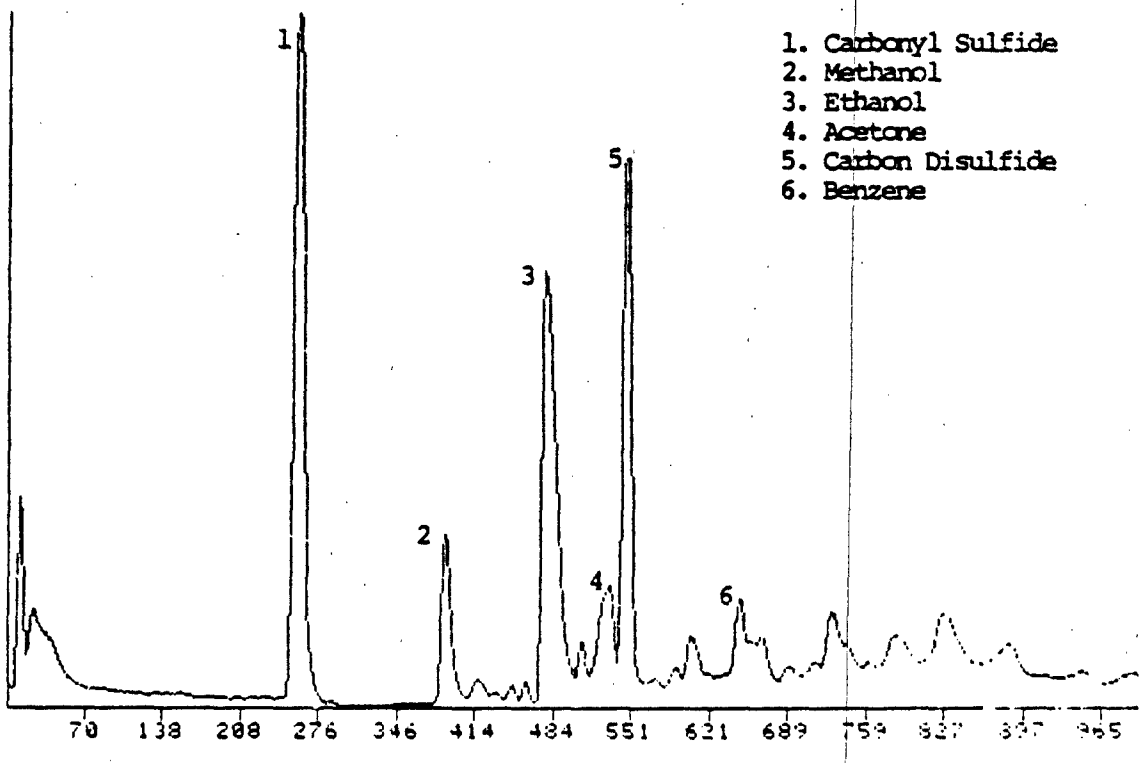


FIGURE 2.9

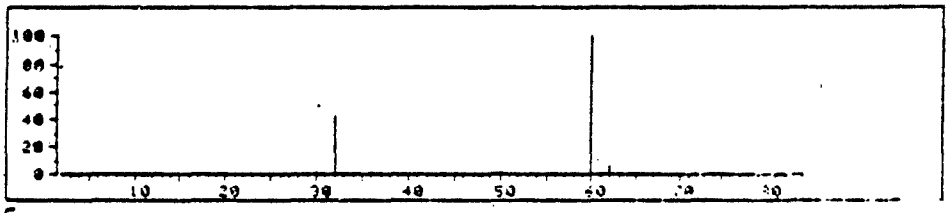
Foam Outgassing Products, 280°F

K-35

Versar inc.

```
(Similarity/Full Search:      MW Range:  60-  62)

AVERAGED SPECTRUM FROM FRN 23741
 + 254  -243

          19 PEAKS,     6 SIGNIFICANT      MAX K   14.0

 LIBRARY  3000     32 SPECTRA SEARCHED,    1 HIT(S)

 .7991 +  Carbon oxide sulfide (COS) (9CI)
        SPEC=  106  LSN=   106. MW=  60  COS
        FRN = 3001 (NBS    106.)  CAS #  0000463581   EPA #  0000000166
        MATCHING PEAKS   CONTAMINATED   MISSING PEAKS  QUAL INDEX=  727
         11.9   5  97%    .0   0   0%    2.7   1   7%  MULTIPLIER=  .96
>PAUSE
```

```
 1 HIT: AVERAGED SPECTRUM (FRN 23741) + 254  -243
```



```
*  1  LFRN  3001 SPECT  106   MW=  60  COS
.7991 Carbon oxide sulfide (COS) (9CI)
```

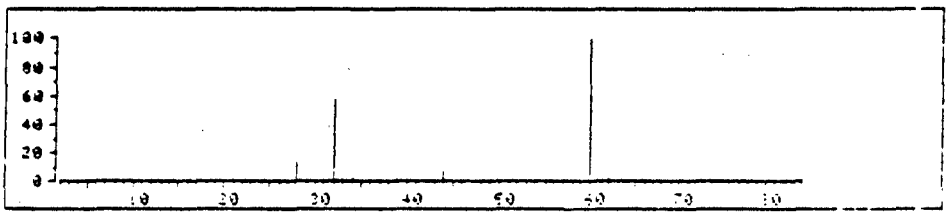


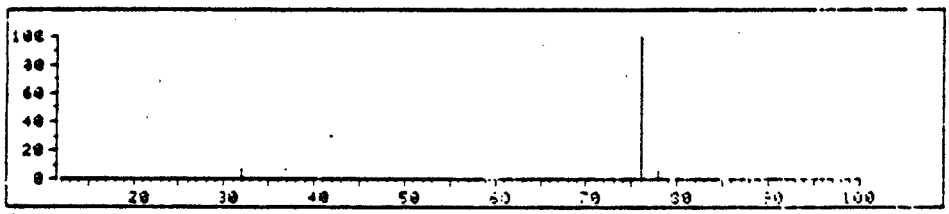
FIGURE 2-10

Carbonyl Sulfide Identification

K-36

Versar inc.

```
[Similarity/Full Search:      MW Range:  76-  90]

AVERAGED SPECTRUM FROM FRN 23741
 + 544  -540

            9 PEAKS,      6 SIGNIFICANT      MAX K   13.5

 LIBRARY  3000    419 SPECTRA SEARCHED,    1 HIT(S)


 .7885 +  Carbon disulfide (8CI9CI)
         SPEC=  313  LSN=   313. MW=  76  CS2
         FRN = 3001 [NBS    313.]  CAS #  6000075150   EPA #  0000034209
         MATCHING PEAKS   CONTAMINATED   MISSING PEAKS  QUAL INDEX=  707
          11.5   5  90%    .0   0   0%    2.7   1  13%  MULTIPLIER= 1.00
>PAUSE


  1 HIT: AVERAGED SPECTRUM (FRN 23741) + 544  -540
```




```
 15.9%
```

```
*  1  LFRN  3001 SPECT  313   MW=  76  CS2
.7885 Carbon disulfide (8CI9CI)
```

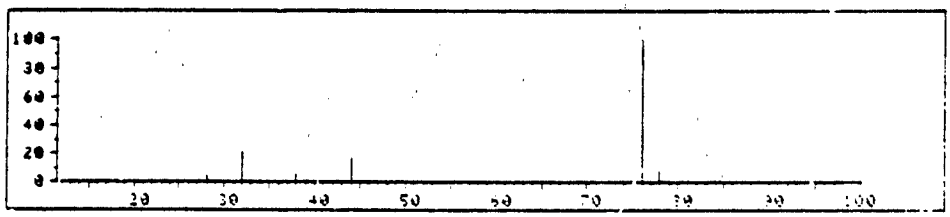


FIGURE 2.11

Carbon Disulfide Identification

K-37

used to obtain the amount of benzene produced per unit weight of foam. Based on the assumption as in the previous FID experiments, that there is no air exchange in the CRG and that 1800 grams of foam are heated to the experimental temperature, a maximum expected concentration in the CRG can be calculated. These calculations are identical to those used to determine whether or not GC/MS experiments were necessary (see Section 2.3.1). With these assumptions the amount of benzene produced at 280°F corresponds to 0.67 mg/m^3, while at 245°F the maximum expected concentration would be 0.11 mg/m^3. The first value is 44 times less than the TLV, the second is over 250 times less than the TLV. Because these are fairly low quantities and the assumptions in this analysis are strongly on the side of safety, it is unlikely that benzene will be a significant problem in the CRG under normal operating conditions.

The carbon disulfide could not be quantified using FID because the detector does not respond to it. The thermal degradation experiments on the black foam were therefore repeated using an electron capture detector in order to estimate the amount of carbon disulfide produced by the foam at various temperatures. These experiments are described in Section 2.3.4.

2.3.3.2 Tygon Tubing

The tygon tubing produced two compounds in appreciable quantities when heated to 280°F. These two compounds were 2-butene and acetone. The TLV for acetone is 2400 mg/m^3, so it is of no concern. There is no TLV for 2-butene, but the TLV for the closely related alkene 1,3 butadiene is 220 mg/m^3. These two compounds were produced in small quantities, and they have low toxicities, so it appears that the tygon tubing poses no hazard at 280°F.

2.3.3.3 Sealer

The sealer produced four compounds in appreciable quantities when heated to 280°F. The experiment was done after allowing the sealer

to air dry overnight. The data are presented in Figure 2.12. The compounds produced were:

1. hexane TLV = 1800 mg/m^3
2. 2-butanone (methyl ethyl ketone) TLV = 640 mg/m^3
3. 4-methyl-2-pentanone (methyl isobutyl ketone) TLV = 410 mg/m^3
4. toluene TLV = 820 mg/m^3

These compounds all have fairly low toxicities, and they are produced in small quantities (see Table 2-8). The sealer used in the PATRIOT Heater/Air Conditioner should present no hazard under typical operating conditions.

2.3.3.4 Adhesive

The adhesive used on the foam (Scotch Green 4518) produced seven compounds in appreciable quantities when heated to 280°F. The adhesive was allowed to air dry overnight before running the experiment in order to simulate the aging and loss of solvents which would occur during manufacturing and shipping. The data are presented in Figure 2.13. The seven compounds were:

1. acetone - TLV = 2400 mg/m^3
2. 3-methyl pentane no data, probably low toxicity (Sax)
3. hexane - TLV = 1800 mg/m^3
4. ethyl cyclobutane no data, probably low toxicity (Sax)
5. heptane - TLV = 220 mg/m^3
6. 3-methyl hexane no data, probably low toxicity (Sax)
7. toluene - TLV = 820 mg/m^3

To exceed the level of concern for the most toxic compound found (toluene) the adhesive would have to release 29500 ug/g of toluene. The data in Table 2-8 show that the level is not exceeded at 194°F. It may, however, be exceeded at higher temperatures. This will depend on the amount of adhesive used in the heater/air conditioners, the amount of time allowed for drying, and the extent to which the toluene can diffuse through the foam once it has been applied. It has been detected in past

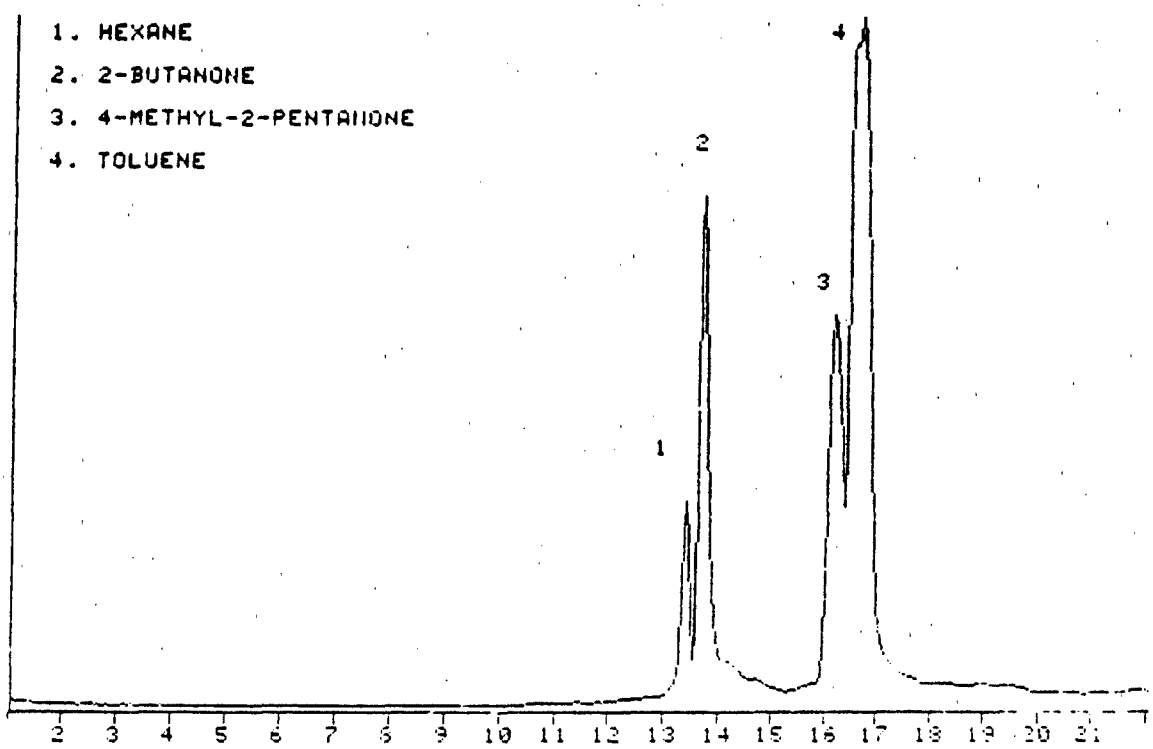


FIGURE 2.12
Sealer Outgassing Products, 280°F

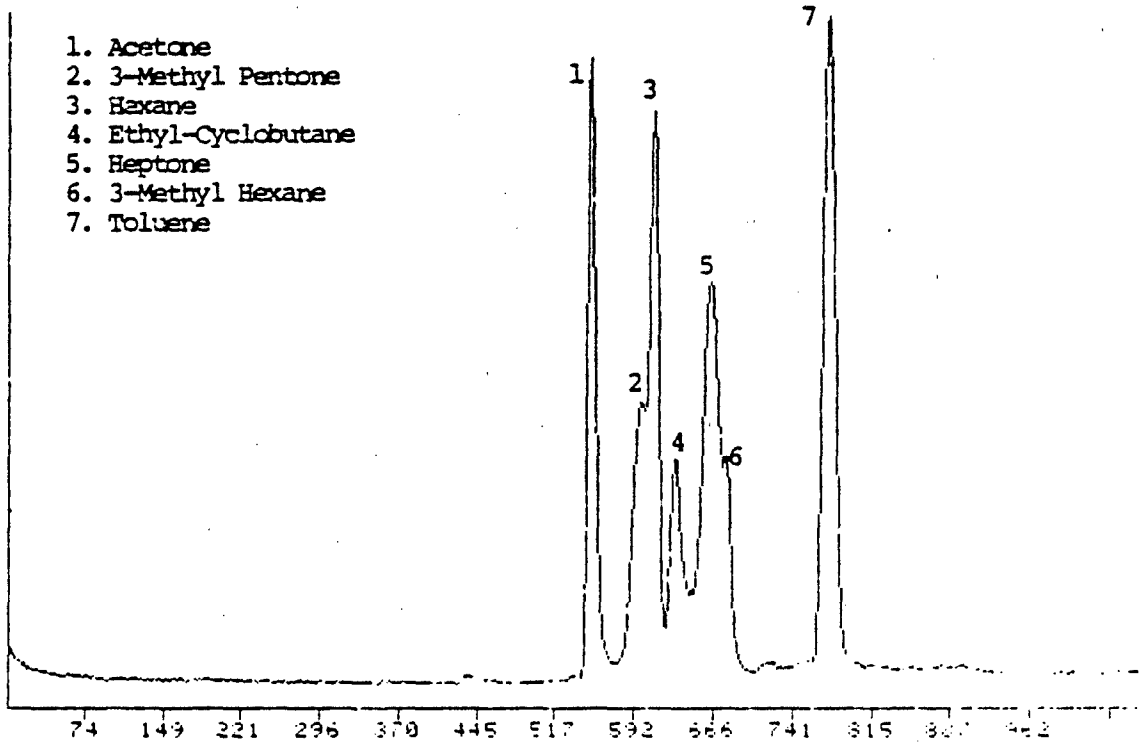


FIGURE 2.13

Adhesive Outgassing Products, 280°F

sampling efforts during this investigation (July 21, 1982 report) but only at trace levels. It should be noted that toluene has a strong and distinct smell at concentrations well below the TLV. Since the personnel working on this project have never smelled toluene while the Heater/Air Conditioners were running it seems unlikely that the solvents in the adhesive pose a significant threat. All of the solvents have relatively low acute toxicities.

2.3.4 Higher Temperature Experiments

Two of the materials in the Heater/Air Conditioners were also tested for outgassing products at higher temperatures. The sampling team in Fort Bliss, Texas, noted that some of the materials in one of the units had apparently been exposed to much higher temperatures than expected (see Section 3.2). For this reason the black foam and the tubing were exposed to temperatures of 340°F in one set of experiments. This temperature is much higher than the highest normal operating temperature measured in Section 2.1.2. It would only be attained in the units during a mechanical or electrical malfunction.

In the GC/FID experiments a sample was heated in a sealed Hypo-Vial for two hours at 340°F. A sample of the headspace was injected into the instrument using a gas tight syringe. The coefficient of variation for duplicate injections of toluene vapors was 3.2%. A 12 ft. Chromosorb 101 column was used in the instrument, and the temperature was programmed at 16°C/min from 40°C to 200°C.

At 340°C the tubing released very small quantities of products. The largest peak in the chromatogram (Figure 2.14) had the same retention time as toluene. Assuming that the peak was toluene, the quantity recovered was 0.0036 mg per gram of tubing. Table 2.7 indicates that this is not a significant amount of material, irrespective of the true identity of the peak. Therefore the GC/MS experiments were not required to identify the peak.

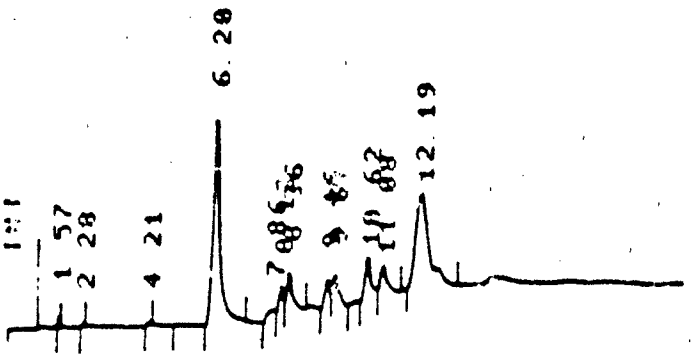


FIGURE 2.11
Tubing Outgassing Products, 340°F

At 340°C the black insulating foam released appreciable quantities of a number of different compounds, so the GC/MS experiments were performed. Some of the data is presented in Figures 2.15 through 2.18. The compounds identified were:

Carbon dioxide, TLV = 9000 mg/m^3
Carbonyl sulfide (COS), no TLV
Sulfur dioxide, TLV = 5 mg/m^3
Carbon disulfide, TLV = 30 mg/m^3
Benzene, TLV = 30 mg/m^3
N,N-dimethylformamide, TLV = 30 mg/m^3

Other compounds were also present, but their spectra could not be conclusively identified.

The amount of benzene released from the foam was quantified using GC/FID. The amounts of carbon disulfide and sulfur dioxide released were quantified using gas chromatography with electron capture detection (GC/ECD). The amount of carbonyl sulfide could not be quantified because no standard was readily available. An estimate was obtained assuming that the response factor for carbonyl sulfide on GC/MS was the same as the response factor for carbon disulfide. The response for dimethyl formamide was small on both GC/FID and GC/MS, so it was not quantified. The sulfur dioxide and carbon disulfide were released in fairly large quantities, so the outgassing experiments were also repeated for these compounds at 280°F and 250°F. The results of the experiments are presented in Table 2-9. A typical chromatogram is presented in Figure 2.19.

Referring to Table 2-7, we estimate that the TLV for carbon disulfide (30 mg/m^3) could not be exceeded unless the foam released greater than 0.24 mg carbon disulfide per gram of foam. At 340°F the quantities found are less than this by a factor of 2.5. At 280°F and 250°F they are less than this by factors of 10 and 20, respectively.

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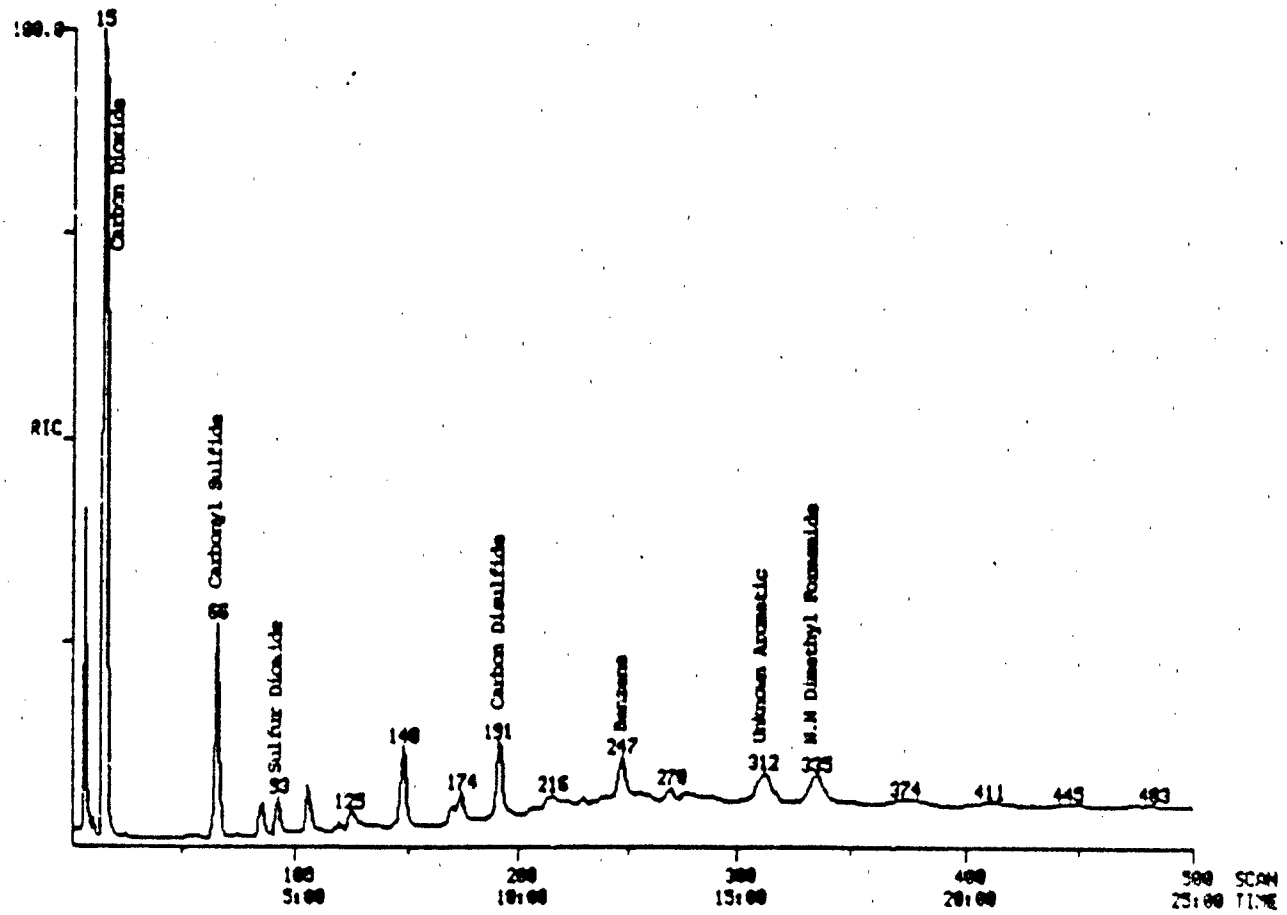

FIGURE 2.15

Foam Outgassing Products, 340°F

K-45

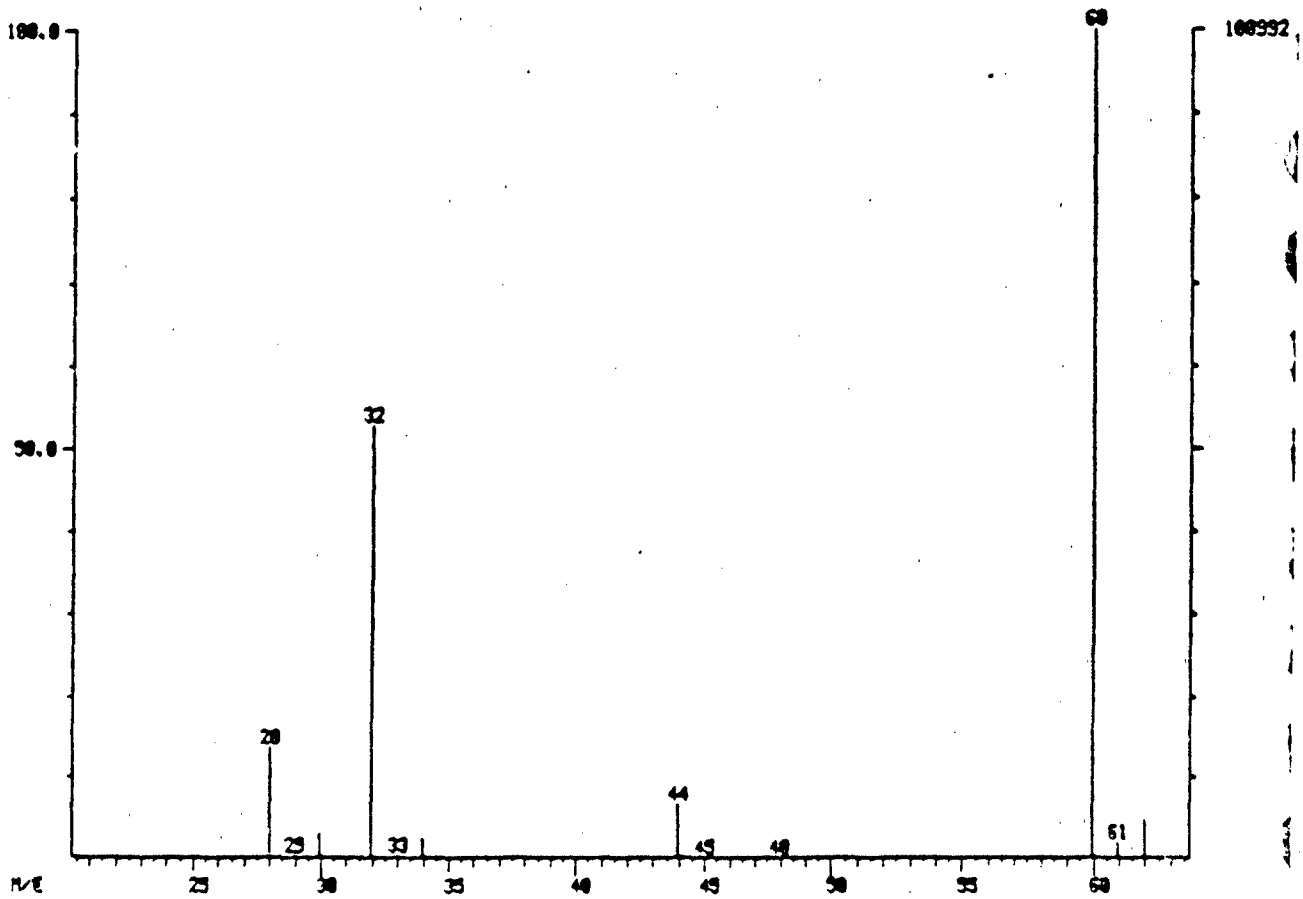

FIGURE 2.16
Identification of Carbonyl Sulfide

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LIBRARY SEARCH DATA: 124 @ 191 BASE M/E: 76
09/24/82 14:54:00 + 9:33 CALI: 60 @ 5 RIC: 63359.
SAMPLE: FOAM FOR EXPERIMENT 170C HEADSPACE 0.5ML
ENHANCED (8 150 2N OT)

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
141 MATCHED AT LEAST 5 OF THE 14 LARGEST PEAKS IN THE UNKNOWN

RANK	IN	NAME
1	272	CARBONDISULFIDE
2	9772	ARSINE
3	179	THIOUREA
4	1103	1-PROPANETHIOL
5	3099	1-PROPENE, 1-CHLORO-

RANK	FORMULA	M. WT	B. PK	PURITY	FIT	RFIT
1	C. S2	76	76	987	996	989
2	H3. AS	78	76	647	654	761
3	C. H4. N2. S	76	76	604	610	749
4	C3. H8. S	76	76	581	639	763
5	C3. H5. CL	76	76	554	598	812

MASS	INTEN	1	2	3	4	5
33		2				
34	3	8				
35					22	
36			3			16
37			1			44
38	56	47	8	30		30
39	10	4	0		74	292
40			0		19	73
41			0	38	171	317
42	13		0	154	209	18
43	3		0	701	219	
44	126	132	0	74		
45	3	2	0		63	
46	3	6	0	23	65	
47				22	236	
48				44	34	
49			0			30
51						30
57	3					
58				13	50	
59				130	40	
60				281		
61					107	40
62				13		39
64	11	14		16		
65		0				
66		1				
67	1					
73						28
75			163			104
76	1000	1004	465	1034	992	759
77	31	27	110	29	39	36
78	93	89	337	48	45	246

FIGURE 2.17

Identification of Carbon Disulfide

Versar inc.

```
LIBRARY SEARCH                    DATA: 124 @  93          BASE M/E.    64
09/24/82 14:34:00 + 4:39          CALI. 60 @   5           RIC.      29567.
SAMPLE: FOAM FOB EXPERIMENT 170C HEADSPACE 0.5ML
ENHANCED (S 150 2N OT)

25409 SPECTRA IN LIBRARYNB SEARCHED FOR MAXIMUM PURITY
  292 MATCHED AT LEAST 3 OF THE  5 LARGEST PEAKS IN THE UNKNOWN

RANK IN NAME
1  9604 SULFURDIOXIDE
2  3168 ETHANESULFONYLCHLORIDE
3   266 ETHANE,CHLORO-
4 12826 1,2-HYDRAZINEDISULFONYLDIFLUORIDE
5   289 ETHENE,1,1-DIFLUORO-

RANK  FORMULA                          M.WT B.PK   PURITY   FIT   RFIT
1 O2.S                                   64   64      994   994    998
2 C2.H5.O2.S.CL                         128   64      615   615    960
3 C2.H5.CL                               64   64      547   547    742
4 H2.O4.N2.S2.F2                        196   64      409   417    818
5 C2.H2.F2                               64   64      326   473    686

MASS   INTEN      1     2     3     4     5
  33              1                     428
  34              4                       5
  35                   98    30
  36                   81    38
  43                                     31
  44                   70               377
  45                  118               658
  46                                     14
  47                  107    19
  48     565   511    417    28   732
  49             4           262
  50      39    24     56    12            34
  51                          80     7     14
  52                                        1
  58                   51
  59                   56    10
  60                   51    27
  61                   68    30
  62                         33            14
  63                         38           138
  64    1000  1034    841   988   736    982
  65       6     9     68    25   320     22
  66      41    50    115   314   125
  67                          8   422
  74                   37
  83                              235
  93                  193
 113                              524
 128                    4
 130                    4
 196                               21
```

FIGURE 2.18

Identification of Sulfur Dioxide

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TABLE 2-9

QUANTITIES OF COMPOUNDS RELEASED FROM FOAM (mg/gram)

	TEMPERATURE		
COMPOUND	340°F	280°F	250°F
Carbon Disulfide	0.094 (0.0087)*	0.025 (0.0023)*	0.013 (0.0059)*
Sulfur Dioxide	1.65 (0.416)*	N.D.	N.D.
Benzene	0.013	----	----
Carbonyl sulfide	0.17**	----	----

* Standard deviation, three replicates.
**Estimate, see text.
N.D. = None Detected.
---- = Not analyzed at this temperature.

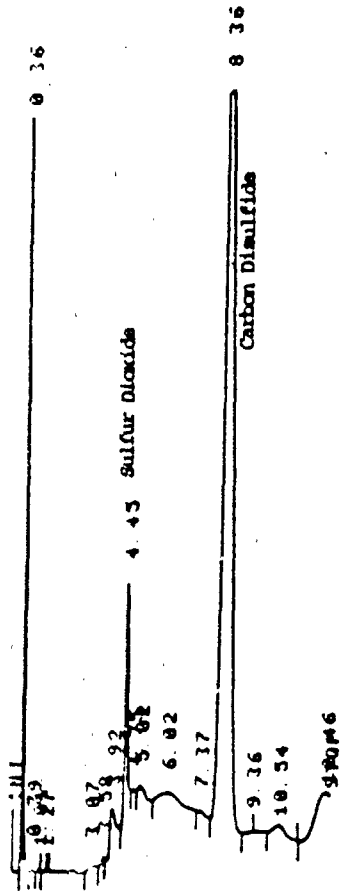

FIGURE 2.19
GC/ECD Chromatogram

Table 2-7 also indicates that the TLV for sulfur dioxide (5 $\mu g/m^3$) would not be exceeded unless the foam released greater than 0.04 mg sulfur dioxide per gram of foam. The quantity released at 340° is greater than this by a factor of 40.

2.4 Conclusions

The normal operating temperature range inside the PATRIOT Heater/Air Conditioners was measured. Outgassing experiments were performed at a number of temperatures on five materials chosen by the Investigative Team. The Investigative Team suggested that the maximum temperature tested should be 15% greater than the maximum observed operating temperature. At these temperatures, the results show that the concentrations of the compounds released will probably not reach hazardous levels.

Two materials (tygon tubing and black insulating foam) were also tested at temperatures much higher than normal operating temperatures. Certain compounds were released from the insulating foam in concentrations which could possibly be hazardous. The assumptions used to estimate the hazard from this release were chosen to overestimate a potential hazard. They were strongly on the side of safety.

The Investigative Team noted a manufacturing flaw in unit SN 801160. A piece of reflective aluminum intended to protect the insulating foam from high temperatures was missing from this unit. The Investigative Team agreed that this was a serious quality control defect.

3.0 TASK 2 - RECOMMENDATIONS 3, 4, & 5

3.1 Summary of Target Parameters

A number of target parameters were suggested in the draft experimental plan dated July 30, 1982. In the meeting of the Investigative Team on August 9, 1982 other parameters were added. The final list of target parameters for the sampling effort at Fort Bliss included:

1. Acrolein
2. Formaldehyde
3. Cyanide
4. Amines
5. Hydrogen Chloride
6. Carbon Dioxide
7. Carbon Monoxide
8. Semi-volatile organics and aromatics collected on charcoal
9. Volatile organics and aromatics collected on Porapak N.

The results show that no acrolein, cyanide or hydrogen chloride was present in the air in the CRG. All samples were below the detection limit of the methods. Traces of formaldehyde were found both inside and outside the CRG shelter, but the levels found were so low that they did not constitute any hazard. An unknown compound was present in the ambient air at Fort Bliss which interfered with the analysis for amines. Therefore, no results were obtained for amines. Carbon dioxide and carbon monoxide levels inside the CRG were not significantly different from the levels found in the ambient air outside the CRG. The charcoal tube test for semi-volatile organics and aromatics did not detect any contaminants at hazardous levels. Trace quantities of volatile organic and aromatic compounds were found in the Porapak N sampling tubes. Again, the compounds were well below levels which could possibly be hazardous.

Earlier reports from site personnel at Fort Bliss indicated that Unit 81013 was missing a piece of reflective aluminum inside the heater box which shields the black foam insulation from exposure to high temperatures created by the heater rods. The visual inspection performed by Versar and VSE personnel showed that this was not in fact the case. All pieces of reflective aluminum were present and properly installed.

The Versar and VSE inspection of Unit 81013 did uncover other significant findings. Two plastic materials, the teflon heater grommets and the tubing, had melted at some previous time. At some point the inside of the heater box on this particular unit reached temperatures which exceeded those for which the internal components were designed. The temperatures required to do this damage were much higher than those measured in the thermal experiments described in Section 2.1.2.

3.2 Sampling

3.2.1 Introduction

Versar was contracted by VSE Corporation to sample the exhaust air from two MERADCOM PATRIOT Heater/Air Conditioners for selected inorganic and organic compounds as described in the "Draft for Comment" Test Plan dated July 30, 1982 (Appendix I). Prior to testing, each individual heater unit was installed in the CRG. Each unit was visually inspected prior to heater operation and testing activities to ensure it was assembled according to specification. Samples were collected inside the shelter using techniques which would allow detection of the target parameters: acrolein, amines, aromatics (less than 120 molecular weight), carbon dioxide, carbon monoxide, formaldehyde, hydrogen cyanide, hydrogen chloride, and a broad range of organic compounds. Corresponding to each of these sample sets collected inside the shelter, an identical sample set was collected outside the shelter at a point near the Heater/Air Conditioner inlet. The sample sets collected outside the shelter were used to establish baseline ambient conditions for comparisons with air inside the shelter during the testing.

3.2.2 Facility Description

As each of the PATRIOT Heater/Air Conditioners was to be tested, it was installed in position on the CRG shelter. The CRG shelter was outfitted with communications equipment which was contained in instrumentation cabinets and was cooled independently from the interior air. The interior dimensions and top view of the CRG are presented in Figure 3.1. The volume of the heated/air conditioned area was approximately 330 cubic feet (9.4 cubic meters).

During the week of sampling activities, the CRG was parked at Abernathy Park in Fort Bliss, Texas, behind a Raytheon facility. The CRG was powered using an in-house source rather than a generator deployed near the CRG. The initial phase of activities prior to sampling was a complete inspection of both the CRG itself and the PATRIOT Heater/Air Conditioner in position on August 23, 1982 (Unit A - SN 81013). Inside the CRG shelter, visual inspection revealed only one major material that was in close proximity to the heated air. This material was a dark porous sound proofing foam. It was located on all four sides inside the heating duct that directs the conditioned air into the shelter. No other materials observed inside the shelter appeared to be potential candidates for further consideration.

The inspection of the PATRIOT Heater/Air Conditioner, Unit A (SN 81013), revealed several operating conditions that were unusual. First, the drain for the heater box was closed, allowing water to accumulate in the box and soak into the black foam. This accumulated water resulted from operation of the air conditioner, not the heater. Before the test the drain was opened, and the water was drained out. Second, during the visual inspection through the side vent (fresh air make-up duct), Versar and VSE personnel observed that two materials in the heater box had been damaged. The first material was the tygon (R-3603) tubing used for the drain from the air conditioning unit through the heater box to the outside. The tygon tube is 3/8" ID, 5/8" OD, 3"

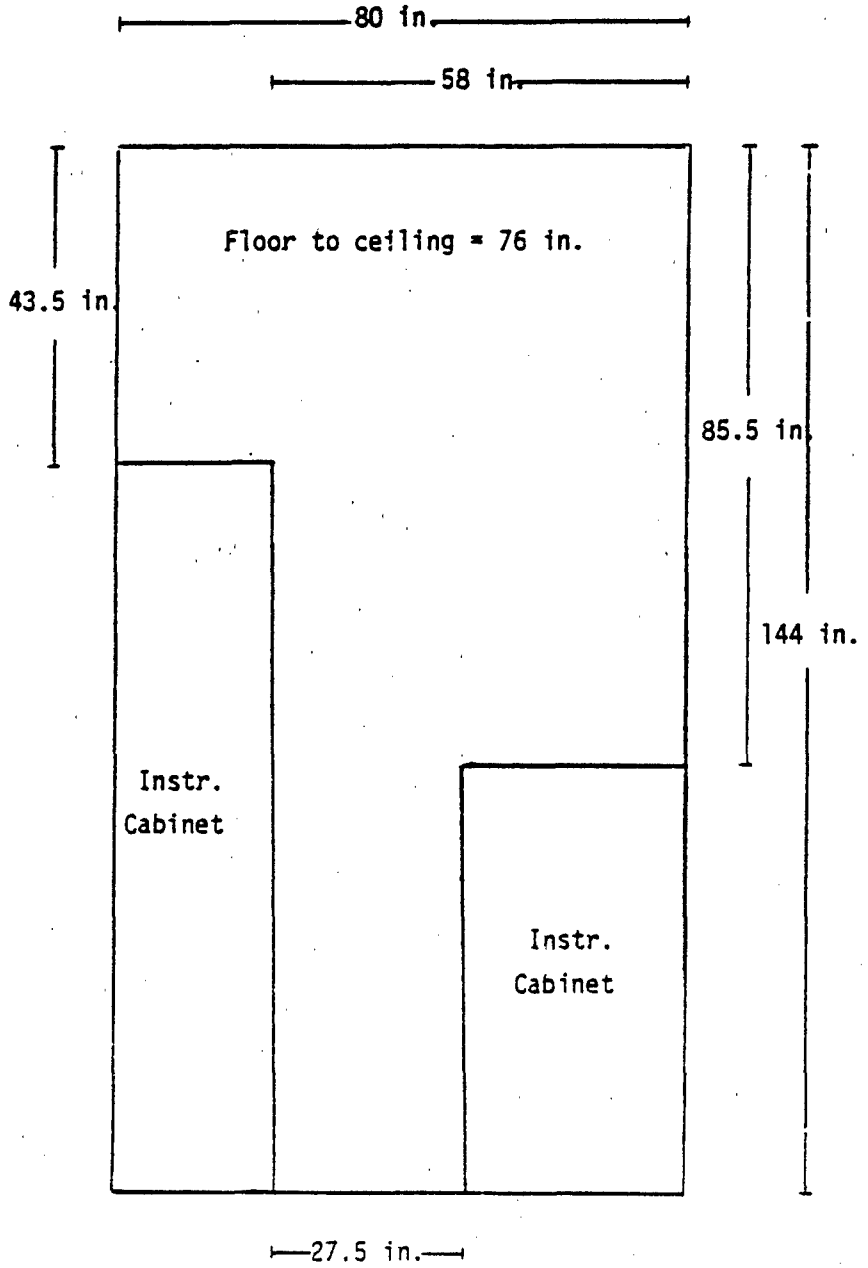

FIGURE 3.1

Interior Dimensions of CRG Shelter

K-55

long, clamped at either end with standard hose clamps. At the time of the inspection this tubing was charred and deformed (damage affected approximately 30% of the surface area). It was therefore removed for visual inspection. This tubing was not placed back into the unit during testing, nor was a section of replacement drain tubing installed. The second material in the heater box that appeared damaged was six (6) teflon grommets that are used to insulate the right end of the heater rod from the metal holder. The grommets were melted. There were several small deposits of molten teflon on the bottom of the box. All other visual features appeared normal, with the black foam properly shielded from the heater rods with reflective aluminum. It appears that during previous operations, the heater box became hot enough to damage the drain tubing and the teflon grommets.

An extensive inspection of the PATRIOT Heater/Air Conditioner, Unit B (SN 801198), was conducted at VSE's facility in Alexandria, Virginia during the week of August 9, 1982. A brief visual inspection at Fort Bliss revealed no apparent problems, and all materials were installed as specified.

3.2.3 Summary of Monitoring Operations

Inspection and testing of the PATRIOT Heater/Air Conditioners were conducted by Versar personnel on August 23 - 26, 1982. The Phase 1 test was the physical inspection of the two units prior to operation. The air sampling tests were conducted in two phases which were designated as Phase 2 and Phase 3. Two Heater/Air Conditioners, labelled A and B, were tested.

Phase 2 sample collection was made up of two 2-hour sample sets inside the CRG when Unit A was operating with the heater off in the air conditioning mode. Similar sample sets were also collected from the outside air to determine ambient baseline conditions. Phase 3 required

the collection of four 1-hour sample sets inside the CRG with first Unit A, and then Unit B, installed and operating in the high heat mode. Outside air sample sets were also collected during Phase 3.

During Phase 2 and 3 tests, make-up air was drawn through the Heater/Air Conditioner. It is believed that similar operating conditions were employed during the April, 1982 incident. One of four covers was removed from the chemical/biological filter intake. During all tests for chemical irritants, this cover remained off.

During Phase 3 sampling both Units A and B were operated with the main switch on high heat and the thermostat set at the highest heat setting. In some previous experiments the over-temperature switch and the thermostat had been bypassed. In this mode the heater operated with all 15 heater rods on continuously. This was not done in this sampling for the following reasons. First, the high ambient air temperatures at Fort Bliss (65 to 80°F) were not characteristic of temperatures encountered during winter months when the heaters will actually be used. The high temperatures that would be achieved could damage the heater unit, and the results would not be representative of typical operating conditions. The second and more important reason for not bypassing the controls was the desire to maintain temperatures in the CRG which would allow the sampling to proceed. Temperatures over 130°F could have damaged either the sampling media or the sampling equipment. These temperatures would also have driven the sampling personnel out of the CRG. Versar sampling personnel were assured by Mr. Robert Sherfy (VSE) that when the heater is set in the high heat mode, approximately 50% of the heater rods are on under all conditions. The unit, therefore, was always exposed to heated conditions. Temperature data collected at the exhaust of the heater indicated that some percentage of the heater rods were on at all times during the sampling.

Post-testing inspections revealed no significant changes to either Unit A or B. Unit B (SN 801198) remained in position on the CRG after Versar concluded testing. Unit A (SN 81013) was for shipment back to VSE in Alexandria, Virginia for additional inspections to be conducted by VSE personnel.

3.2.4 Sample Collection Equipment and Preparation

The following list represents the equipment used to collect the first-hour sample sets during each of the three tests:

9 Porapak N tubes (3 were field blanks)
9 Charcoal tubes (3 were field blanks)
1 CO_2 dosimeter tube
2 Midget impingers, standard
10 Midget impingers, fritted
8 Liquid traps
8 High flow sampling pumps
4 Electric vacuum pumps
1 Low flow sample pump
4 Three-tube manifolds
12 Sample bottles
80 ml 1% sodium bisulfite ($NaHSO_3$) stock solution
30 ml 0.1M sodium hydroxide (NaOH) stock solution
30 ml 1:100 hydrochloric acid - isopropanol stock solution
1 Carbon Monoxide monitor
Cooling manifolds and ice
Tygon tubing

Before collecting the first sample set, the impingers were cleaned according to the following procedure:

a) Wash with mild detergent
b) Rinse with water
c) Rinse with 1:1 nitric acid
d) Rinse six times with deionized water
e) Shake out excess water

In the field, the impingers were cleaned between sampling sets by first rinsing with deionized water and then rinsing with the particular solution to be used in the impinger.

3.2.5 Phase 2: Characterization of the CRG

The purpose of the Phase 2 test was to verify that none of the target parameters were present inside the CRG when the Heater/Air Conditioner was operating in other than the high heat mode. For this test, the unit installed on the CRG (Unit A) was operated with the air conditioner compressor and fan on but the heater off. Two 2-hour sample sets were scheduled to be collected inside the CRG and two corresponding 2-hour sets were collected outside. Each sample set utilized the following trapping media under the specified conditions:

Charcoal - 3 charcoal tubes (400 mg front section; 200 mg break-through section SKC catalogue No. 226-09) were connected in parallel, using tygon tubing, to an electric vacuum pump. A needle valve, installed at the pump inlet, was used to adjust the air sampling rate to approximately 250 ml/min for each tube. Cooling manifolds were used to cool the tubes to approximately 50°F. The charcoal tubes were activated and sealed at the factory.

Porapak N - 3 Porapak tubes (18 cm x 6 mm OD glass packed with 6 cm of Porapak N) were connected in parallel, using tygon tubing, to an electric vacuum pump. A needle valve, installed at the pump inlet, was used to adjust the air sampling rate to approximately 100 ml/min for each tube. Cooling manifolds were used to cool the tubes to approximately 50°F. Prior to use, the Porapak tubes were pre-conditioned at 190° with a helium (99.999%) flow rate of 5 ml/min for 12 hours and sealed in the Versar laboratories.

Sodium Bisulfite ($NaHSO_3$) - 2 sampling trains were used per set. Each train consisted of 2 midget fritted impingers, each containing 10 ml of 1% $NaHSO_3$ solution, connected in series to a high flow sampling pump. The sampling pumps were calibrated to draw air through the impingers at the rate of 1.0 liter/min.

Sodium Hydroxide (NaOH) - One standard midget impinger, containing 15 ml of 0.1M NaOH, was connected to a high flow sampling pump. The pump was calibrated to draw air through the impinger at the rate of 1.0 liter/min.

Acidified Isopropanol - One fritted midget impinger, containing 15 ml of 1:100 hydrochloric acid - isopropanol solution, was connected to a high flow sampling pump. The pump was calibrated to draw air through the impinger at the rate of 1.0 liter/min.

Collection of the first sample sets began at approximately 2140 hours MDT on August 24 and continued for 2 hours as scheduled. Collection of the second sample sets began at approximately 0020 hours MDT on August 25. Outside (ambient) sampling was terminated at 0050 hours because of heavy rain showers. Inside sampling was terminated at 0140 hours, when power to the CRG was lost as a result of a severe electrical storm.

As each sampling period ended, the charcoal and Porapak tubes were labelled and sealed with appropriate caps and placed inside screw cap culture tubes. The solution from each impinger was poured into a labelled sample bottle and refrigerated at 4°C.

Phase 2 testing also included the collection of field blanks during the first two-hour test. The following field blanks were collected:

3 Porapak N tubes
3 Charcoal tubes
2 Sodium Bisulfite solution
2 Sodium Hydroxide solution
1 Acidified Isopropanol solution

The Porapak N and charcoal blanks were prepared by opening the ends of the tubes and then resealing them with appropriate caps. The sodium hydroxide and acidified isopropanol impinger solution blanks were prepared by pouring 15 ml of the appropriate solution into a clean impinger bottle and then into a labelled sample bottle. The sodium bisulfite blanks were prepared in an identical manner, except that 10 ml of solution was used. All impinger solution blanks were then placed in a cooler at 4°C and stored until shipment to the analytical laboratories.

In addition to the above listed sampling activities, a continuous-reading carbon monoxide (CO) analyzer was used to monitor the CO levels both inside and outside the CRG. Both levels remained constant at approximately 0.2 ppmv. Also, the air temperature, both inside and outside the CRG, was recorded every 20 minutes. The inside air temperature ranged from 68°F to 75°F during the Phase 2 tests. Meanwhile, the outside air temperature ranged from 72°F to 85°F.

A summary of all samples collected during Phase 2 testing is presented in Table 3-1.

3.2.6 Phase 3: Testing in the High Heat Mode

The purpose of the Phase 3 tests was to determine whether any of the target parameters were introduced into the CRG when the PATRIOT Heater/Air Conditioners were operated in the high heat mode. Two heater/air conditioners, designated Unit A (SN 81013) and Unit B (SN 801198), were subjected to Phase 3 testing.

First, Unit A was switched to the high heat mode. Four consecutive inside air sample sets were collected for one-hour each, with the exception of the isopropanol sample which was collected only during the first 30 minutes of each one-hour period (the sampling time for the isopropanol impinger was reduced from one hour to 30 minutes because of evaporation of the impinger solution). So, four outside air sample sets were collected, corresponding to each of the inside air sample sets, to determine if the outside air used for CRG make-up air was contributing potential irritants to the shelter.

The sample collection apparatus was identical in both sample number and sampling rates to that described for Phase 2 sampling in 3.2.5. Also, as in Phase 2 testing, CO concentration and temperature measurements, both inside and outside the CRG, were recorded during the collection of each sample set.

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TABLE 3-1

SAMPLING DESIGN FOR AIR SAMPLES COLLECTED IN THE CRG SHELTER WITH THE PATRIOT HEATER/AIR CONDITIONER UNIT A DURING PHASE 2 CONSISTING OF TWO 2-HOUR SAMPLING SETS

	Shelter Air	Make-up Air	Blanks Field	Blanks Lab	1st Set Summary	2nd Set Summary	Total Summary
Porapak N Tubes	3*	3*	3**	3**	12	6	18
Charcoal Tubes	3*	3*	3**	3**	12	6	18
0.1 M NaOH	1	1	1***	---	3	2	5
1% $NaHSO_3$	2+	2+	2+	---	6	4	10
Isopropanol	1	1	1	---	3	2	5
CO/CO_2	1++	---	---	---	1	1	2
			TOTAL SAMPLES		37	21	58

* Triplicate samples were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman.

** Blank traps were collected during the first sampling set only.

*** A blank for 0.1 M NaOH impinger solution was collected during the first sampling set.

\+ Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples were collected during both sampling sets, and a blank sample were collected during the first sampling set. These duplicate samples and blanks were submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology.

++ Carbon monoxide (CO) was monitored continuously and carbon dioxide was monitored using a dosimeter.

Collection of the first Unit A sample sets began at 0310 hours MDT on August 25, 1982. During this hour, the temperature inside the CRG increased from 82°F to 101°F, while the outside air temperature reached 69°F. The CO concentration inside and outside the CRG shelter was measured at 0.2 ppmv. A full set of field blanks, as described in 3.2.5, was prepared during this first hour.

Collection of the second Unit A sample sets began at 0455 hours. During this hour, the temperature inside the CRG increased from 106°F to 109°F, while the outside air temperature reached 72°F. The CO concentration measured inside the CRG, 0.3 ppmv, was only negligibly higher than the outside air concentration of 0.2 ppmv.

Collection of the third Unit A sample sets began at 0625 hours. During this hour, the temperature inside the CRG increased from 108°F to 118°F, while the outside air temperature reached 78°F. The CO concentration inside the CRG remained at 0.3 ppmv, while the outside air concentration continued to be 0.2 ppmv.

Collection of the fourth Unit A sample sets began at 0752 hours. During this hour, the temperature inside the CRG reached 124°F while the outside air temperature reached 82°F. Again, the CO concentration inside the CRG remained only negligibly higher than the outside air concentration. Also during this time, additional sets of Porapak N and charcoal field blanks were prepared.

After the fourth Unit A sample sets were completed, Unit A was removed and replaced with Unit B. Unit B was then subjected to the same tests as those performed on Unit A. Again, all samples were collected for one-hour, with the exception of the isopropanol impinger, which was collected for 30 minutes.

Collection of the first Unit B sample sets began at 2133 hours MDT on August 25, 1982. During this hour, the temperature inside the CRG increased from 72°F to 109°F, while the outside air temperature reached

72°F. The CO concentration inside the CRG was equal to the outside air concentration of 0.2 ppmv. Also during this hour, a full set of field blanks was prepared.

Collection of the second Unit B sample sets began at 2307 hours. During this hour, the temperature inside the CRG increased from 112°F to 120°F, while the outside air temperature reached 74°F. The CO concentration inside the CRG was again equal to the outside air concentration of 0.2 ppmv.

Collection of the third Unit B sample sets began at 0043 hours on August 26. During this hour, the temperature inside the CRG increased from 118°F to 124°F, while the outside air temperature reached 74°F. The CO concentration inside the CRG remained equal to the outside air concentration of 0.2 ppmv.

Collection of the fourth Unit B sample sets began at 0215 hours. During this hour, the temperature inside the CRG increased from 124°F to 128°F, while the outside air temperature decreased to 72°F. The CO concentration inside the CRG remained equal to the outside air concentration of 0.2 ppmv. Also during this hour, additional Porapak N and charcoal field blanks were prepared. A summary of samples collected from each unit is presented in Table 3.2.

In addition to the sampling techniques used in the Phase 3 sampling for Unit A, a long-term color dosimeter tube was used to measure the carbon dioxide (CO_2) concentration inside the CRG during Phase 3 testing of Unit A (pump failure caused the dosimeter tube used for Phase 3 Unit A tests to be invalid). A sampling pump was used to draw air through the tube at the rate of 20 ml/min from 2133 hours until 0315 hours (342 min). The tube indicated that, during that period, the average CO_2 concentration inside the CRG was 691 ppmv.

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TABLE 3-2

SAMPLING DESIGN FOR AIR SAMPLES COLLECTED IN THE CRG SHELTER EQUIPPED WITH THE PATRIOT HEATER/AIR CONDITIONER DURING PHASE 3 CONSISTING OF FOUR 1-HOUR SAMPLING SETS PER UNIT A AND PER UNIT B

	Shelter Air	Make-up Air	Blanks Field	Blanks Lab	Samples Hourly	Samples Total
Porapak N Tubes	3*	3*	3*	3*	12	33
Charcoal Tubes	3*	3*	3*	3*	12	33
0.1 M NaOH	1	1	1**	---	3	9
1% $NaHSO_3$	2+	2+	2+	---	6	18
Isopropanol	1	1	1**	---	3	9
CO/CO_2	1++	---	---	---	1	4
			TOTAL SAMPLES		37	106

* Triplicate samples and blank traps were collected and submitted to U.S. AEHA and Raytheon/Skinner & Sherman. Field blanks were collected only during sampling sets 1 and 4; lab blanks were submitted only for sampling set 1.

** A field blank for these samples was collected during the first sampling set only.

\+ Duplicate 1% $NaHSO_3$ (sodium bisulfite) impinger samples and field blanks were collected and submitted to Raytheon/Skinner & Sherman for analysis of acrolein using NIOSH P&CAM 211 methodology. Field blanks were only collected during the first sampling set.

++ Carbon monoxide (CO) was monitored continuously and carbon dioxide was monitored using a dosimeter.

3.2.7 Sample Distribution

After samples were collected, they were prepared for shipment to Raytheon/Skinner & Sherman, U.S. Army Environmental Hygiene Agency, and Versar Laboratories. Samples were shipped via Federal Express to the respective laboratories. Shipments containing impinger solutions contained ice packs to maintain the samples at 4°C.

The laboratories received the samples indicated in Tables 3-3, 3-4, and 3-5, with the exception of the laboratory blanks. The laboratory blanks were shipped directly from the Versar Laboratory. Chain-of- custody records, listing the enclosed samples, were included with each shipment. Chain-of-custody forms are presented in Appendix V.

3.3 Analysis of Target Parameters

3.3.1 Acrolein In Air

Acrolein in air was determined on site using NIOSH Method P&CAM 211. Two midget impingers cooled to 4°C and connected in series, each containing 10 ml of 1% sodium bisulfite ($NaHSO_3$) solution, were used to collect air samples for acrolein determinations. A sampling rate of approximately 1 liter/min for approximately one-hour provided a detection limit of 0.05 mg acrolein/m^3 in a sample volume of 53 liters of air. No acrolein was found in samples collected at Fort Bliss, Texas. Two samples, each spiked at 0.24 mg acrolein/m^3, gave 98% and 96% spike recoveries respectively. The data are presented in Table 3-6.

3.3.2 Formaldehyde in Air

Formaldehyde in air samples were collected and analyzed following NIOSH Method P&CAM 125. Two midget impingers cooled to 4°C and connected in series, each containing 10 ml of 1% sodium bisulfite ($NaHSO_3$) solution, were used to collect air samples for formaldehyde determinations. An air volume of 53 liters provided a detection limit of

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TABLE 3-3

SAMPLES SUBMITTED TO RAYTHEON/SKINNER & SHERMAN COLLECTED FROM TESTS CONDUCTED IN THE CRG SHELTER WITH THE PATRIOT HEATER/AIR CONDITIONER DURING PHASES TWO AND THREE

	Shelter Air	Make-up Air	Blanks Field	Blanks Lab	Total Summary
Phase 2 (SN 81013)					
Porapak N Tubes	2	2	1	1	6
Charcoal Tubes	2	2	1	1	6
1% $NaHSO_3$	2	2	1	--	5
			TOTAL SAMPLES		17
Phase 3 (SN 81013 & 801198)					
Porapck N Tubes	8	8	4	2	22
Charcoal Tubes	8	8	4	2	22
1% $NaHSO_3$	8	8	2	--	18
			TOTAL SAMPLES		62

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TABLE 3-4

SAMPLES SUBMITTED TO U.S ARMY ENVIRONMENTAL HYGIENE AGENCY COLLECTED FROM TESTS CONDUCTED IN THE CRG SHELTER WITH THE PATRIOT HEATER/AIR CONDITIONER DURING PHASES TWO AND THREE

	Shelter Air	Make-up Air	Blanks Field	Blanks Lab	Total Summary
Phase 2 (SN 81013)					
Porapak N Tubes	2	2	1	1	6
Charcoal Tubes	2	2	1	1	6
			TOTAL SAMPLES		12
Phase 3 (SN 81013 & 801198)					
Porapak N Tubes	8	8	4	2	22
Charcoal Tubes	8	8	4	2	22
			TOTAL SAMPLES		44

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TABLE 3-5

SAMPLES SUBMITTED TO THE VERSAR LABORATORY
COLLECTED FROM TESTS CONDUCTED IN THE CRG SHELTER
WITH THE PATRIOT HEATER/AIR CONDITIONER DURING
PHASES TWO AND THREE

	Shelter Air	Make-up Air	Blanks Field	Blanks Lab	Total Summary
Phase 2 (SN 81013)					
Porapak N Tubes	2	2	1	1	6
Charcoal Tubes	2	2	1	1	6
0.1 M NaOH	2	2	1	--	5
1% $NaHSO_3$	2	2	1	--	5
Isopropanol	2	2	1	--	5
			TOTAL SAMPLES		27
Phase 3 (SN 81013 & 801198)					
Porapak N Tubes	8	8	4	2	22
Charcoal Tubes	8	8	4	2	22
0.1 M NaOH	8	8	2	--	18
1% $NaHSO_3$	8	8	2	--	18
Isopropanol	8	8	2	--	18
			TOTAL SAMPLES		98

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TABLE 3-6

ACROLEIN IN AIR

Field Sample No.	Acrolein (mg/m^3)	Volume of Air Sampled (liters)
A-H-1-B-1 Blank	<0. 25mg/L	---
A-H-1-B-1a	<0.05	53
A-H-1-B-1b	<0.05	53
A-HA-2-B-1a	<0.05	53
A-HA-2-B-1b	<0.05	53
A-H-2-B-1a	<0.05	53
A-H-2-B-1b	<0.05	53
A-HA-2-B-1a	<0.05	53
A-HA-2-B-1b	<0.05	53
A-C-1-B-1 Blank	<0.25 mg/L	---
A-CA-1-B-1a	<0.02	107
A-CA-1-B-1b	<0.02	107
A-CA-2-B-1a	<0.09	27
A-CA-2-B-1b	<0.09	27
A-C-1-B-1a	<0.02	107
A-C-1-B-1b	<0.02	107
A-C-2-B-1a	<0.04	71
A-C-2-B-1b	<0.04	71
A-H-3-B-1a	<0.05	53
A-H-3-B-1b	<0.05	53
A-HA-3-B-1a	<0.05	53
A-HA-3-B-1b	<0.05	53
A-H-4-B-1a	<0.05	53
A-H-4-B-1b	<0.05	53
A-HA-4-B-1a	<0.05	53
A-HA-4-B-1b	<0.05	53
B-H-1-B-1 Blank	<0.25 mg/L	---
B-H-1-B-1a	<0.05	53
B-H-1-B-1b	<0.05	53
B-H-2-B-1a	<0.05	53
B-H-2-B-1b	<0.05	53
B-H-3-B-1a	<0.05	53
B-H-3-B-1b	<0.05	53
B-H-4-B-1a	<0.05	53
B-H-4-B-1b	<0.05	53
B-HA-1-B-1a	<0.05	53
B-HA-1-B-1b	<0.05	53
B-HA-2-B-1a	<0.05	53
B-HA-2-B-1b	<0.05	53
B-HA-3-B-1a	<0.05	53
B-HA-3-B-1b	<0.05	53
B-HA-4-B-1a	<0.05	53
B-HA-4-B-1b	<0.05	53

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0.05 mg formaldehyde/m^3. As shown in Table 3-7, trace levels of formaldehyde were detected both inside and outside the CRG shelter during various collection episodes. The levels are consistently less than 1/15 of the TLV of 3.0 mg formaldehyde/m^3. Spike recoveries of 60% and 30% respectively were found on two samples spiked at 0.5 mg formaldehyde/m^3.

3.3.3 Cyanide In Air

Cyanide as hydrogen cyanide was collected following NIOSH Method P&CAM 116 using midget impingers containing 15 ml of 0.1 M sodium hydroxide (NaOH). Air was drawn through the impinger at a rate of approximately 1 liter per minute for approximately one-hour. The samples and controls were stored at 4°C in a refrigerator prior to analysis. A potentiometric determination of cyanide in samples and controls showed no cyanide to be present at levels above the detection limit. A recovery of 100% was obtained for a spike of 0.06 mg CN^-/m^3 on sample A-H-3-H-1. The data are presented in Table 3-8. The TLV for cyanide is 7 mg/m^3, so the levels were less than the TLV by more than a factor of 100.

3.3.4 Amines in Air

Primary and secondary amines in air were determined using APHA Method 124 - Tentative Method of Analysis for Primary and Secondary Amines in the Atmosphere (Ninhydrin Method). Air samples were collected using midget impingers containing 10 ml of acidified isopropanol. The absorbing solution was reacted with ninhydrin (1,2,3-trikstohydrindene). Primary and secondary amines produce a purple complex whose absorbance is read at 575 nm and compared to a calibration curve prepared from n-butylamine standards. All samples, excluding blanks, collected at Fort Bliss, Texas failed to develop a color response after the addition of the ninhydrin. The blanks, as expected, developed a normal color response. A chemical interference of an unknown nature inhibited color development in all samples collected inside and outside the CRG shelter. Spiked CRG

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TABLE 3-

FORMALDEHYDE IN AIR

Field Sample No.	Formaldehyde (mg/m^3)	Volume of Air Sampled (liters)
A-H-1-8-1 Blank	<0.25 mg/L	---
A-H-1-8-1A	<0.05	53
A-H-1-8-1B	<0.05	53
A-H-2-8-1A	<0.05	53
A-H-2-8-1B	<0.05	53
A-H-3-8-1A	<0.05	53
A-H-4-8-1A	0.09	53
A-HA-1-8-1A	<0.05	53
A-HA-1-8-1B	<0.05	53
A-HA-2-8-1A	<0.05	53
A-HA-2-8-1B	0.09	53
A-HA-3-8-1A	<0.05	53
A-HA-4-8-1A	0.09	53
A-C-1-8-1 Blank	<0.25 mg/L	---
A-C-1-8-1A	<0.02	107
A-C-1-8-1B	<0.02	107
A-C-2-8-1A	<0.04	71
A-CA-1-8-1A	<0.02	107
A-CA-2-8-1A	<0.09	27
B-H-1-8-1 Blank	<0.25 mg/L	---
B-H-1-8-1A	0.09	53
B-H-1-8-1B	0.05	53
B-H-2-8-1A	0.05	53
B-H-2-8-1B	0.05	53
B-H-3-8-1A	<0.05	53
B-H-3-8-1B	<0.05	53
B-H-4-8-1A	<0.05	53
B-H-4-8-1B	0.09	53
B-HA-1-8-1A	<0.05	53
B-HA-1-8-1B	<0.05	53
B-HA-2-8-1A	0.19	53
B-HA-2-8-1B	<0.05	53
B-HA-3-8-1A	0.05	53
B-HA-3-8-1B	<0.05	53
B-HA-4-8-1A	<0.05	53
B-HA-4-8-1B	<0.05	53

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TABLE 3-8

CYANIDE IN AIR

Field Sample No.	Cyanide (mg/m^3)	Volume of Air Sampled (liters)
A-C-1-H-1 Blank	<0.1 mg/L	---
A-C-1-H-1	<0.01	107
A-C-2-H-1	<0.02	71
A-CA-1-H-1	<0.01	107
A-CA-2-H-1	<0.06	27
A-H-1-H-1 Blank	<0.1 mg/L	---
A-H-1-H-1	<0.03	53
A-H-2-H-1	<0.03	53
A-H-3-H-1	<0.03	53
A-H-4-H-1	<0.03	53
A-HA-1-H-1	<0.03	53
A-HA-2-H-1	<0.03	53
A-HA-3-H-1	<0.03	53
A-HA-4-H-1	<0.03	53
B-H-1-H-1 Blank	<0.1 mg/L	---
B-H-1-H-1	<0.03	53
B-H-2-H-1	<0.03	53
B-H-3-H-1	<0.03	53
B-H-4-H-1	<0.03	53
B-HA-1-H-1	<0.03	53
B-HA-2-H-1	<0.03	53
B-HA-3-H-1	<0.03	53
B-HA-4-H-1	<0.03	53

sample absorbing solutions also failed to give the expected color development. N-Butylamine was added to CRG sample absorbing solutions after collection but prior to color development. Spike levels were 3.7 mg n-butylamine/m^3 and spike recoveries were zero. A detection limit of 0.8 mg n-butylamine/m^3 in a 27 liter air sample was provided. The data are presented in Table 3-9.

Control samples at the Versar Laboratories in Springfield, Virginia, were handled to duplicate the field sampling effort in order to determine if the sampling methodology itself caused the chemical interference. Analysis of the controls showed no color inhibition as experienced with the samples collected in El Paso, Texas. Figure 3.2 is a pictura of the solutions after color development in Fort Bliss. The dark tubes on the right are the blanks which developed the blue color. The remaining tubes are the samples which did not develop the blue color.

3.3.5 Hydrogen Chloride in Air

The samples for hydrogen chloride in air used the same impinger solutions as the determinations of cyanide in air. Approximately 60 liters of air were drawn through a midget impinger containing 15 ml of 0.1 M sodium hydroxide (NaOH). The chloride ion levels were measured potentiometrically. The results are presented in Table 3-10. Chloride was detected in all of the samples at concentrations near [illegible] of the blank. The chloride in the blank is probably due to trace impurities in the reagent grade NaOH used in the impinger solutions. Even without adjusting for the error introduced by the blank, all of the values reported are at least 3.5 times less than the TLV of 7 mg/m^3. Most measurements are less than the TLV by a factor greater than 10. The results indicate that hydrogen chloride released from the PATRIOT Heater/Air Conditioners does not present a hazard to personnel working in the CRG.

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TABLE 3-9

AMINES IN AIR

Field Sample No. (liters)	Amines (mg/m^3)	Volume of Air Sampled
A-C-1-I-1 Blank	<2. mg/L	---
A-C-1-I-1	CI	107
A-C-2-I-1	CI	71
A-CA-1-I-1	CI	107
A-CA-2-I-1	CI	13
A-H-A-I-1 Blank	<2. mg/L	---
A-H-1-I-1	CI	27
A-H-2-I-1	CI	27
A-H-3-I-1	CI	27
A-H-4-I-1	CI	27
A-HA-I-1	CI	27
A-HA-1-I-1	CI	27
A-HA-8-I-1	CI	27
A-HA-4-I-1	CI	27
B-H-1-I-1 Blank	<2. mg/L	---
B-H-1-I-1	CI	27
B-H-2-I-1	CI	27
B-H-3-I-1	CI	27
B-H-4-I-1	CI	27
B-HA-1-I-1	CI	27
B-HA-2-I-1	CI	27
B-HA-3-I-1	CI	27
B-HA-4-I-1	CI	27

CI = Chemical Interference

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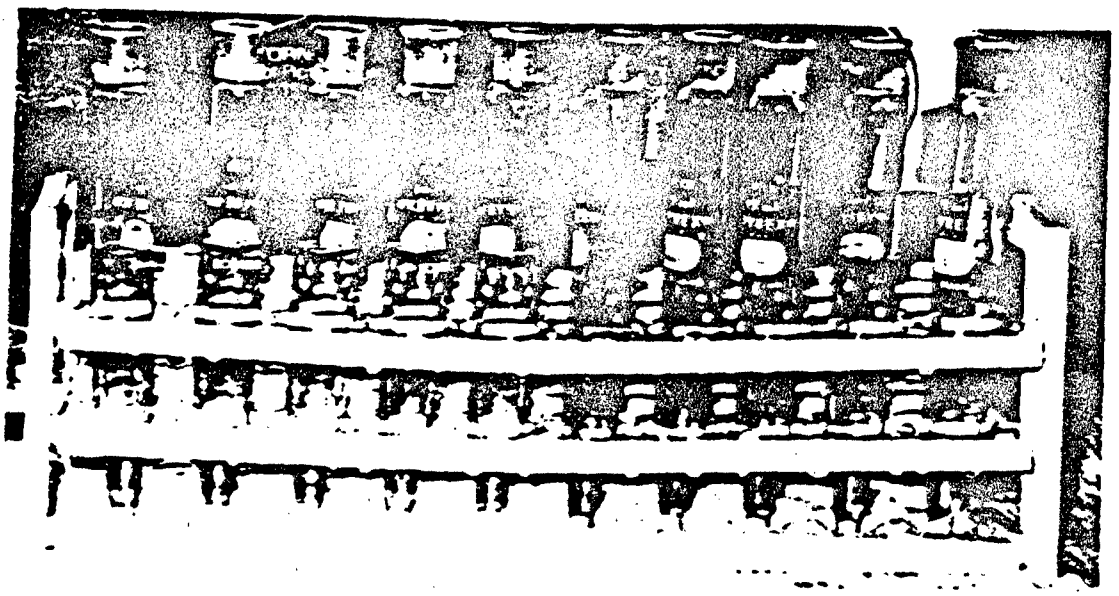

FIGURE 3.2

Interference in Amines Analysis at Fort Bliss

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TABLE 3-10

RESULTS OF SAMPLES FOR
HYDROGEN CHLORIDE IN AIR

Lab Sample No.	Field Sample No.	Volume of Air Sampled (liters)	Chloride (mg/m^3)
3705	A-C-1-H-1-Blk	106.79	0.98
3706	A-C-1-H-1	53.39	1.1
3707	A-C-2-H-1	71.19	0.42
3708	A-CA-1-H-1	106.79	0.42
3709	A-CA-2-H-1	26.70	1.1
3710	A-H-1-H-1-Blk	53.39	0.56
3711	A-H-1-H-1	53.39	0.28
3712	A-H-2-H1	53.39	0.56
3713	A-H-3-H-1	53.39	2.0
3714	A-H-4-H-1	53.39	0.84
3715	A-HA-1-H-1	53.39	0.56
3716	A-HA-2-H-1	53.39	1.1
3717	A-HA-3-H-1	53.39	0.28
3718	A-HA-4-H-1	53.39	0.28
3719	B-H-1-H-1-Blk	53.39	0.28
3720	B-H-1-H-1	53.39	0.56
3721	B-H-2-H-1	53.39	0.28
3722	B-H-3-H-1	53.39	0.28
3723	B-H-4-H-1	53.39	0.28
3724	B-HA-1-H-1	53.39	0.28
3725	B-HA-2-H-1	53.39	0.28
3726	B-HA-3-H-1	53.39	0.56
3727	B-HA-4-H-1	53.39	0.14
3713 Dup		53.39	2.52
3713 Spike (1.0 mg/l)			100% Recovery

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3.3.6 Carbon Monoxide in Air

As mentioned in Section 3.2, the carbon monoxide levels inside the CRG were not elevated to a significant extent. The highest levels observed were 0.3 mg/m^3 which is less than the TLV of 55 mg/m^3 by a factor of 180.

3.3.7 Carbon Dioxide in Air

The dosimeter reading after the sampling operation mentioned in Section 3.2 indicated that the carbon dioxide levels were not significantly elevated in the CRG. The observed value of 691 ppm is approximately 7-fold less than the TLV of 5,000 ppm.

3.3.8 Charcoal Tube Analysis for Organic Contaminants

Samples were standard charcoal tubes (SKC Catalogue No. 2236-09). The fronts and backs were placed into separate screw cap vials fitted with teflon lined septa.

On the day of analysis 3 ml CS_2 was added to the vials and gently agitated. After 30 minutes 1 ml was placed into an injection vial and spiked with 10 ul 2 mg/ml d-10 anthracene. Injection volumes were 2 ul using the solvent flush technique.

Capillary GC/FID was used to screen the extracts before possible GC/MS analysis.

GC Conditions

Instrument	Varian 3700 gas chromatograph
Column	28.5 m x 0.3 mm ID non-polar fused silica capillary
Injector	Splitless
Inlet Vent	Close 10 sec, inject, open after 30 sec; 60 ml/min
Temps: Inlet	250°C
Detector	300°C
Oven	45°C for 4 min, 10°C/min to 280°C, hold 9 min
Gases: Carrier	15 psi He
Make-up	26 ml/min N_2
FID	30 ml/min H_2; 300ml/min Air

Prior to the days injections, a mixture of compounds was injected to serve as retention time markers. The mixture contained 10ppm each benzene, toluene, ethyl benzene, naphthalene, 20ppm d-10 anthracene, and 100ppm benzo(ghi)perylene in CS_2.

The screening criteria was detection of peaks eluting after benzene larger than the response for 1ppm toluene. Extracts that showed peaks were reanalyzed and, if confirmed by FID, were analyzed by GC/MS.

The initial injection of each day showed some large peaks at 17.3 and 20.98 minutes. Since the column was left at 45°C overnight, these peaks indicate cold trapping of impurities in the carrier gas.

Table 3-11 presents the results of the charcoal tube analysis. A typical chromatogram is presented in Figure 3.3. The charcoal tube technique did not detect any contamination in the air in the CRG. The screening criteria were only exceeded by three of the tubes. GC/MS analysis showed that the contaminant in these tubes was toluene. However, one of the three tubes containing toluene was a sampling blank. This indicates that the source of the contamination was an intermittent sample contamination problem, and that the toluene was not actually present in the air of the CRG. Even if the toluene was present in the CRG, the levels found indicate that it is of no concern. The quantities found corresponded to 230 ug/m^3 in sample B-H-1-C-1-blk, 130 ug/m^3 in B-H-1-C-1, and 150 ug/m^3 in B-H-1-C-2. The highest value here is 3500 times less than the TLV for toluene.

3.3.9 Volatile Organic and Aromatic Compounds

Air samples collected on Porapak N sample tubes were analyzed by thermal desorption packed column GC/MS procedures. The methodology used as a reference was EPA Method 603, Federal Register, Vol. 44, No. 233, Monday, December 3, 1979.

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TABLE 3-17

VSE III - SAMPLED AUGUST 24-26, 1982

A = SN81013
B = SN801198

Sampler's #	Lab #	Screen Results/Comments
A-C-1-C-1-blk	3682	Neg.
A-CA-1-C-1	3681	Neg.
-2-	3684	Neg.
A-C-1-C-1	3680	Neg.
-2-	3683	Neg.
A-H-1-C-1-blk	3687	Neg.
-4-	3694	N/I
A-HA-1-C-1	3686	Neg.
-2-	3689	N/I
-3-	3691	N/I
-4-	3693	Neg.
A-H-1-C-1	3685	Neg. GC/MS analyzed
-2-	3688	Neg.
-3-	3690	Neg.
-4-	3692	Neg.

Neg. = No peaks after benzene larger than 1ppm toluene.
N/I = Not Injected

VSE III - SAMPLED AUGUST 24-26, 1982

Sampler's #	Lab #	Screening Results/Comments
B-H-1-C-1-blk	3697	Neg.
-4-	3704	Positive toluene-GC/MS analyzed
B-HA-1-C-1	3696	Neg.
-2-	3699	Neg.
-3-	3701	Neg.
-4-	3703	Neg.
B-H-1-C-1	3695	Positive toluene-GC/MS analyzed
-2-	3698	Positive toluene-GC/MS analyzed
-3-	3700	Neg.
-4-	3702	Neg.

Neg. = No peaks after benzene larger than 1ppm toluene.

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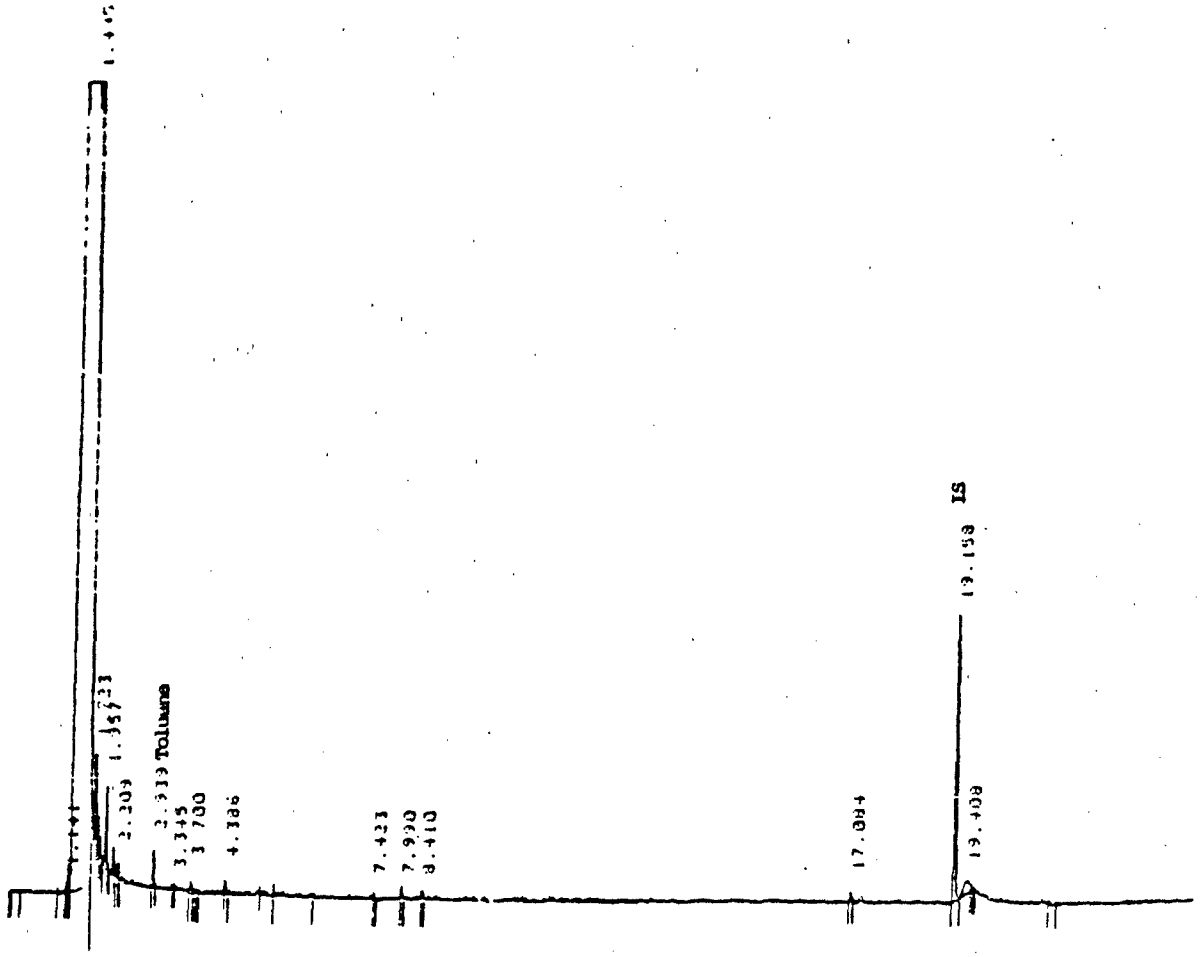

FIGURE 3.3

Charcoal Tube Chromatogram
Sample B-H-1-C-1

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Prior to analysis of samples the GC/MS was calibrated to FC 43 and DFTPP. The instrument response factors were then produced by analysis of standard reference materials. These internal standard response factors were then used for quantitation of identified materials. Unknowns were identified by library search using the EPA NIH 32000 spectra library.

The Porapak N sample tubes were spiked with surrogate spikes prior to sampling. The surrogate spikes were 2.1 micrograms acrylonitrile d3 and 2.6 micrograms 2-fluorobenzene d5. These surrogate spikes were used to monitor the retention capability of the Porapak N.

Upon analysis the sample tubes were spiked with 1.2 micrograms of benzene d6 as an internal standard. The sample tubes were assembled in the desorption unit and purged of air with helium. The sample was then heated to 180°C for eight minutes and injected onto a Chromosorb 101 6 foot glass column at 80°C. After injection the GC oven was programmed to 225°C at 14° per minute and the sample chromatographed into the mass spectrometer. The mass spectrometer parameters were as follows:

Scan Range	20 - 450 AMU
Scan Rate	2.95 seconds/scan
Electron Impact	70 ev

One large early eluting peak was present in all of the samples collected both inside and outside the CRG. It was not present in the blank. Since the peak was present in samples collected both inside and outside the CRG, there apparently is a contaminant present in the ambient air at Fort Bliss, Texas. The spectrum of this peak is presented in Figure 3.4. The spectrum could not be identified using either computer searches or manual interpretation. This suggests that the peak is actually a mixture of compounds. Since the peak is not produced by the PATRIOT Heater/Air Conditioners or the CRG, it is of no concern to this investigation.

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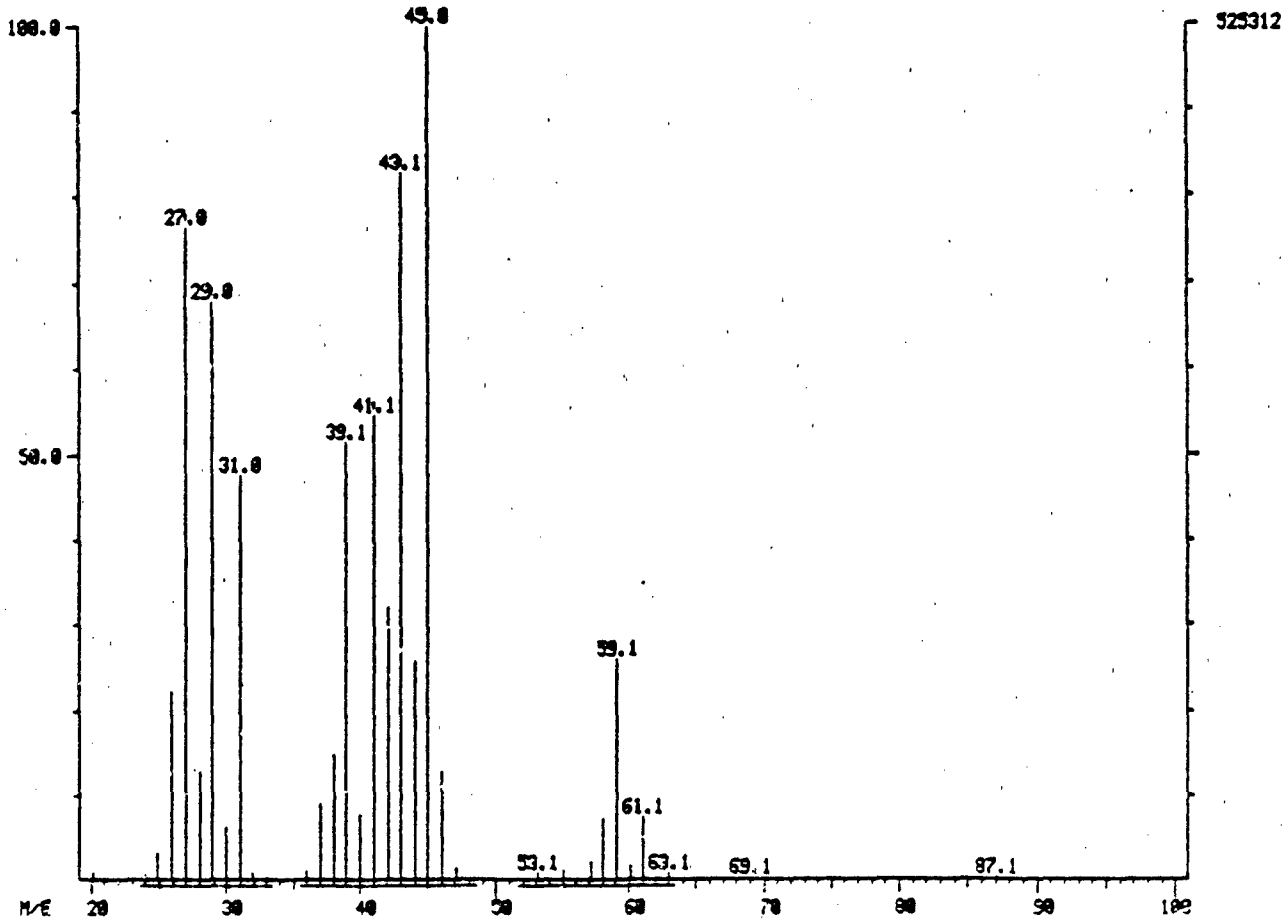

FIGURE 3.4

Mass Spectrum of Fort Bliss Air Contaminant

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The peak was typically present in higher concentrations in the inside of the CRG. This, however, is not surprising. All of the surfaces in the Heater/Air Conditioners and in the CRG have probably been exposed to this contaminant most of the time they have been at Fort Bliss. During the tests the Heater/Air Conditioner and the CRG were heated to the highest temperatures they have been at in months. It is highly plausible that this would cause a release of contaminants which had been accumulated from the air.

Small amounts of some aromatic compounds were found in the CRG. Benzene was found at concentrations near the detection limit for the method. Small amounts were also present in the blanks. The highest concentration of benzene was found in the first hour sample from unit A in the cooling cycle (sample A-C-1-P-1). The concentration in this sample corresponded to an airborne benzene concentration of 0.07 mg/m^3. This is over 400 times less than the TLV for benzene.

Toluene was also found in low concentrations in certain samples. Toluene was not present in the blanks. The highest concentration was found in the sample from unit B, hour 4 in the heating mode (sample B-H-4-P-1). The concentration found was 0.46 mg/m^3. This is over 800 times less than the TLV of 375 mg/m^3. The data for benzene and toluene are presented in Table 3-12.

A number of compounds other than benzene and toluene were also identified in the Porapak N tubes. The compounds are listed in Table 3-13. These compounds were found in small quantities, and they all have fairly high TLV's. The compounds were found both inside and outside the CRG, so they are probably contaminants in the ambient air at Fort Bliss. Typical chromatograms for the samples are presented in Figures 3.5 and 3.6.

Acrolein is a potential contaminant which has received considerable attention throughout this study. We used mass chromatograms

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TABLE 3-12

BENZENE AND TOLUENE IN AIR (mg/m^3)

SAMPLE CODE	BENZENE	TOLUENE
A-H-1-P-1 (in)	0.04	0.06
A-HA-1-P-1 (out)	0.03	0.015
B-H-1-P-1 (in)	0.04	0.26
B-HA-1-P-1 (out)	0.06	0.12
A-C-1-P-1 (in)	0.07	0.33
A-CA-1-P-1 (out)	0.04	0.04
A-H-4-P-1 (in)	0.02	0.06
B-H-4-P-1 (in)	0.03	0.46
A-C-1-P-1 (blank)	0.04	ND

ND = Not Detected.

TABLE 3-13

MISCELLANEOUS COMPOUNDS IN PORAPAK TUBES

SAMPLE NO.	IDENTITY	SCAN NO.
A-H-1-P-1	MEK	304
A-H-1-P-1	Methyl cyclopentane	318
A-H-1-P-1	3-methylbutanol	375
A-H-1-P-1	2-methylpentane	331
A-HA-1-P-1	MEK	308
B-H-1-P-1	MEK	307
B-H-1-P-1	Methyl cyclopentane	317
B-H-1-P-1	Cyclohexane	332
B-HA-1-P-1	MEK	306
B-HA-1-P-1	Methyl cyclopentane	317
B-HA-1-P-1	Cyclohexane	332
A-C-1-P-1	MEK	305
A-C-1-P-1	Butyl acetate	394
A-C-1-P-1	Possibly xylene or ethylbenzene	506
A-CA-1-P-1	Acetic acid	298
A-CA-1-P-1	MEK	308
A-CA-1-P-1	C6 hydrocarbon	318
A-H-4-P-1	MEK	313
A-C-1-P-1	Acetone	257
A-C-1-P-1	Acetic acid	302

MEK = methyl ethyl ketone (2-butanone)

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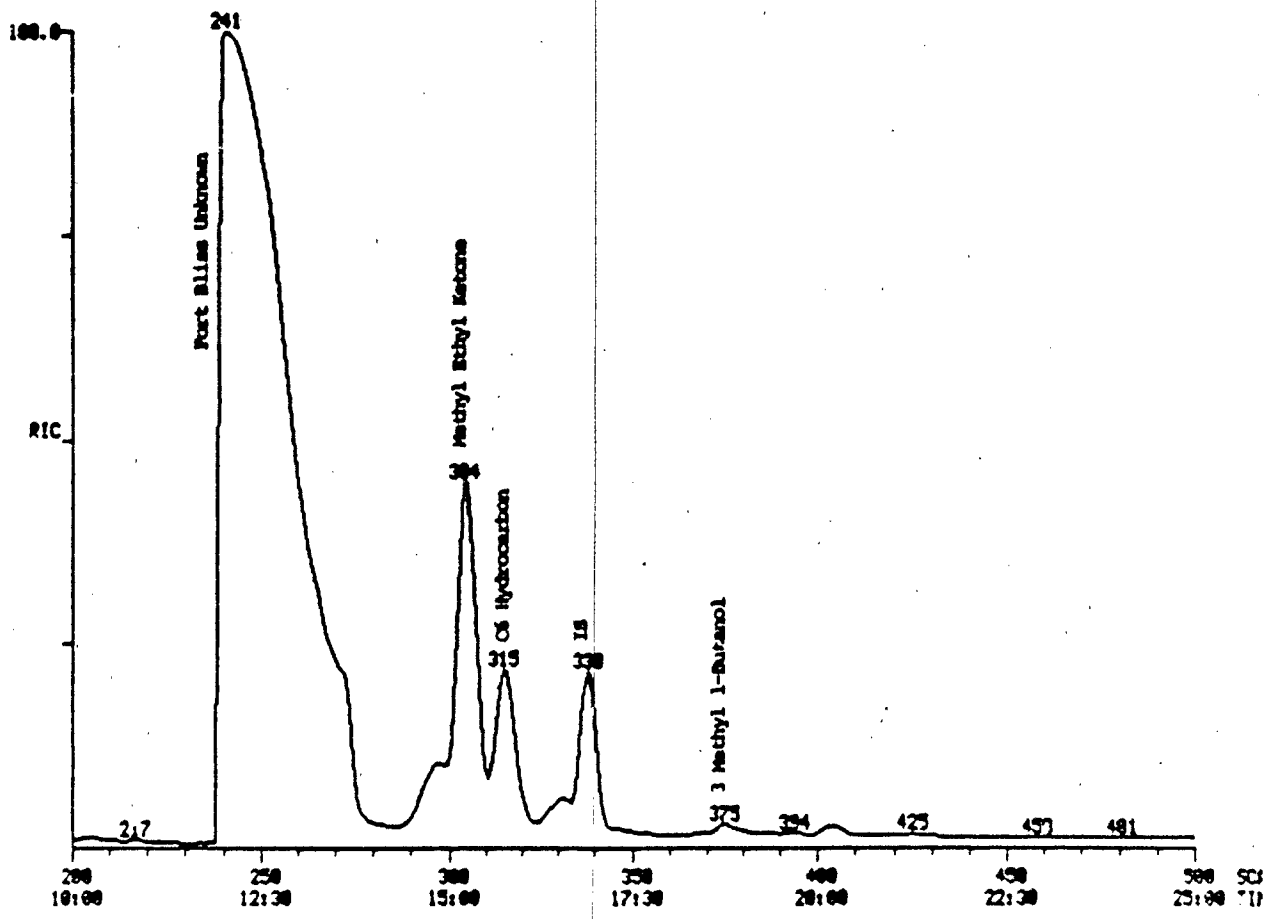

IS = Internal Standard

FIGURE 3.5

Heating Discharge, Inside Air, Unit 81013

K-87

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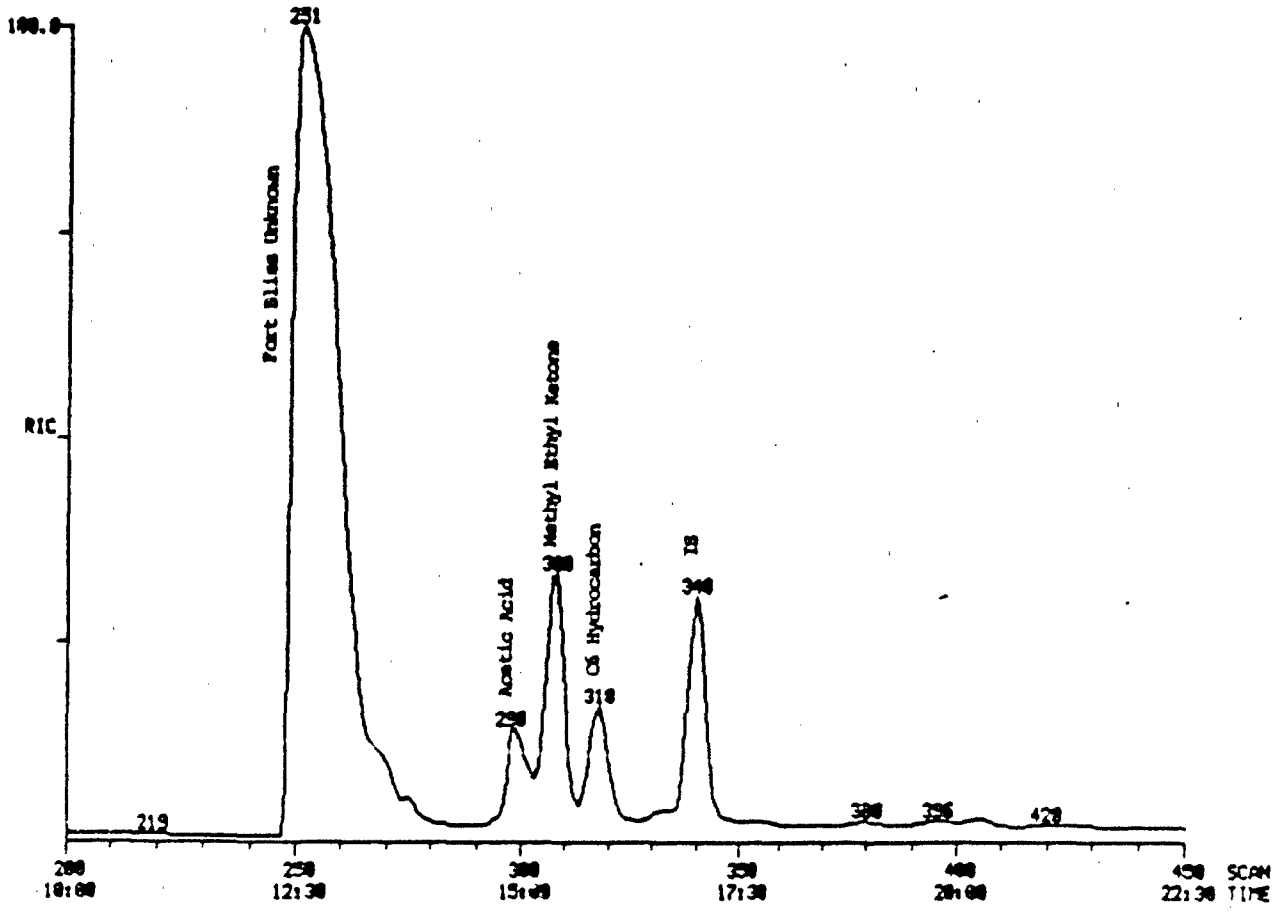

IS = Internal Standard

FIGURE 3.6

Outside Air, Unit 81013

to scan the data for the presence of acrolein. Acrolein would elute under the peak due to the Fort Bliss contaminant if it was present. The total ion current chromatogram normally displayed as GC/MS output would not show a peak for acrolein even if it were present. We therefore used computer reconstructed mass chromatograms to scan for the presence of acrolein. A mass chromatogram plots the intensity of one ion versus time while a total ion current chromatogram plots the intensity of all ions versus time. If one ion, characteristic of a particular compound, is absent throughout a chromatogram; then the compound is not present in the sample. Acrolein has characteristic ions at masses 56 and 27. A mass chromatogram for an acrolein standard containing a propanal contaminant is presented in Figure 3.7. The acrolein peak is at scan number 250 while the propanal peak is at scan number 258. Both compounds have characteristic ions with masses of 27, so there is a peak for both compounds at mass 27. Propanal, however, does not have a characteristic ion with a mass of 56, so only acrolein causes a response at mass 56. This standard contained one microgram of acrolein. The peak height at mass 56 was 18640 counts.

The contaminant present in Fort Bliss air also has an ion at mass 27 but does not have an ion at mass 56. The area under the contaminant peak was scanned for the presence of mass 56. A typical mass chromatogram for a sample is presented in Figure 3.8. It is clear from this that acrolein is not present. The responses at mass 56 are around the noise level of the instrument. The highest peak observed at mass 56 was 401 counts. Assuming (probably falsely) that this peak was due to the presence of acrolein, the calculated amount reaching the mass spectrometer is 0.022 ug. This corresponds to a airborne concentration of 0.004 mg/m^3, which is a factor of 70 less than the TLV of 0.25 mg/m^3. This confirms the results of Section 3.3.1, Acrolein in Air. No acrolein was present in the air in the CRG at Fort Bliss.

Versar

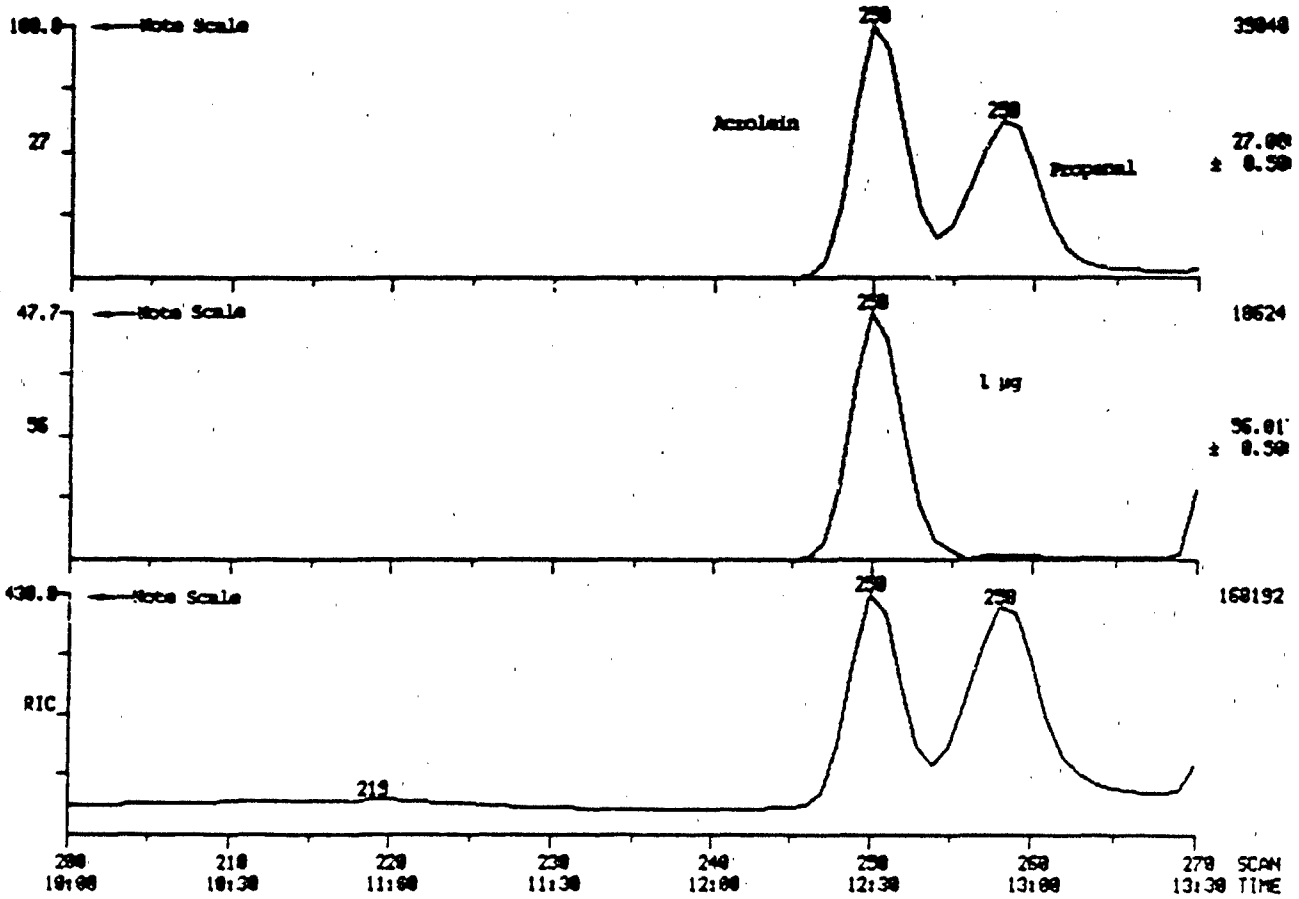

FIGURE 3.7

Reference Acrolein Mass Chromatogram

K-90

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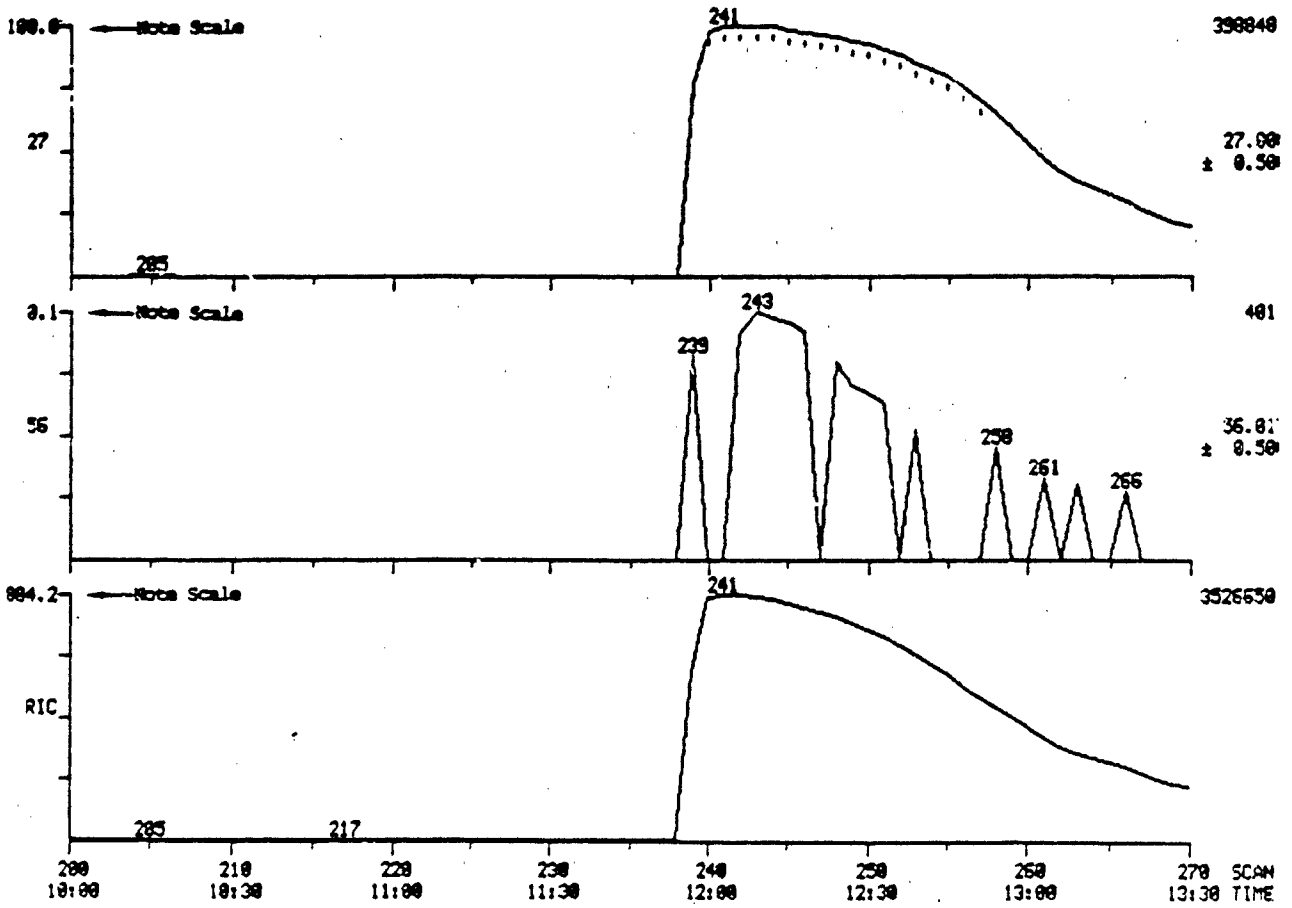

FIGURE 3.8

Unknown Fort Bliss Air Mass Chromatogram
Sample A-H-1-P-1

K-91

All of the samples from the hour one sampling were analyzed. The samples taken inside the CRG during hour four for both units were also analyzed. The data collected up to this point indicated that no useful information would come from analyzing the remainder of the samples, so they were not analyzed.

The recoveries of the surrogate spikes were variable. The results are presented in Table 3-14. The blanks had both been chipped during the sampling trip, so both were exposed to the air before analysis. This could have resulted in some losses. For the samples the recoveries of d-3 acrylonitrile ranged from 0% to 56%, while the recoveries of fluorobenzene ranged from 61% to 103%. The inconsistent recoveries could be due to variations in the temperature during sampling, variations in the humidity during sampling, or variations in the flow rate through the tubes during sampling.

In conclusion, the Porapak N tubes did not detect any significant contamination coming from the CRG of the PATRIOT Heater/Air Conditioners. Small amounts of benzene and toluene were present. The Porapak N tubes did detect a compound (or compounds) present in fairly high concentrations in the ambient air at Fort Bliss.

3.4 Conclusions

The samples taken at Fort Bliss were analyzed for a broad spectrum of irritants and toxic compounds chosen by the Investigative Team. No irritants or toxic compounds were detected in the CRG at Fort Bliss at hazardous concentrations. All materials were found at concentrations well below their Threshold Limit Value (TLV). Most of the materials found in the CRG appeared to be contaminants present in the ambient outside air at Fort Bliss.

The sampling team visually inspected the CRG and the PATRIOT Heater/Air Conditioners at Fort Bliss. They found evidence that unit SN 81013 overheated at some point in the past. This is the unit which caused the original incident.

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TABLE 3-14

RECOVERIES OF SPIKES

SAMPLE	ACRYLONITRILE % RECOVERED	FLUOROBENZENE % RECOVERED
A-H-1-P-1 (in)	0	81
A-HA-1-P-1 (out)	0	88
B-H-1-P-1 (in)	36	77
B-HA-1-P-1 (out)	44	99
A-C-1-P-1 (in)	0	85
A-CA-1-P-1 (out)	56	103
A-H-4-P-1 (in)	0	61
B-H-4-P-1 (in)	0	94
B-H-1-P-1 (blank)	36	75
A-C-1-P-1 (blank)	67	137

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4.0 VALIDATION OF NIOSH METHOD P&CAM 211 - ACROLEIN IN AIR

The performance of NIOSH Method P&CAM 211 with respect to detection limit and efficiency of sorption of acrolein in air was investigated. To determine acrolein in the atmosphere, air is drawn through two midget impingers containing 1% sodium bisulfite ($NaHSO_3$) solution. Acrolein is determined colorimetrically after reaction with 4-hexylresorcinol in an alcoholic trichloroacetic acid solvent medium in the presence of mercuric chloride. The absorbance of the blue colored product, having a strong absorption maximum at 605 nm, is read in a spectrophotometer.

To establish the lowest concentration of acrolein which may be distinguished from zero, a series of seven measurements of one microgram acrolein standard solutions were made. This is presented in Table 4-1. The detection limit was defined as the concentration of acrolein which would yield an absorbance equal to twice the standard deviation of the measurements of the dilute acrolein standard solutions. A detection limit of 0.07 mg acrolein/m^3 in a 50-liter air sample was calculated as follows:

Twice the standard deviation of the absorbances of the seven replicate 1 ug acrolein standards equals 0.010 abs. units. 0.010 abs. units is equivalent to 0.9 ug acrolein.

$$\frac{0.9 \text{ ug acrolein}}{\text{4.0 ml absorbing solution taken for analysis}} \times \frac{\text{15.0 ml total absorbing solution volume}}{\text{50-liter air sample}}$$

$$= 0.0675 \text{ ug/l} = 0.067 \text{ mg/m}^3$$

NIOSH reports a detection limit of 0.023 mg acrolein /m^3 in a 50 liter air sample. The detection limit calculation used here has been referred to by others as the sample and blank definition.[3] It is the lowest concentration of acrolein which can be distinguished from the blank with 95% confidence. This calculation is similar to the method detection limit recently defined by EPA.[4]

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TABLE 4-1
ACROLEIN DETECTION LIMIT

Standards	Absorbance at 605 nm in 1 cm cells	
1 ug	0.015	
1 ug	0.023	
1 ug	0.010	$\bar{x}$ = 0.15
1 ug	0.016	S = 0.005
1 ug	0.022	
1 ug	0.010	
1 ug	0.011	

STANDARD CURVE

Standard (ug)	Absorbance	
1	0.015	
2	0.030	Slope = 0.011
5	0.065	Intercept = 0.008
10	0.139	Correlation = 0.9955
20	0.215	
50	0.358	

$$\text{Detection Limit} = \frac{25}{\text{slope}} = \frac{0.01}{0.011} = 0.91 \text{ ug}$$

K-95

Efficiency of collection of acrolein is reported to be approximately 95% when two impingers are used in series. The NIOSH procedure suggests an air sampling rate of 2 liters/min for a duration of 60 minutes. To determine if acrolein was stripped from the 1% $NaHSO_3$ impinger solutions, ten replicate solutions of 1% $NaHSO_3$ were spiked at 0.5 ug, 1.0 ug and 2.0 ug acrolein. Five solutions at each spike level were sparged with air for 60 minutes at a rate of 2 liters/min. The remaining five solutions at each spike level served as controls and were not sparged. Colorimetric analysis of each impinger solution showed that no losses of acrolein occurred during sampling (see Table 4-2).

A similar, but smaller, scheme was performed to duplicate Versar's sampling technique where air is sampled at a rate of 1 liter/min for a duration of 60 minutes through two midget impingers. The results of this study are shown in Table 4-3.

It appears that no acrolein is stripped from the 1% $NaHSO_3$ absorbing solutions. The detection limit calculated by Versar is three times higher than that reported by NIOSH, but still significantly lower than the threshold limit value of 0.25 mg acrolein/m^3. It should be noted also that the data indicate that the reported detection limit is probably a maximum value. The data from the controls on the stripping experiments can also be used to calculate detection limits. For the experiment at 0.5 ug the detection limit found is 0.015 mg/m^3. The experiments at 1.0 and 2.0 ug give limits of 0.03 mg/m^3 and 0.05 mg/m^3 respectively. These can be compared to the first detection limit determination of 0.07 mg/m^3. It should be noted that the detection limits are lower in the samples with lower spike values, and that the detection limits determined in the stripping experiments are all lower than the original determination. There are probably two reasons for this. First, individual standards were prepared in the first determination, while the stripping experiments used aliquots of one standard solution. Some of the variability in the first determination

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TABLE 4-2

STRIPPING POTENTIAL OF ACROLEIN IN 1% $NaHSO_3$
(NIOSH TECHNIQUE)

CONTROL SPIKES		ACROLEIN FOUND (ug/g)	
0.5 ug	A	0.45	
	B	0.54	$\bar{x}$ = 0.50 ug
	C	0.54	S = 0.09 ug
	D	0.36	
	E	0.63	
SPARGED SPIKES			
0.5 ug	A	0.36	
	B	0.28	$\bar{x}$ = 0.43 ug
	C	0.54	S = 0.10 ug
	D	0.54	
	E	0.45	
CONTROL SPIKES			
1.0 ug	A	0.72	
	B	0.80	$\bar{x}$ = 0.80 ug
	C	0.54	S = 0.18 ug
	D	0.89	
	E	1.07	
SPARGED SPIKES			
1.0 ug	A	0.89	
	B	0.98	$\bar{x}$ = 0.80 ug
	C	0.63	S = 0.15 ug
	D	0.89	
	E	0.63	

K-97

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TABLE 4-2 (Continued)

STRIPPING POTENTIAL OF ACROLEIN IN 1% $NaHSO_3$
(NIOSH TECHNIQUE)

CONTROL SPIKES		
2.0 ug A	1.94	
B	2.38	$\bar{x}$ = 2.01 ug
C	1.77	S = 0.28 ug
D	2.30	
E	1.68	

SPARGED SPIKES	ACROLEIN FOUND (ug)	
2.0 ug A	1.77	
B	1.77	$\bar{x}$ = 1.89 ug
C	2.12	S = 0.28 ug
D	2.30	
E	1.51	

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TABLE 4-3

STRIPPING POTENTIAL OF ACROLEIN IN 1% $NaHSO_3$
(VERSAR TECHNIQUE)

CONTROL SPIKES	ACROLEIN FOUND (ug)
0.5 ug	0.54
1.0 ug	1.07
2.0 ug	1.94
SPARGED SPIKES	
0.5 ug	0.45
1.0 ug	1.07
2.0 ug	2.03

could be due to variation in the standards. Second, the analysts were more experienced in the technique by the time the stripping experiments were done. These observations indicate that the reported detection limit of 0.07 mg/m^3 is probably a maximum value. The validation work done here leaves little doubt NIOSH Method P&CAM 211 as performed by Versar will detect acrolein at levels well below the TLV.

Several procedural changes may be able to increase the sensitivity of the NIOSH Method P&CAM 211. First, longer path length cells can be used to increase absorbance values. Second, a decrease in the immersion time in the boiling water bath from 5 - 6 minutes to 3 - 4 minutes increases color intensity. Finally, immersion in an ice water bath for approximately 10 minutes after removal from the boiling water bath also increases color intensity.

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5.0 RECOMMENDATIONS AND CONCLUSIONS

5.1 Summary

No chemical irritants' concentrations approach the TLV level for any air sample taken.

The outgassing experiments on the PATRIOT Heater/Air Conditioner materials selected by the Investigative Team indicated that no concentration of the chemical irritants found approached the TLV for those materials.

Failure of some aspect of Unit SN 81013 would indicate very high temperatures occurred at some time in the units use cycle.

The key missing thermal shield in Unit SN 801160 indicates a quality control defect.

5.2 Recommended Actions

An Army review panel of perhaps AEHA and the DARCOM Surgeons Office needs to review the materials analysis and assumptions that were employed in this study.

A detailed electrical and mechanical review of the Unit SN 81013 should be undertaken to determine any design deficiencies that could have resulted in its failure.

A detailed review and upgrade of the quality control checks required in the manufacturing process should be defined and implemented.

5.3 Conclusions

Based on successful review by the Army of analysis and assumptions used in this study, nothing has been uncovered that would prevent the PATRIOT Heater/Air Conditioners from operating in High Heat Mode provided they are operated in accordance with prescribed procedures.

APPENDIX L

Report of Test - Internal Temperature Tests of the 18,000 BTUH Split-Package PATRIOT Air Conditioner

REPORT OF TEST

Subject: Internal Temperature Tests of the 18,000 BTUH Split-Package PATRIOT Air Conditioner

Contract: DAAK70-81-D-0109, PJO 0300.039

Test Location: VSE Corporation

Test Personnel: R. Beahm and R. Sherfy

Test Dates: October 8 - 18, 1982

Report Writer: Robert B. Sherfy, Project Engineer

Test Objectives:
a. Determine critical internal air conditioner (A/C) temperatures with return air blocked.
b. Investigate "quick fix" possibilities to minimize hazards under adverse operating conditions.

BACKGROUND

In ~~February~~ April 1982, several employees of Raytheon Corporation (prime contractor for the PATRIOT Missile System development and production) were working in a closed PATRIOT Communications Relay Group (CRG) shelter in the Boston area. They were adversely affected by an irritant which, it is believed, came from the 18,000 BTUH split-package air conditioner operating in the high heat mode on the shelter. A Raytheon retained chemical analysis company, Skinner and Sherman Laboratories, Inc., and the VSE retained chemical analysis company, VERSAR, of Springfield, Virginia, have found no conclusive evidence of an offending irritant in recent and exhaustive tests of other identical air conditioners.

In order to test the actual air conditioner (S/N 81013) which reportedly caused the problem, several VERSAR chemical analysts and the writer visited Fort Bliss, El Paso, Texas on August 23 - 26, 1982, where the suspect air conditioner and CRG shelter had been delivered. (See Trip Report by R. B. Sherfy, Subject: Irritant Testing of PATRIOT Air Conditioners on CRG Shelter, August 23 - 26, 1982.)

Prior to testing and chemical sampling of S/N 81013, an inspection of the unit through the right hand fresh air opening revealed evidence that this air conditioner had been extremely overheated at some time. The right hand drain hose, located below the heater assembly, had melted to the extent that it was badly misshappen and flattened on the bottom where it rested on the unit bottom. Furthermore, the hose top was scorched and had a hole melted or burned into it. The black foam cabinet insulation was surface crusted where it was close to the heaters but not protected by reflective material. Several of the teflon bushings, which cushion the electrical heating elements from their mounting bracket, had partially melted and were found in the bottom of the unit. Later, the air conditioner operating in the high heat mode did not appear to produce the normal amount of heat, indicating that some of the heating elements may have been burned out or that one of the over-temperature switches tripped.

Consideration of these overheat indications led the writer to the opinion that the only way this unit could have been made to overheat to this extent is for the return air to have been severely restricted. This could have happened from an extremely dirty return air filter or a loose piece of newspaper or packaging paper sucked against the return air opening, located at floor level in the shelter (See Figure 1). No remaining evidence of an occurrence of this type existed inside the CGR shelter at Ft. Bliss. Following extensive air sampling, S/N 81013 was removed from the shelter and shipped back to VSE for further investigation.

DISCUSSION

The over-temperature (O.T.) switches in S/N 81013 were tested to assure that they opened at reasonable settings to protect the system. Specified settings are: open at 150°F ±5°F, close at 110°F ±10°F (drawing 13216E6224). Testing was done using thermocouples located at the sensing disc of each switch and an electric heat gun to heat the switches. Although the setting of switch S2, the

low heat O.T. switch was not within specified tolerance, it's setting under the unit operating conditions was probably of no consequence (See Table 1, Test No. 6).

The CRG shelter, at the time of the incidence at the Raytheon plant, was located outdoors in very cold weather with the air conditioner operating in the high heat mode. The fresh air intake duct is mounted on the right (curb) side of the air conditioner on this shelter (See Figure 2). With this configuration, if the return air is severely restricted, a large quantity of cold, fresh air is induced into the air conditioner, bathing the over-temperature switches in cold air and preventing them from sensing the true temperatures in the inner evaporator compartment. Therefore, they will not turn the heaters off and cannot protect the heaters or evaporator compartment materials under this abnormal operating condition.

Our first test simulated this operating condition on an identical air conditioner (S/N 801185) with a blocked return air opening, and cool air entering the fresh air intake. Dry ice in a fabricated intake cooling box kept the fresh makeup air cool enough so that the over-temperature switches never tripped during tests 1 and 2. S/N 801185 was instrumented similar to previous units tested for irritants at VSE with the exception of thermocouples 1, 10, 15, 16, 17 and 18 (See List 1). Thermocouple #10 measures the right condensate drain temperature, a point which appears to get hotter than any other in the evaporator section, except for the heater elements themselves. Data taken during Test No. 1 is presented in Table 2. This test was run in low heat, with the fresh air intake duct on the right side of the air conditioner, and with the return air duct blocked various amounts from wide open to completely closed. The drain tube temperature reached 322°F even under low heat operation. The last two runs of Test No. 1 were with 75% of the return duct blocked and the fresh air intake completely blocked to determine the fresh air cooling ability at the over-temperature switches and elesewhere in the evaporator. Temperature differences between the tests make it

obvious that considerable cooling of the O.T. switches and other areas in the upper right portion of the evaporator section results from cool air entering the right fresh air intake.

Test No. 2 (Table 3) was similar to Test No. 1, but in the high heat mode. A maximum drain tube temperature of 386°F was reached before the heaters were manually turned off because of a burned rubber odor coming from the unit.

Disassembly and inspection of S/N 801185 following these tests revealed that the right side plastic drain tube had melted and burned exactly like the one found in S/N 81013.

Mr. Franklin P. Good, MERADCOM Project Engineer for this air conditioner, and the writer, discussed possible quick fixes to keep outside air from affecting the over-temperature switches and to reduce temperatures at and near the right plastic drain hose. After extensive consideration, two methods appeared possible for a quick fix, and worthy of additional testing. One possibility was a metal baffle to shield the right drain tube from heat radiation, which originates at the heater elements and is reflected off of the reflective metal which protects the foam rubber wall insulation. The other considered fix was a small air deflector in the right side fresh air opening to deflect the incoming air away from the O.T. switches and downward toward the right drain tube (See Figure 4). Test Nos. 3 and 4 were performed (with limited thermocouple locations) to determine critical temperatures with various combinations of drain baffle and fresh air diverter. Test No. 3 used the fresh air intake on the right side of the unit and Test No. 4, a left fresh air intake. Note that the air diverter would serve no purpose in the left air intake opening because of its distance from the over-temperature switches and the right condensate drain tube. Therefore the diverter could only be used for an air conditioner with the fresh air intake installed on the right side. Results of these two tests are presented in Tables 4 and 5.

Test No. 5 was used as a control test with no fixes installed, but with the return air completely blocked again to verify temperatures at the drain tube and O.T. switches. Temperatures very similar to previous results were found with a drain tube high temperature of 385°F (See Table 6). List 2 indicates instrumentation used for all tests.

RESULTS: Exception for the heater elements, the right condensate drain appears to be the hottest component (within the evaporator compartment), which might be adversely affected by high temperatures under very restricted return air conditions. Tests indicate a repeatable drain tube temperature of approximately 385°F with the return air completely restricted, and the fresh air intake duct on the right side. Over temperature switches generally will not trip with outside air temperatures below about 68°F.

Under the same conditions, but with the fresh air intake on the left side, the over-temperature switches repeatedly tripped, limiting the right drain tube to about 307°F.

Unless the return air duct opening is restricted more than 90%, no excessive temperatures are evident in the evaporator compartment.

When the return air is completely blocked, evaporator fan operation is extremely unstable with air flow coming out of only one fan discharge, and a slight air flow entering the other fan discharge. At times this flow would reverse between the two fan outlets, creating entirely new flow patterns in the evaporator compartment.

The installation of the baffle reduced the drain tube temperature by about 115°F to a high of 270°F with a normal fresh air intake on the right side. (return air blocked). With a left side fresh air intake, high temperature of the tube was about 307°F.

The fresh air diverter did an excellent job of deflecting the cold air away from the O.T. switches, and kept the right drain tube temperature from exceeding 160°F. However, the diverter is not usable with a left air intake duct, and the drain hose attains about 307°F in this configuration before the O.T. switches reduce the heat.

CONCLUSIONS: With the return air blocked, temperatures of degradable materials inside the air conditioner can reach critical temperatures. As an example, the Tygon tubing, which has a normal maximum working temperature of approximately 180°F, actually reached temperatures of around 385°F under this severe operating condition. In addition, the lower right rear wall reflective metal reaches about 340°F under the same condition. This metal is adhered directly to a synthetic foam insulation material, which can also be adversely affected by temperatures in this range.

These extraordinary internal temperatures can only be caused by a severe restriction of the return air.

It is the opinion of this writer that no easily applied "quick fix" to the air conditioner will offer adequate protection to internal materials of the evaporator section. However, a program, including an engineer change proposal (ECP82HE0387), initiated more than eleven months ago to correct an unnecessarily high heater element failure rate, has the ability to completely protect the unit, regardless of careless external blockage of the return air. This ECP changes the bare heater elements to finned elements, drastically reducing their surface temperature, and therefore the resultant radiant heat. At the same time, the over-temperature switches are relocated to be more responsive to heater and internal temperatures, and less affected by fresh air intake.

RECOMMENDATIONS:

1. Provide a method, within the shelter, to prevent the blockage of the return air filter (but still allow for easy filter cleaning).

2. Investigate an alternate drain tube material, such as silicone, which is more temperature resistant than the existing plastic tubing.

3. Immediately implement ECP82HE0387 for redesigned heaters, to include retrofit of existing air conditioners.

AIR FLOW CIRCUITS

(SIMILAR TO CRG SHELTER)

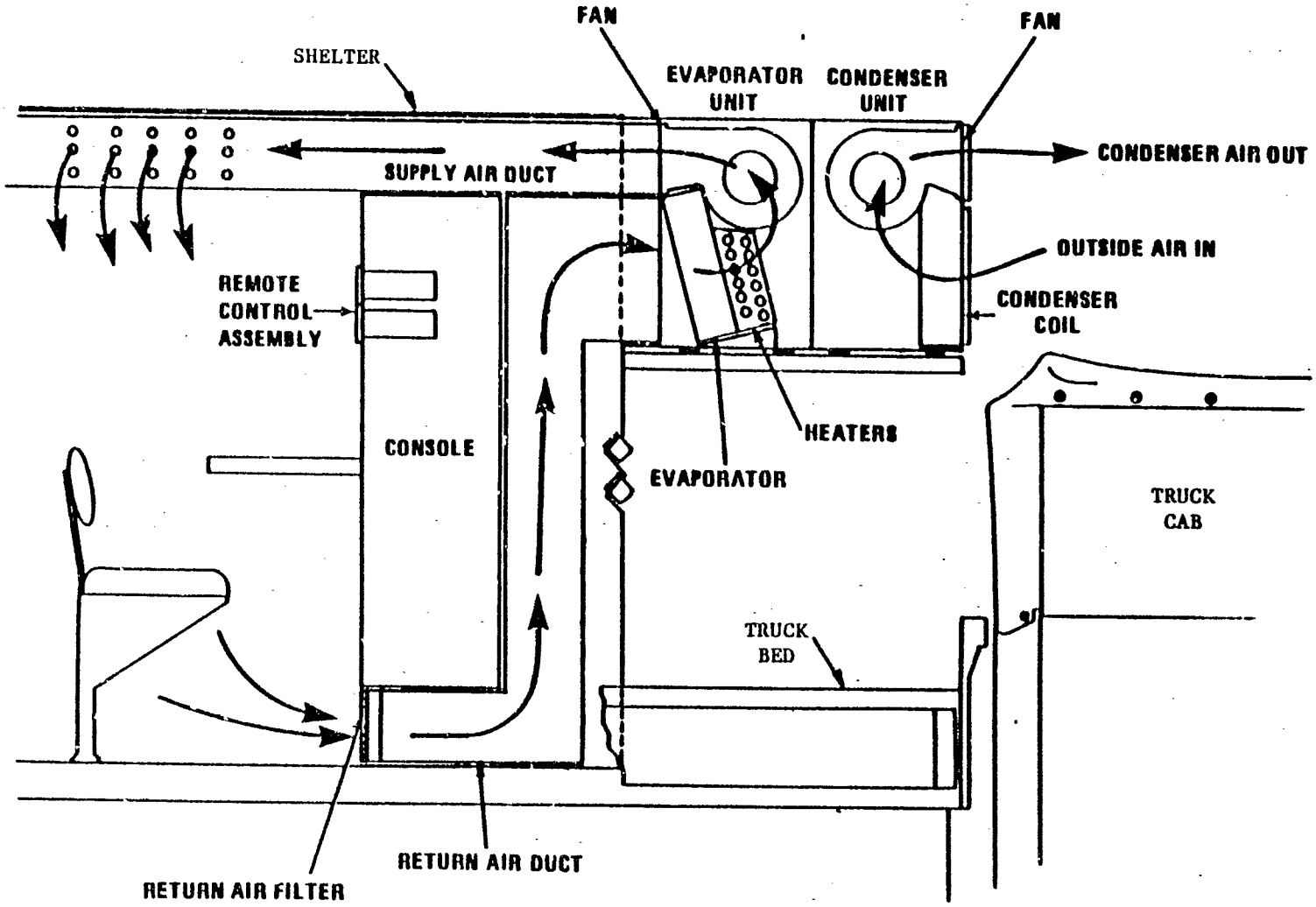


FIGURE 1

SHELTER INTERFACE
(SIMILAR TO CRG SHELTER)

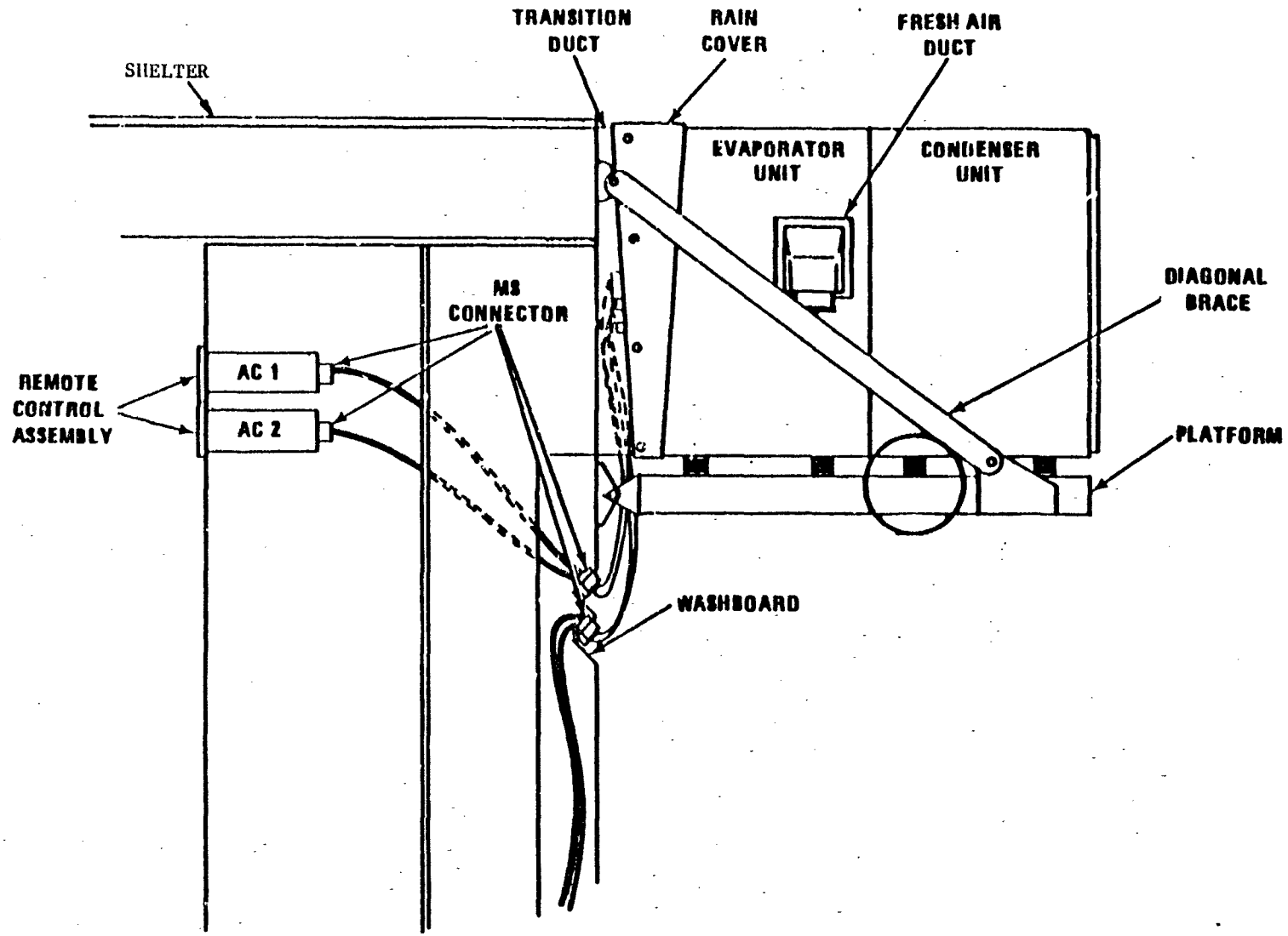


FIGURE 2

18,000 BTUH SPLIT-PACKAGE AIR CONDITIONER OVERHEAT TESTS

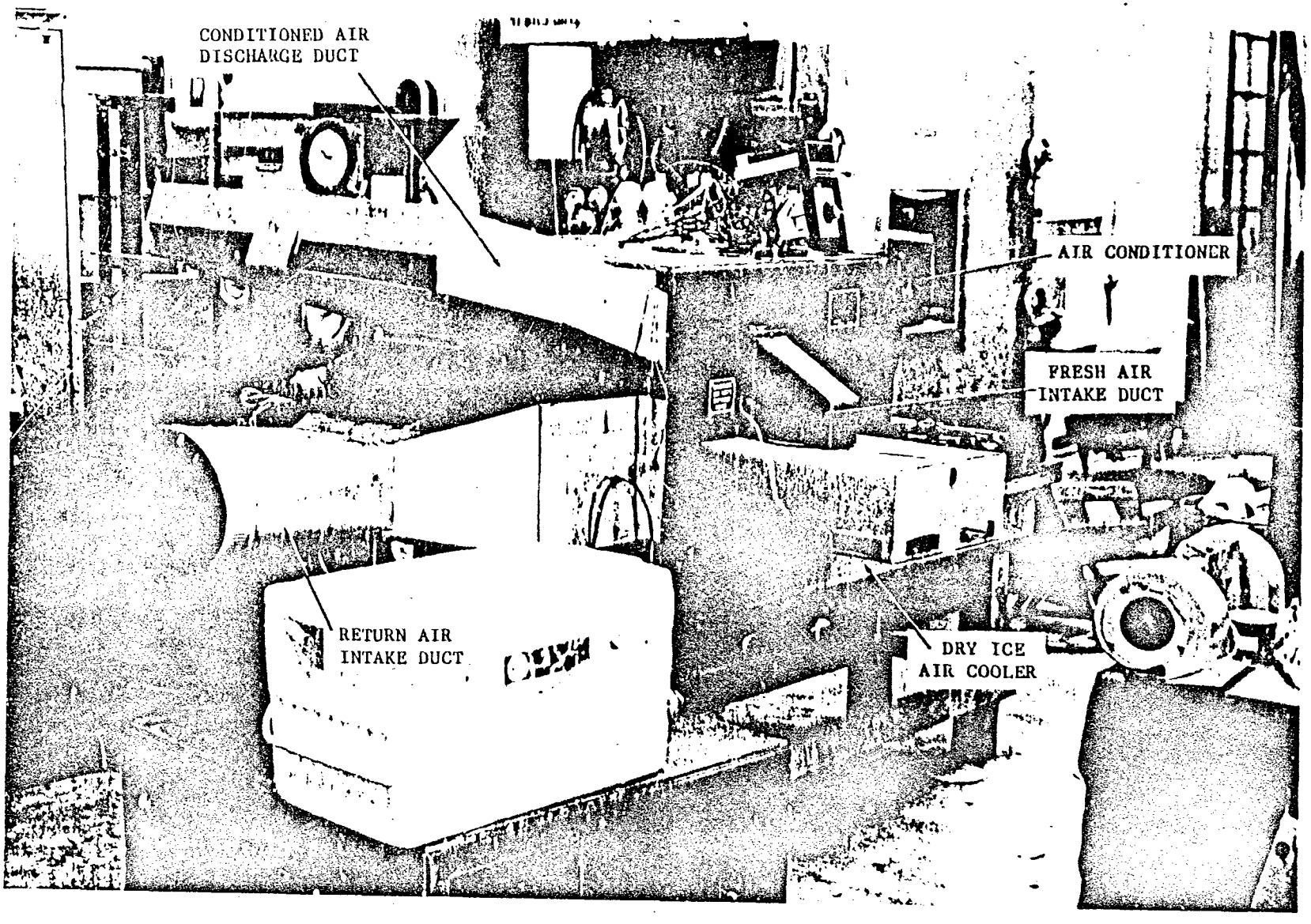


FIGURE 3

FRESH AIR DIVERTER AND DRAIN TUBE BAFFLE
INSTALLATION IN 18,000 BTUH SPLIT PACKAGE
AIR CONDITIONER (SECTION THROUGH FRESH AIR INTAKE)

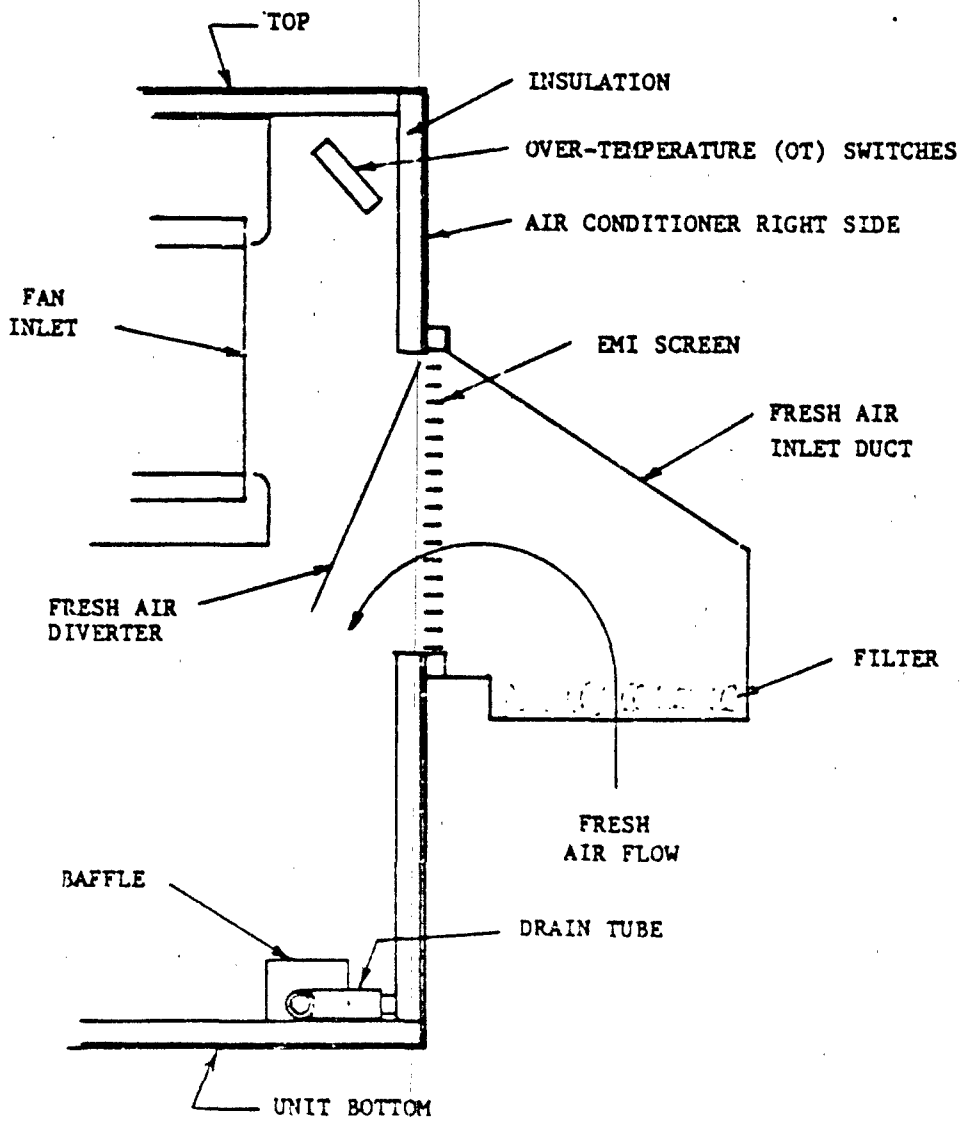
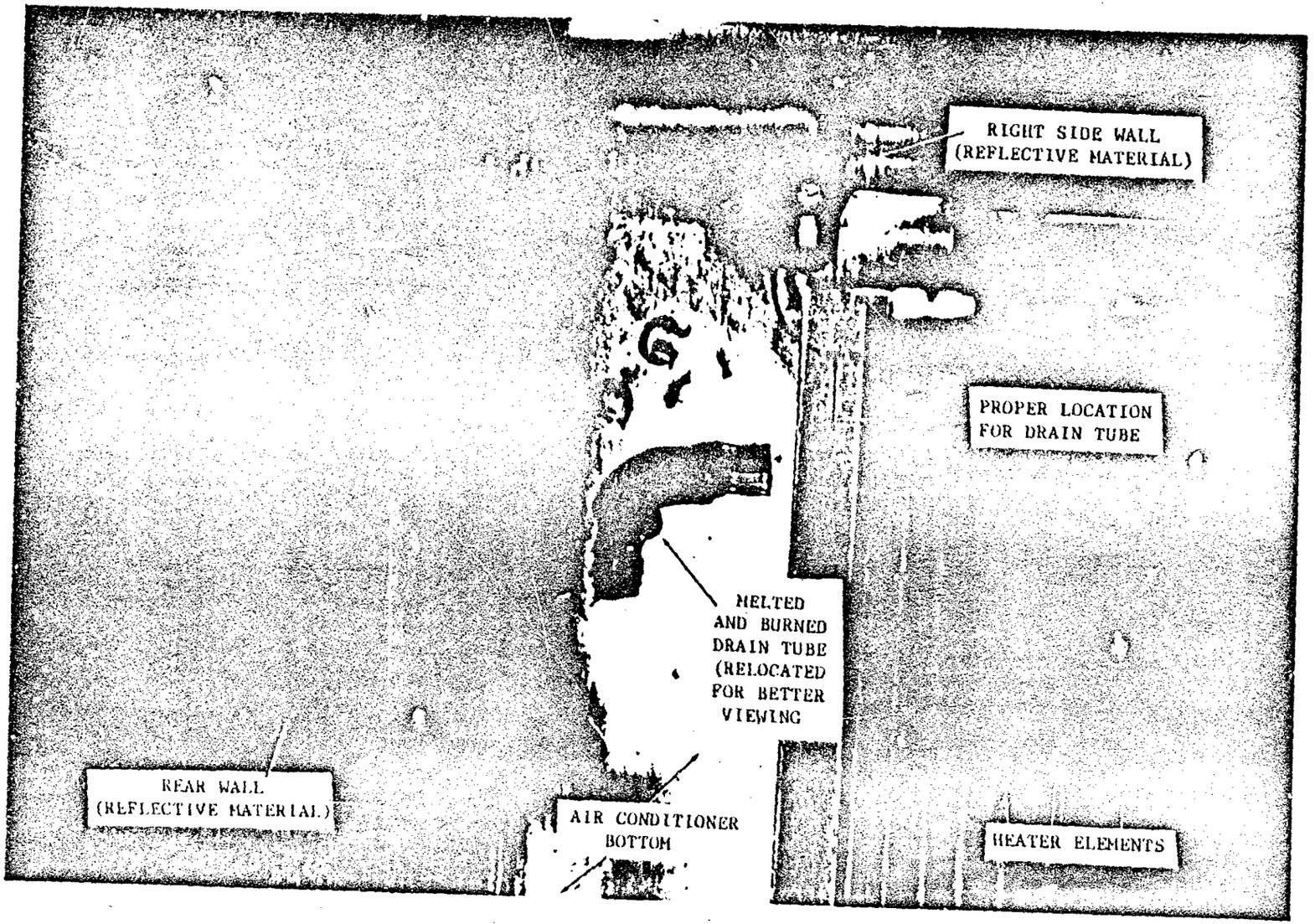


FIGURE 4

DOWNWARD VIEW INSIDE A/C 81013



PLACEMENT OF THERMOCOUPLES FOR TESTS 1 AND 2

1. Fresh air inlet. Placed in Fresh air filter. No Epoxy.

2. Return air. Placed in intake duct. No epoxy.

3. Exit air. Placed in discharge duct. No epoxy.

4. Thermal bulb tape (insulation tape). Imbedded in the thermal bulb tape, a few inches to the left side of the heater. No epoxy.

5,6,7&8. Rear Bulkhead. Four thermocouples places left to right across the rear bulkhead, attached with epoxy to the reflective aluminum, six to nine inches off the bottom of the unit.

9. Rear bulkhead. Attached with epoxy, rear bulkhead, approximately two inches from the bottom of the unit, and two inches from the right side.

10. Tygon tube drain. Located against the right drain tube. No epoxy.

11. Right wall rear. Attached with epoxy on the right side wall on the reflective aluminum, six to nine inches from the bottom of the unit, near the rear corner.

12. Right wall. Attached with epoxy on the right side wall on the reflective aluminum, directly to the right of the hearing elements. Approximately two inches from the bottom of the unit.

13. Right wall rear. Attached with epoxy to the right side wall near the rear corner. Approximately two inches from the bottom of the unit.

14. Rear wall. Attached with epoxy to the rear wall insulation near the right corner on the cut out for the Riv nut. Approximately two inches from the bottom of the unit.

15. Heating element. Wired to low heat heating element. Thermocouple was <u>not</u> attached with epoxy. Actual measurement is an air measurement very close to the surface. This is true for point 16 also.

16. Heating element. Wired to high hear heating element. See point 15.

17. Over temperature switch S3. Mounted against front O.T. switch disk for high heat control. No epoxy.

18. Over temperature switch S2. Mounted against rear O.T. switch disk for low heat contro. No expoy.

LIST 1

INSTRUMENTATION

The following instrumentation was used for all testing involved in this report.

Current Transformer, Weston Model 461, MERADCOM CT #6B.4
Current Transformer, Weston Model 461, MERADCOM CT #6B.3
Wattmeter, Weston Model 432, VSE S/N 1481
Voltmeter, Weston Model 904, MERADCOM #4B.6
Temperature Indicator, Thermo Electronic Model LLPH3, VSE S/N 0209, 18 point digital temperature indicator, 1° resolution, 1% accuracy, used with chromel-alumel thermocouples

LIST 2

TEST NO. 6

OVER-TEMPERATURE (O.T.) SWITCH SETTING

Date: October 15, 1982

S/N: 81013

Personnel: R. Beahm
R. Sherfy

	FRONT O.T. SWITCH (S3) (THERMOCOUPLE 17)	BACK O.T. SWITCH (S2) (THERMOCOUPLE 18)
SWITCH OPENS	147°F	176°F
SWITCH CLOSES	107°F	96°F

TABLE 1

51-7

TEST NO. 1

HIGH TEMPERATURE TESTING OF EVAPORATOR COMPARTMENT OF
18,000 BTUH SPLIT-PACKAGE AIR CONDITIONER (PATRIOT)

Date: October 8, 1982
S/N: 801185
Mode Switch: Low Heat
Thermostat: Warmer
Volts: 208V AC, 400 Hz
Watts: 5,700
Personnel: R. Beahm
R. Sherfy

RETURN AIR INLET	FRESH AIR INLET	TIME	THERMOCOUPLE NUMBERS AND LOCATIONS																	
			FRESH AIR IN	RETURN AIR IN	AIR OUT	TXV BULB INSUL	BACK WALL LEFT	BACK WALL #2	BACK WALL #3	BACK WALL RIGHT	BACK WALL L.R. COR	TYGON TUBE DRAIN	RIGHT WALL, REAR	RIGHT WALL NR HTRS	RIGHT WALL, LOW	BACK WALL ON INSUL	LOW HEAT ELEMENT	HIGH HEAT ELEMENT	FRONT O.T. SWITCH	BACK O.T. SWITCH
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
OPEN	RIGHT	1051	56	74	97	100	115	128	137	140	144	166	128	115	133	132	639	152	93	93
50% OPEN	RIGHT	1059	58	74	100	104	128	143	149	150	162	170	135	121	142	140	707	170	97	95
50% OPEN	RIGHT	1110	59	75	102	108	129	143	149	150	163	177	137	123	144	143	705	171	99	97
25% OPEN	RIGHT	1120	60	75	108	119	145	163	162	151	188	202	162	137	165	162	757	200	102	97
25% OPEN	RIGHT	1130	62	76	110	128	147	165	163	153	190	206	163	138	167	164	751	200	104	100
CLOSED	RIGHT	1135	62	77	115	128	158	197	164	162	220	231	181	165	185	177	800	383	120	106
CLOSED	RIGHT	1140	63	78	133	124	189	235	190	187	265	293	217	194	220	203	848	512	139	120
CLOSED	RIGHT	1150	65	79	142	138	201	249	199	196	281	322	233	211	238	217	875	548	149	130
OPEN	RIGHT	1200	74	77	103	118	121	134	144	146	151	179	132	120	140	143	665	151	102	102
OPEN	RIGHT	1230	-24*	78	102	109	118	129	139	136	146	165	129	120	134	136	632	144	111	108
25% OPEN	CLOSED	1400	81	82	123	119	149	167	191	183	192	224	173	145	173	171	768	212	139	126
25% OPEN	CLOSED	1405	85	82	124	126	152	170	192	184	193	230	174	145	175	174	768	211	144	135

*Ice blocked F.A. filter. Filter removed.
NOTE: O.T. switches remained closed

TABLE 2

TEST NO. 2

HIGH TEMPERATURE TESTING OF EVAPORATOR COMPARTMENT OF

18,000 BTUH-SPLIT PACKAGE AIR CONDITIONER (PATRIOT)

Date: October 8, 1982
S/N: 801185
Mode Switch: High Heat
Thermostat: Warmer
Volts: 200V AC, 400 Hz
Watts: 8,700
Personnel: R. Beahm
R. Sherfy

RETURN AIR INLET	FRESH AIR INLET	TIME	THERMOCOUPLE NUMBERS AND LOCATIONS																	
			FRESH AIR IN	RETURN AIR IN	AIR OUT	TXV BULB INSUL	BACK WALL LEFT	BACK WALL #2	BACK WALL #3	BACK WALL RIGHT	BACK L. RT. COR	TYGON TUBE DRAIN	RIGHT WALL, REAR	RIGHT WALL NR HTRS	RIGHT WALL,LOW	BACK WALL ON INSUL	LOW HEAT ELEMENT	HIGH HEAT ELEMENT	FRONT O.T. SWITCH	BACK O.T. SWITCH
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
OPEN	RIGHT	1420	60	81	117	136	163	185	195	186	221	243	179	154	202	192	678	643	107	106
OPEN	RIGHT	1430	66	81	118	140	163	184	195	192	221	246	181	154	204	193	677	653	110	109
50% OPEN	RIGHT	1505	67	82	123	154	175	189	197	196	236	276	195	172	216	203	709	678	110	107
50% OPEN	RIGHT	1520	78	82	125	154	177	195	202	200	243	282	203	177	225	211	711	677	114	112
25% OPEN	RIGHT	1531	59	81	129	178	194	217	166	184	269	365	234	204	257	242	782	738	106	110
CLOSED	RIGHT	1533	60	83	138	176	217	273	196	215	339	374	293	265	321	294	890	1048	139	134
CLOSED	RIGHT	1536	SMELLED BURNED RUBBER.								340	386						SHUT OFF HEATERS.		

NOTE: O.T. switches remained closed

TABLE 3

TEST NO. 3

HIGH TEMPERATURE TESTING OF EVAPORATOR COMPARTMENT OF

18,000 BTUH SPLIT-PACKAGE AIR CONDITIONER

Date: October 15, 1982
S/N: 801185
Mode Switch: High Heat
Thermostat: Warmer
Personnel: R. Beahm

RETURN AIR INLET	FRESH AIR INLET	FRESH AIR DIVERTER	DRAIN TUBE BAFFLE	TIME	VOLTS	WATTS	THERMOCOUPLE NOS. AND LOCATIONS: FRESH AIR IN 1	AIR OUT LEFT 3	AIR OUT RIGHT 4	TYGON TUBE DRAIN 10	FRONT O.T. SWITCH 17	BACK O.T. SWITCH 18
OPEN	RIGHT	IN	IN	1032	202	8750	69	101	97	120	98	102
CLOSED	RIGHT	IN	IN	1035	203	8600	69	159	179	137	122	143
CLOSED	RIGHT	IN	IN	1037	203	8550	69	183	183	158	148	176
THERMAL SWITCH OPENED. COOL UNIT TO REPEAT TEST												
OPEN	RIGHT	IN	IN	1045	203	8700	69	108	102	149	103	108
CLOSED	RIGHT	IN	IN	1047	203	8550	70	167	172	149	125	147
CLOSED	RIGHT	IN	IN	1048	203	8550	70	187	176	160	150	178
THERMAL SWITCH OPENED. UNIT COOLED TO REPEAT TEST												
OPEN	RIGHT	OUT	IN	1100	203	8700	70	99	99	118	87	88
OPEN	RIGHT	OUT	IN	1102	203	8700	70	105	104	143	95	95
CLOSED	RIGHT	OUT	IN	1104	203	8550	70	99	145	171	123	113
CLOSED	RIGHT	OUT	IN	1106	203	8550	70	119	165	229	147	133
CLOSED	RIGHT	OUT	IN	1107	203	8550	70	129	174	253	157	144
CLOSED	RIGHT	OUT	IN	1108	203	8550	70	138	180	270	175	152
THERMAL SWITCH OPENED. COOLED UNIT TO RETEST												
CLOSED	RIGHT	OUT	IN	1113	203	8550	70	90	142	177	124	113
CLOSED	RIGHT	OUT	IN	1115	203	8550	70	120	164	235	146	133
CLOSED	RIGHT	OUT	IN	1116	203	8550	70	129	174	260	157	142
THERMAL SWITCH OPENED. COOLED UNIT TO RETEST												
OPEN	RIGHT	IN	OUT	1128	202	8750	70	102	99	136	95	101
OPEN	RIGHT	IN	OUT	1130	202	8700	70	107	102	154	100	106
CLOSED	RIGHT	IN	OUT	1132	202	8550	70	156	157	136	120	138

TABLE 4

RETURN AIR INLET	FRESH AIR INLET	AIR DIVERTER	DRAIN TUBE BAFFLE	TIME	VOLTS	WATTS	1	3	4	10	17	18
CLOSED	RIGHT	IN	OUT	1133	202	8550	71	178	177	144	132	154
CLOSED	RIGHT	IN	OUT	1134	202	8550	71	189	197	145	149	170
			THERMAL SWITCH OPENED. COOLED UNIT TO RETEST									
CLOSED	RIGHT	IN	OUT	1138	202	8550	71	132	164	122	116	130
CLOSED	RIGHT	IN	OUT	1140	202	8550	71	177	166	139	133	153
				THERMAL SWITCH OPENED.								

TABLE 4 (CONTINUED)

TEST NO. 4

HIGH TEMPERATURE TESTING OF EVAPORATOR COMPARTMENT OF 18,000 BTUH SPLIT-PACKAGE AIR CONDITIONER

Date: October 18, 1982
S/N: 801185
Mode Switch: High Heat
Thermostat: Warmer
Personnel: R. Beahm

RETURN AIR INLET	FRESH AIR INLET	FRESH AIR DIVERTER	DRAIN TUBE BAFFLE	TIME	VOLTS	WATTS	THERMOCOUPLE NOS. AND LOCATIONS: FRESH AIR IN 1	AIR OUT LEFT 3	AIR OUT RIGHT 4	TYGON TUBE DRAIN 10	FRONT O.T. SWITCH 17	BACK O.T. SWITCH 18
OPEN	LEFT	NA	IN	0815	204	8700	67	95	103	119	110	117
CLOSED	LEFT	NA	IN	0818	205	8650	67	149	68*	250	130	143
				0821		THERMAL	66	179		SWITCH OPENED		
OPEN	LEFT	NA	IN	0827	204	870	67	92	101	137	113	117
CLOSED	LEFT	NA	IN	0829	205	8650	68	145	68*	266	137	148
CLOSED	LEFT	NA	IN	0831	205	8600	68	162	68*	305	149	169
						THERMAL SWITCH OPENED						
OPEN	LEFT	NA	IN	0850	204	8700	68	91	99	118	112	114
CLOSED	LEFT	NA	IN	0852	205	8600	68	130	69*	219	129	134
CLOSED	LEFT	NA	IN	0854	204	8625	68	152	69*	271	148	153
CLOSED	LEFT	NA	IN	0856	204	8625	68	164	69*	307	153	171
CLOSED	LEFT	NA	OUT	0858	204	8625	68	108	69*	192	115	119
CLOSED	LEFT	NA	OUT	0900	204	8625	68	136	69*	245	129	139
CLOSED	LEFT	NA	OUT	0902	204	8625	68	152	69*	280	141	150
CLOSED	LEFT	NA	OUT	0903	204	8625	69	164	69*	305	-	-
						THERMAL SWITCHES OPENED						
CLOSED	LEFT	NA	OUT	0909	207	3900	-	-	-	170	-	104
CLOSED	LEFT	NA	OUT	0914	207	3900	68	118	69*	225	120	127

TEST TERMINATED. EXPERIENCE INDICATED THAT LOW HEATERS WILL NOT AGAIN COME ON SINCE HIGH HEAT HEATERS WILL PREVENT O.T. SWITCH RESET.

* Faulty Thermocouple

TABLE 5

TEST NO. 5

HIGH TEMPERATURE TESTING OF EVAPORATOR COMPARTMENT OF

18,000 BTUH SPLIT-PACKAGE AIR CONDITIONER

Date: October 18, 1982
S/N: 801185
Mode Switch: High Heat
Thermostat: Warmer
Personnel: R. Beahm

RETURN AIR INLET	FRESH AIR INLET	FRESH AIR DIVERTER	DRAIN TUBE BAFFLE	TIME	VOLTS	WATTS	THERMOCOUPLE NOS. AND LOCATIONS					
							FRESH AIR IN	AIR OUT LEFT	AIR OUT RIGHT	TYGON TUBE DRAIN	FRONT O.T. SWITCH	BACK O.T. SWITCH
							1	3	4	10	17	16
OPEN	RIGHT	OUT	OUT	0953	204	8600	68	90	101	127	114	115
CLOSED	RIGHT	OUT	OUT	0955	204	8600	68	133	69*	274	133	136
C[illegible]D	RIGHT	OUT	OUT	0957	204	8600	68	150	69*	325	144	150
CL[illegible]ED	RIGHT	OUT	OUT	0958	204	8600	68	158	70*	385	159	172
				BURNED ODOR DETECTED. HEATERS MANUALLY SHUT OFF.								

* Faulty Thermocouple.

TABLE 6

APPENDIX M

Minutes of Meeting - 19 October 1982

DEPARTMENT OF THE ARMY
US ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA 22060

DRDME-EPAT

DEC 13 1982

MEMORANDUM FOR RECORD

SUBJECT: Minutes, Meeting to Review Results of Final Phase of Irritant Testing of PATRIOT Production Air Conditioners, UII, 19 Oct 82.

1. Short Concise Synopsis of Meeting: The results of following were discussed: a) investigative team inspection of two (2) Patriot Production Air Conditioners, b) materials evaluation, c) sampling, d) observation of CRG Shelter at Ft. Bliss, and e) air sampling analysis of the CRG Shelter. Representatives from Patriot Missile Office, Raytheon, Army Environmental Hygiene Agency (AEHA), DARCOM Surgeon General, VSE, VERSAR, Skinner and Sherman, and MERADCOM were in attendance. It was concluded that no suspected chemical irritants for which tests were made (e.g., acrolien, cyanide) were emitted from the Patriot Air Conditioner when operating in the high heat mode and that it was safe to operate in the high heat mode of operation.

Also, the results of an investigation into possible causes for overheating of Patriot Air Conditioner S/N 81013 were discussed at length. S/N 81013 is the air conditioner that was mounted on the CRG Shelter in which Raytheon personnel became ill during April 1982. It was demonstrated on another air conditioner (S/N 801185) that by blocking the return air, the overheated condition of S/N 81013 could be duplicated. This was confirmed by comparing materials removed from S/N 81013 to that of S/N 801185. It was concluded that somehow the return air duct in the CRG shelter must have become clogged/closed-off accidently while the Raytheon personnel were working in it in April 1982, thus causing the overheating.

It was agreed that MERADCOM would: a) forward a message to PATRIOT Missile Office (PMO) indicating that the Production Air Conditioner was safe to use in the high heat mode as long as return air flow is not blocked, b) recommend to the PMO that all tags should be removed from the Air Conditioner so that the air conditioners can be used in the high heat mode, and c) request that Raytheon add a warning label in the shelter against blocking the shelter return air ducts.

2. Personnel Present: See attached list.

3. Discussion:

A. VERSAR provided a review of their draft final report "Patriot Heater/Air Conditioner Investigation: Results of Implementation of July 21, 1982 Recommendations", dated October 4, 1982. Copies of this report had been distributed the week of 4 October 1982. The report covered in detail the following:

1) Investigation into the various types of materials used in the air conditioner. Five materials were selected that would require further testing due to the amount used in the unit and their proximity to the heating elements. These included the black insulating foam, thermal bulb insulating tape, adhesive for foam, sealer for condensate trap, and tubing for condensate drain.

2) Temperature survey of the air conditioner as it was operated in the high heat mode. The maximum temperature was 247°F. with the return air duct 50% blocked off.

3) Air Sample Testing of the CRG Shelter at Ft. Bliss using Air Conditioner S/N 81013 and S/N 801198. S/N 801198 was tested earlier at VSE Corp. with no evidence of chemical irritants being emitted while operating in the high heat mode. The target parameters for the sampling effort were as follows: Acrolien, Formaldehyde, Cyanides, Amines, Hydrogen Chloride, Carbon Dioxide, Carbon Monoxide, Semi-volatile organics, volatile organics, and aromatics. The sampling and analysis were in accordance with a draft plan dated 30 July 1982 and changes as result of comments by AEHA, Raytheon/Skinner & Sherman, and MERADCOM. A proposed sampling experiment by Raytheon/Skinner & Sherman was not included because of insufficient time for validation prior to the testing of the CRG Shelter at Ft. Bliss.

4) Inspection of Patriot Air Conditioner S/N 81013 upon its removal from the CRG Shelter revealed that it had overheated. A number of teflon grommetts and the tagon drain tubing were either burned or had melted.

5) Outgassing experiments on the five selected materials which were subjected to a maximum temperature of 280°F. It was agreed that the maximum temperature found in the Air Conditioner would be increased by approximately 15% which would establish the maximum temperature. At these temperatures, the results showed that the concentration of the compounds released would probably not reach hazardous levels.

B. VSE provided a review of their investigation into the possible causes for the over-heating of Air Conditioner S/N 81013. They showed that the inside condition of S/N 81013 of burned grommetts and melted tubing could be duplicated by blocking off the return air to the air conditioner. This was accomplished by operating a similar production Air Conditioner (S/N 801185) in the high heat mode with the return air duct completely blocked off. Since there was no air moving across the heater elements, the heater elements reached their maximum temperature in a matter of minutes. The unit was shut down and an inspection revealed grommetts and tubing very similar to those found in S/N 81013. VSE showed that the April 1982 incident at Raytheon with the CRG Shelter could have been caused by some foreign object (drawing sheet, coat, etc.) falling in front of and clogging the shelter return air duct. The return air duct is located about 1" off the floor of the shelter and would be vulnerable to something like this happening. A copy of VSE's report on this investigation will be part of the final report on this phase of Irritant Testing.

C. Raytheon/Skinner & Sherman indicated that the results of their analysis was essentially in agreement with those of VERSAR's. Also, they had compared material samples received from KECO via VERSAR and those material samples removed from S/N 81013. Skinner & Sherman concluded that the material was essentially the same.

D. AEHA indicated that they had not analyzed any of the samples as agreed to by the plan of test. However, they considered the approach, experiments and conclusion of the VERSAR's draft report to be valid.

4. Conclusion: It was concluded that:

A. Nothing had been uncovered (based on the list of suspected irritants) in the testing and analysis of Patriot Air Conditioner/Heater that would prevent it from operating in the high heat mode; that the Air Conditioner/Heater is safe to use in the high heat mode provided the return air flow is not blocked.

B. A warning sign should be incorporated in the shelters that warns against blocking the shelter return air ducts.

C. There should be an increased QA surveillance at the contractor's plant. Poor quality of workmanship was exhibited in a number of the Air Conditioners/Heaters that were inspected/tested.

D. All Air Conditioners/Heaters that have been delivered prior to the increased QA surveillance should be re-inspected.

E. The over-temperature switch on the Air Conditioner/Heater should be relocated to a position where it would not be effected by the temperature of the make-up air. It should be located where it can sense the temperature of the heater elements and shut down the heater if an over-temperature condition developes.

FOR THE COMMANDER:

Robert M. McKechnie

ROBERT M. MCKECHNIE
DPO, PATRIOT Support
Project Office

George F. Sams

GEORGE F. SAMS
PATRIOT Support Office

1 Incl

19 Oct 82

MEETING ON IRRITANT TESTING
OF PATRIOT AIR CONDITIONERS

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APPENDIX N

VERSAR Report (Draft Final Report) "The Role of TFE Grommets in PATRIOT Heater/Air Conditioner - Shelters Irritant Gas Incidents"

Versar inc.

DRAFT FINAL REPORT

THE ROLE OF TFE GROMMETS IN PATRIOT HEATER/AIR CONDITIONER-SHELTERS IRRITANT GAS INCIDENTS

Submitted to:

VSE Corporation
2550 Huntington Avenue
Alexandria, Virginia 22303

Attention: Mr. George Sams

Versar No. 787

Submitted by:

VERSAR INC.
6850 Versar Center
Springfield, Virginia 22151

January 20, 1983
Revised February 7, 1983

N-1

Versar inc.

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Appendix I - Neil Jurinski Trip Report

Versar inc.

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EXECUTIVE SUMMARY

MERADCOM has been investigating the source of irritant gas production in PATRIOT Heater/Air Conditioners - shelters since the original reports at Raytheon in April 1982. During this investigation over 1,500 samples have been analyzed for a number of parameters. Exhaust air from the PATRIOT Heater/Air Conditioners has been monitored for hydrolyzable fluoride, hydrogen cyanide, hydrogen chloride, acrolein, formaldehyde, organic amines, sulfur dioxide, carbon monoxide, carbon dioxide, some semi-volatile organic compounds and volatile organic compounds. None of the samples taken before the Fort Bliss hydrolyzable fluoride tests had any material identified at a sufficiently high concentration to explain the personnel symptoms. This report is a summary of the role of polytetrafluoroethylene (TFE) grommets in the PATRIOT irritant gas incidents. The report details the incident 3 November 1982 at Fort Bliss, the absence of hydrolyzable fluoride in seven shelters with grommetless heaters, and lastly, a detailed reconstruction of the original incident. The reconstruction of the incident was accomplished in the laboratory on a single heater rod, in a stand-alone Heater/Air Conditioner and lastly in an actual CRG/ICC shelter. TFE grommets used in the PATRIOT Heater/Air Conditioner-CRG/ICC shelter have been shown to thermally decompose to a sufficient extent and in a short enough time to produce a concentration of TFE decomposition products that could produce the chemical irritation reactions described. After removal of these grommets, hydrolyzable fluoride, the major TFE decomposition product monitored, was not observed.

Grommets have been removed from all units. In virtually every case (some 30 units investigated to date) major TFE loss was observed. The standard Army issue M8 chemical agent alarm was used to monitor the air. It can detect the decomposition products of TFE, but it is not sensitive enough to be useful. TFE grommets should not be used in direct contact with the heater rods or in any environment where the temperature is high enough to decompose the TFE. Decomposition of TFE will begin between

332°F and 572°F.[1] NIOSH recommends that "exposure to the decomposition products of fluorocarbon polymers be controlled by the use of engineering and administrative controls and by strict adherence to work practices that will minimize worker contact with pyrolysis products of fluorocarbon polymers or with potentially pyrolyzable dust."[1]

I. OVERVIEW

A. Background

Army and Raytheon personnel were exposed to an irritant gas during the testing of the PATRIOT Army Air Defense System - CRG shelter in Andover, Massachusetts on 5 April 1982. Initial gas tests were conducted by Raytheon/Skinner-Sherman and shortly after by VSE/Versar on stand-alone PATRIOT Heater/Air Conditioners. Different observations were made by the two investigating laboratories. On 8 June 1982, a meeting was called by MERADCOM to define and eliminate the irritant gas problem. Present at that meeting were representatives of:

- MERADCOM PATRIOT Office
- U.S. Army Environmental Hygiene Agency (U.S.AEHA)
- MERADCOM Safety
- DARCOM Surgeon General (staff were not present until actual tests and report evaluation)
- Raytheon
- VSE
- Skinner/Sherman
- Versar

A plan was developed that addressed all relevant target parameters and the most appropriate sampling methodologies. Standard sampling and analytical methods were used whenever possible, exceptions were discussed and if used documented. This plan and the detailed report were presented (16 July 1982) and reviewed (21 July 1982). (16 July 1982 Results of Sampling and Analysis conducted on four PATRIOT Heater/Air Conditioners at the VSE Corporation facility in Alexandria, Virginia.) No irritant chemical was identified that was produced in sufficient concentration to have caused the original incident.

During the review process a detailed set of chemical and engineering evaluations were suggested. A second plan was developed, reviewed, and implemented. This plan and detailed report were presented (4 October 1982) and reviewed (19 October 1982). (4 October 1982 PATRIOT Heater/Air Conditioner Investigation: Results of Implementation of 21 July

1982 Recommendations.) At this meeting it was concluded that sufficient data was on hand to begin the use of the PATRIOT Heater/Air Conditioner.

On Wednesday, 3 November 1982, (before any official order to use had been given) Army and Raytheon staff working at Fort Bliss, Texas were exposed to an irritant gas during the testing of the PATRIOT Army Air Defense System - ICC Shelter (similar to a CRG shelter, but equipped with two heater/air conditioner units). MERADCOM on Friday, 5 November 1982 contacted Versar and asked that an appropriate investigation be undertaken. This report is a summary of that investigation.

B. Incident at Fort Bliss, Texas, 3 and 5 November 1982

An industrial hygiene investigative team was dispatched (reported on Thursday, 4 November 1982 - team interviews Monday, 8 November 1982) by MERADCOM to define the exposure problem. A detailed account of that trip is given in Section II.B. They found that seven individuals had been exposed to some form of chemical irritation over a period of two weeks. The chemical exposures happened when the heater was used. Significant damage to teflon grommets of both heaters was observed. Coughing and dryness of throat are the most commonly reported effects first noted. Other symptoms of sleeplessness, severe headaches, and chest pains were also reported.

Based on these observations and discussions with the AEHA staff it was determined that the air would be monitored for hydrolyzable fluoride, chloride, sulfur dioxide, acrolein, contaminants detected by the M8 chemical agent alarm, organics trapped on charcoal tubes and organics trapped on Porapak N tubes. The unit would be tested at low heat and high heat, with and without grommets.

No chemical irritants were detected except hydrolyzable fluoride. The fluoride concentration went from 0.01 mg/m^3 to not detected after the grommets were removed. The 30 teflon grommets in the shelter lost

over 4.5 grams of fluoride. This could have raised the internal concentration of hydrolyzable fluoride to over 250 mg/m^3 (using the assumptions developed in the October 4, 1982 report "PATRIOT Heater/Air Conditioner Investigation: Results of Implementation of July 21, 1982 Recommendations".

C. Hydrolyzable Fluoride Analysis in PATRIOT Shelters at Fort Bliss and White Sands Missile Range After Grommet Removal

Based on the finding of the investigation of the 3 November 1982 incident at Fort Bliss, TFE grommets were removed from all field units. All units showed some signs of thermal decomposition of grommets. It was decided and concurred by PATRIOT Missile Office to subject all enclosures to the same tests done on the 3 November 1982, Fort Bliss unit. This plan was reviewed by US AEHA who supplied additional support equipment. These tests were all conducted and no significant levels of irritants were detected.

D. Reconstruction of the Incident Conditions

In detailed discussions with US AEHA and others it became apparent to MERADCOM that a reconstruction of the decomposition of TFE grommets was worthwhile. A three phase plan was developed with the advice and help of US AEHA. This is discussed in Section IV. The phases are as follows:

- Phase 1 - Laboratory Experiments
- Phase 2 - PATRIOT Heater/Air Conditioner Alone
- Phase 3 - Total Shelter

The laboratory experiments showed that the heater rod produced significant TFE damage. The products of this decomposition were hydrolyzable fluoride (approximately 20 percent), particulate TFE and a large number of organic flouride materials. The analytical methods and target parameters were the same used in all efforts. Only hydrolyzable

fluoride would be produced in significantly high enough concentrations to be detected. The experiments also showed that the M8 chemical agent alarm did respond to the decomposition products of TFE.

In the second phase samples were taken from a stand-alone PATRIOT Heater/Air Conditioner and demonstrated a good correspondence between hydrolyzable fluoride and M8 chemical agent alarm response and loss of weight of TFE grommets. The study showed that the air conditioner alone did not destroy TFE, but only under the normal conditions created when approximately one-half of the return air was blocked. Lastly, the M8 detector response appears to be directly related to hydrolyzable fluoride concentration.

In the third and final phase the concentration of hydrolyzable fluoride, the air flow characteristics, and the M8 chemical agent alarm response were investigated in a real shelter. This study showed that a single heater/air conditioner operated in an ICC shelter will destroy substantial amounts of TFE and will release hazardous amounts of hydrolyzable fluoride. If the other air handling equipment in the shelter is turned on, more TFE is destroyed, and more hydrolyzable fluoride is released. It is important to note that this case, air handling equipment on, is the normal operating condition for the shelter. These experiments, like the second phase experiments, showed that the M8 chemical agent alarm response was related to the hydrolyzable fluoride concentration. However, the study also showed that the M8 chemical agent alarm was not sensitive enough to be a useful warning.

II. INCIDENT AT FORT BLISS, TEXAS, 3-5 NOVEMBER 1982

A. Introduction

During routine evaluation, Wednesday, 3 November 1982, of a PATRIOT Army Air Defense System - ICC shelter at Fort Bliss, Texas, Army and Raytheon personnel were exposed to an irritant gas. On Friday, 5 November 1982, MERADCOM personnel asked Versar to investigate the incident.

Dr. Neil Jurinski (NU CHEMCO) and Mr. John Richards (Versar Inc.) traveled to El Paso, Texas to interview Raytheon Corporation and US Army personnel who had reported adverse health effects during the period from 3-5 November 1982, while working in an ICC shelter equipped with two PATRIOT Heater/Air Conditioners operated in the heat mode. Dr. Jurinski and Mr. Richards interviewed six personnel to determine what the adverse health effects were among the six interviewee's (the seventh person was unable for an interview). This information provided direction in terms of what types of air samples to collect and parameters to look for. The results of the interviews, the exposure assessment, and sampling activities are provided in this section. Also, Dr. Jurinski has described the first phase of the trip to El Paso, Texas in the enclosed trip report submitted to Versar on 12 November 1982 (see Appendix I). During the interviews it was confirmed that all illnesses occurred when the units were operated in one of the heating modes. The second phase of this trip was to provide air sampling to attempt to identify the chemical irritants that may be present in the shelter during heater operation and relate these irritants back to the adverse health effects observed earlier (see Section II.C. for specific details).

B. Industrial Exposure Assessment Results

The results of the interviews indicated that an irritant was being released into the air of the ICC shelter during heater operations. The presence of this irritant in the air caused all personnel involved to be uncomfortable about working in the ICC shelter, therefore, the PATRIOT Heaters/Air Conditioners were turned off and the shelter vacated.

Versar determined that additional on-site testing was required and scheduled the tests for 10 November 1982. Dr. Jurinski was not present during the on-site testing. His trip report for activities conducted on 8-9 November 1982 are presented in Appendix I.

C. Field Sampling

Field sampling was conducted on 10 November 1982, in the ICC shelter located at Abernathy Park in Fort Bliss (El Paso, Texas). Sampling activities began at 0400 and ended at approximately 1240. Samples were collected for the following target parameters:

- Sulfur dioxide
- Hydrogen fluoride
- Hydrogen chloride
- Acrolein
- Semi-volatile organic compounds
- Volatile organic compounds

In addition, an irritant gas detector developed for the US Army was used as a real time monitor of possible irritants in the air. This chemical agent alarm is referred to as the "M8", and is used by US Army personnel to detect gases such as carbonyl chloride (Phosgene). During sampling, personnel wore respirators when inside the ICC shelter when monitoring sampling equipment and collecting data inside.

The development of the above list of target parameters was as a result of both recommendations from US AEHA and review of analytical data obtained from the thermal degradation studies conducted earlier by Versar. The use of the M8 chemical agent alarm was recommended by US AEHA.

C.1 Sampling

All sampling procedures were either recommended or approved EPA or NIOSH methods for the target parameters of interest. As described above, air samples were collected for the above chemical constituents and

general chemical groups using impinger solutions, Porapak sorbent tubes, and charcoal sorbent tubes. In addition, the M8 chemical agent alarm, plus a second M8 chemical agent alarm from the Fort Bliss NBC school, were operated continuously during all phases of sampling to provide a real time monitor for the possible presence of chemical irritants like carbonyl chloride. A total summary of samples collected is presented in Table 1.

The following sampling scheme was conducted with TFE grommets in position on both heater units and operated as described below:

- 0.5 hr sampling run with both units on high heat.
- 1.0 hr sampling run with both units on high heat.
- 1.0 hr sampling run with both units on low heat.
- 1.0 hr sampling run outside shelter - referred to make-up air.

All TFE grommets were removed from both heater units and were submitted to the laboratory for gravimetric analysis after the above sampling runs were completed. Then a final sampling run was performed to determine if conditions inside the ICC shelter were different than those observed when the TFE grommets were in position. The sampling run was conducted under the following conditions:

- 1.0 hr sampling run with both units on high heat.

All samples were submitted to Versar's analytical laboratory on November 11, 1982 at 0930 for analyses.

C.2 On-site Observations

Inspection of the ICC shelter revealed that the inside configuration was similar to the CRG shelter and was equipped with electronic equipment. The ICC shelter has two PATRIOT Heater/Air Conditioner units rather than one like the CRG shelter. The units in

TABLE 1

SUMMARY OF AIR SAMPLES COLLECTED ON 10 NOVEMBER 1982
FROM THE ICC SHELTER EQUIPPED WITH TWO
PATRIOT HEATER/AIR CONDITIONER UNITS*

	Shelter Air	Make-up Air	Field Blanks	Total Summary
0.3N H_2O_2 impinger	4	1	2	7
0.1N NaOH impinger	8	2	2	12
1 percent $NaHSO_3$ impinger	8	2	4	14
Porapak Tubes	8	8	5	21
Charcoal Tubes	8	7	2	17
M8 Continuous	1	--	--	1
TOTALS	37	20	15	72

*Curbside unit was SN 81014; Roadside unit was SN 801163.

position on the shelter were SN 81014 on the curbside and SN 801163 on the roadside. It was observed that the foam dust filter at the face of the floor-level return air duct was extremely dirty. A slight touch with a pencil resulted in many dust particules falling off. Also, all horizontal surfaces inside the shelter were covered with a thin layer of dust. The general condition of the shelter appeared as if neither housekeeping activities nor dust filter maintenance had been been recently performed.

Inspection of the heater/air conditioner units was performed and the following was observed:

SN 81014 (curbside)

- heater rods - slightly discolored entire length of rod.
- TFE grommets - eight disfigured, but none melted to the point that they had apparently dripped.
- tygon tubing - appeared good.
- aluminum shielding - all in place.
- foam - pliable and showed only signs of having standing water for long periods.
- general - inside of box was dirty on bottom.

SN 801163 (roadside)

- heater rods - all discolored with a light black dust present on all. Discoloration covered approximately 50 percent of rod and did not go all the way to the free end.
- TFE grommets - all appeared in good condition and none were disfigured.
- tygon tubing - appeared good.
- aluminum shielding - all in place.
- foam - pliable and showed signs of having standing water for long periods.
- general - inside of box was extremely dirty at the bottom.

During sampling, the inside air temperature ranged from a low of 74°F to a high of 140°F, dependent upon whether the heaters were just

turned on and positioned to either the low or high heat mode. Samples were located approximately six inches the floor in the middle of the shelter. The return air duct located on the floor was clear of blockage and the foam dust filter was in place. The dust filter was not cleaned before sampling activities began.

Each time the heaters were started up, there was an initial burning smell which lasted for a period from 30 seconds to 2 minutes. The smell was similar to the one encountered when a new electrical stove element is turned on. There were no other obvious smells detected during sampling.

During the entire sampling period, two M8 chemical agent alarms were operated continuously. There were no audible signals produced, nor did the zero needle show a deflection greater than zero. The M8 chemical agent alarms were operated by a Sgt. Lee from the NBC school who was thoroughly knowledgeable about the operation of the detector.

D. Fort Bliss Sampling Trip and Incident Investigation, 8-9 November 1982

Samples were collected for hydrogen fluoride (HF), sulfur dioxide, acrolein, semi-volatile organic compounds with charcoal tubes, and volatile organic compounds on Porapak N tubes. The TFE grommets in the units tested were removed and sent to the laboratory after the initial air testing was completed.

Hydrogen Fluoride

Fluoride samples were analyzed using a modification of NIOSH method. The NIOSH method states that the samples should be collected in impingers containing 0.1 N NaOH. The samples collected in 0.1 N NaOH were damaged during shipping, so they could not be analyzed. As an alternative, we analyzed the fluoride in the impinger solutions used for sulfur dioxide. These impinger solutions contain a hydrogen peroxide

solution adjusted to pH = 5. This change in the impinger solution from the standard method may reduce the collection efficiency, so the results reported may be low. They should, however, be comparable, so any trends observed in the data will reflect actual conditions in the ICC shelter. The data is presented in Table 2. The highest fluoride levels observed were during the first 30 minutes of heating in the high heat mode. The next hour of heating had a lower fluoride level. The next hour of heating was done on the low heat mode, and even lower fluoride levels were observed. Fluoride was not detectable in the air samples after the TFE grommets were removed. It was not detectable in the ambient air.

Sulfur Dioxide

Sulfur dioxide was analyzed using NIOSH method P&CAM 146. The results are presented in Table 2. The results indicate that the ambient air at Fort Bliss contains low levels of sulfur dioxide. These levels are typical for many areas in the United States. There is no evidence that the sulfur dioxide levels are elevated inside the ICC shelter.

Acrolein

Acrolein was analyzed using NIOSH method P&CAM 118. The results are presented in Table 2. No acrolein was found either inside or outside the ICC shelter.

Semi-Volatile Organic Compounds

Semi-volatile organic compounds were collected on standard charcoal tubes purchased from SKC Corp. (Catalogue No. 226-09). The collected organic compounds were eluted with carbon disulfide and were analyzed by capillary gas chromatography with flame ionization detection. The method has been described in detail in an earlier report. The results are presented in Table 2. No compounds less volatile than toluene were detected in significant amounts in the ICC shelter.

TABLE 2

SUMMARY OF AIR SAMPLE CHEMICAL ANALYSIS TAKEN ON 10 NOVEMBER 1982 FROM ICC SHELTER EQUIPPED WITH TWO PATRIOT HEATER/AIR CONDITIONER UNITS

Sample Description	Reported Fluoride in Air* mg/m^3 F^-	ug/m^3	SO_2 mg/m^3	Semi-Volatile Organics	Acrolein
High heat with teflon 0.5 h at 1.45 l/min	0.010	10.	0.1	ND	< 0.06
High heat with teflon 1.0 h at 1.45 l/min	0.004	4.	0.5	ND	< 0.06
Low heat with teflon 1.0 h at 1.45 l/min	0.002	2.	0.2	ND	< 0.06
High heat without teflon 1.0 h at 1.45 l/min	0.002	2.	0.1	ND	< 0.06
Ambient air 1.0 h at 1.45 l/min	0.002	2.	0.5	ND	< 0.06
Method Detection Limit	0.002	2.	0.1	**	0.06

*H_2O_2 solution.

**ND = No blank corrected peaks larger than 0.53 mg/m^3 toluene eluting after toluene.

Volatile Organic Compounds

Volatile organic compounds were collected on Porapak N tubes following EPA Method 603, Federal Register, Vol. 44, No. 233, Monday, 3 December 1979 as a guideline. Prior to sample collection the Porapak N sampling tubes were spiked with surrogate tracer material to monitor the retention of the adsorbent. The analysis was performed by thermally desorbing the volatile organics from the sample tube into the GC/MS using packed column chromatography. The method is described in detail in the 4 October 1982 report. The results are summarized in Table 3. No volatile organics were detected during the first half hour of operation. During the next three hours, very low levels of several solvents were detected. Those solvents were toluene, pentane, and 2-ethoxyethanol- acetate. Toluene was confirmed by standard reference material, whereas the other solvents have only been tentatively identified by library search. No acrolein was detected and no evidence of fluorinated hydrocarbons was detected by the method. Porapak N studies discussed in detail in Section IV.A of this report, have shown that Porapak N would effectively trap many of the expected decomposition products of TFE.

Surrogate recoveries are summarized in Table 4. The recovery for both surrogates was quantitative (+100 percent) during the first half hour of sampling. No spike was included on the sample tube for the second 1.0 hour sample tube. The third and fourth 1.0 hour sample tube recoveries were variable, with 0 percent recovery for acrylonitrile-d3 and quantitative recovery of 2-fluorobenzene at 77 and 85 percent respectively.

The volatile organic analysis chromatograms for the four samples collected on 10 November 1982 at Fort Bliss, Texas, are shown in Figures 1 through 5 with the spiked trip blank. The largest peak in all RIC chromatograms (the bottom graph) at scan 480 $\pm$ 2 scans is the surrogate 2-fluorobenzene-5 and the internal standard benzene-d6. The peak represents 3.2 ug of materials. In the 0.5 hour air sample it would

TABLE 3

SUMMARY OF RESULTS OF VOLATILE ORGANICS SAMPLES COLLECTED 10 NOVEMBER 1982 FROM ICC SHELTER

SAMPLE DESCRIPTION	COMPOUNDS	CONC. (mg/m^3
High heat with TFE 0.5 hour	None detected	ND
High heat with TFE 1.0 hour	Pentane	0.07(1)
	Toluene	0.01
	Xylene	0.01(1)
Low heat with TFE 1.0 hour	Toluene	0.06
	2-Ethoxyethanolacetate	0.07(1)
High heat without TFE 1.0 hour	Toluene	0.03
	2-Ethoxyethanolacetate	0.1(1)

(1) Estimated concentrations based on internal standard response.

TABLE 4

SURROGATE RECOVERIES

SAMPLE DESCRIPTION	ACRYLONITRILE-d3	2-FLUOROBENZENE-d5
High heat with TFE 0.5 hour	122	104
High heat with TFE 1.0 hour	No spike added	No spike added
Low heat with TFE 1.0 hour	0	77
High heat without TFE 1.0 hour	0	85

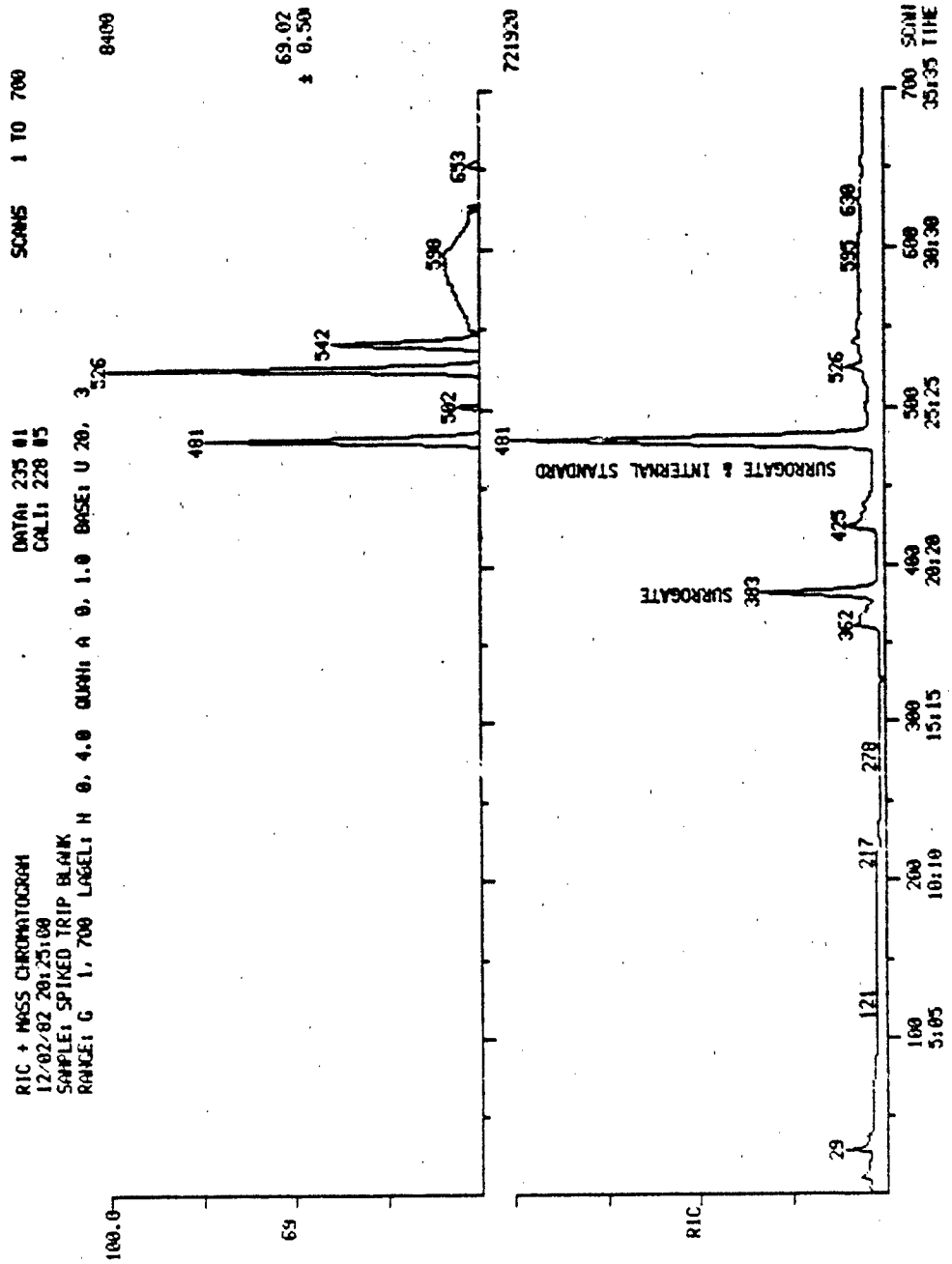


FIGURE 1

SPIKED TRIP BLANK, 8-9 NOVEMBER 1982

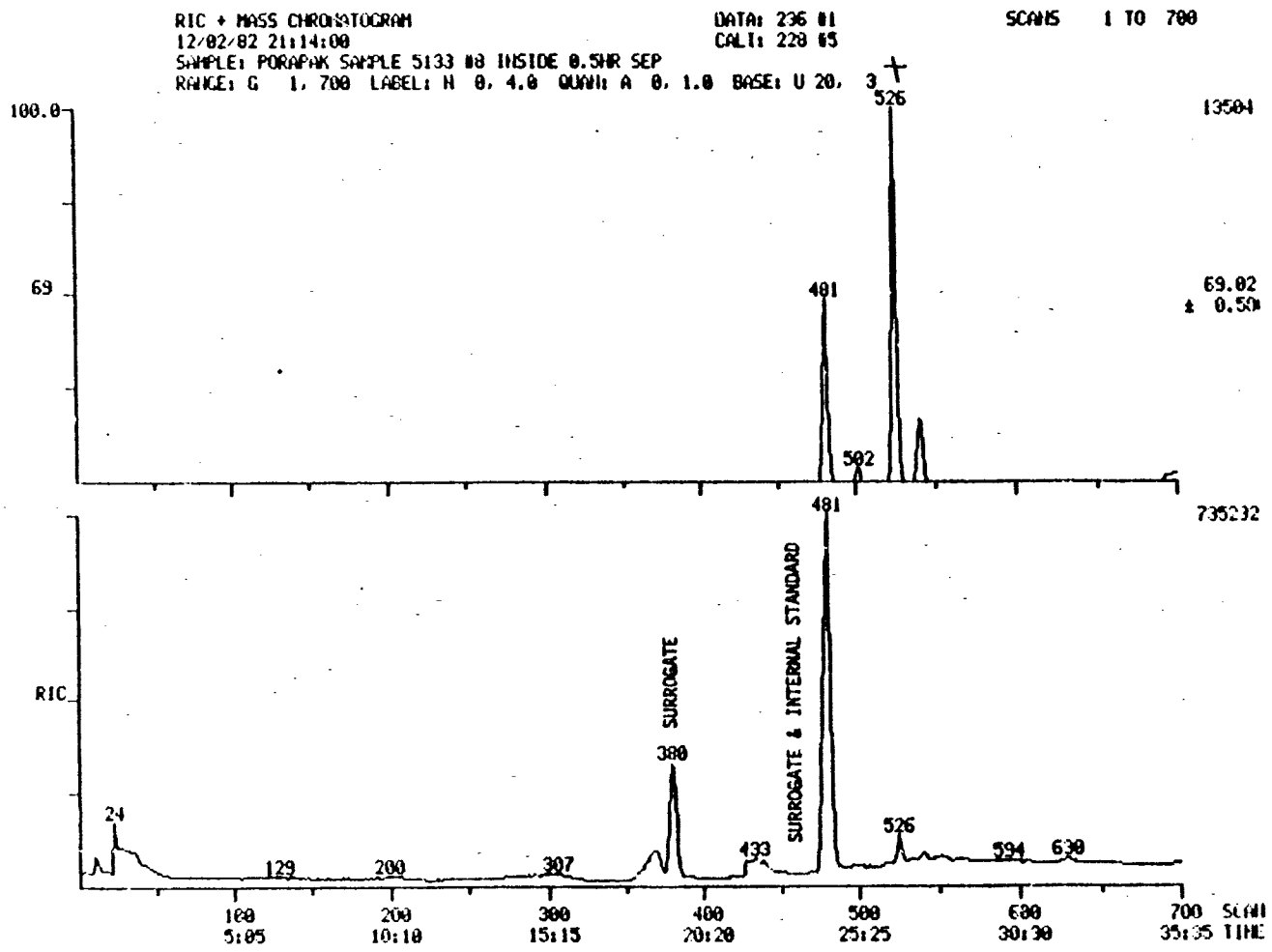


FIGURE 2

INSIDE AIR, 0.5 HR, HIGH HEAT

N-25

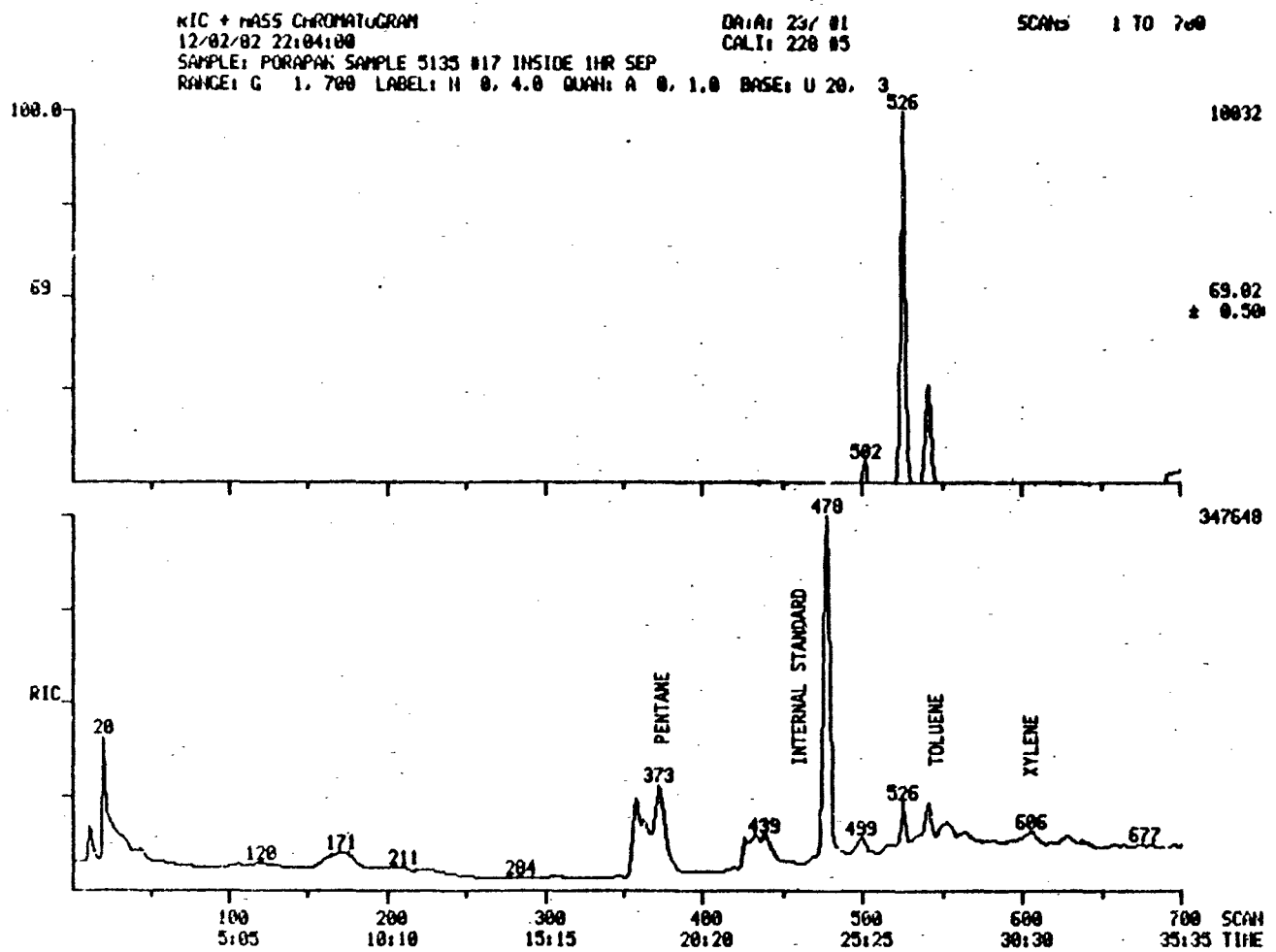


FIGURE 3

INSIDE AIR, 1.0 HR, HIGH HEAT

N-26

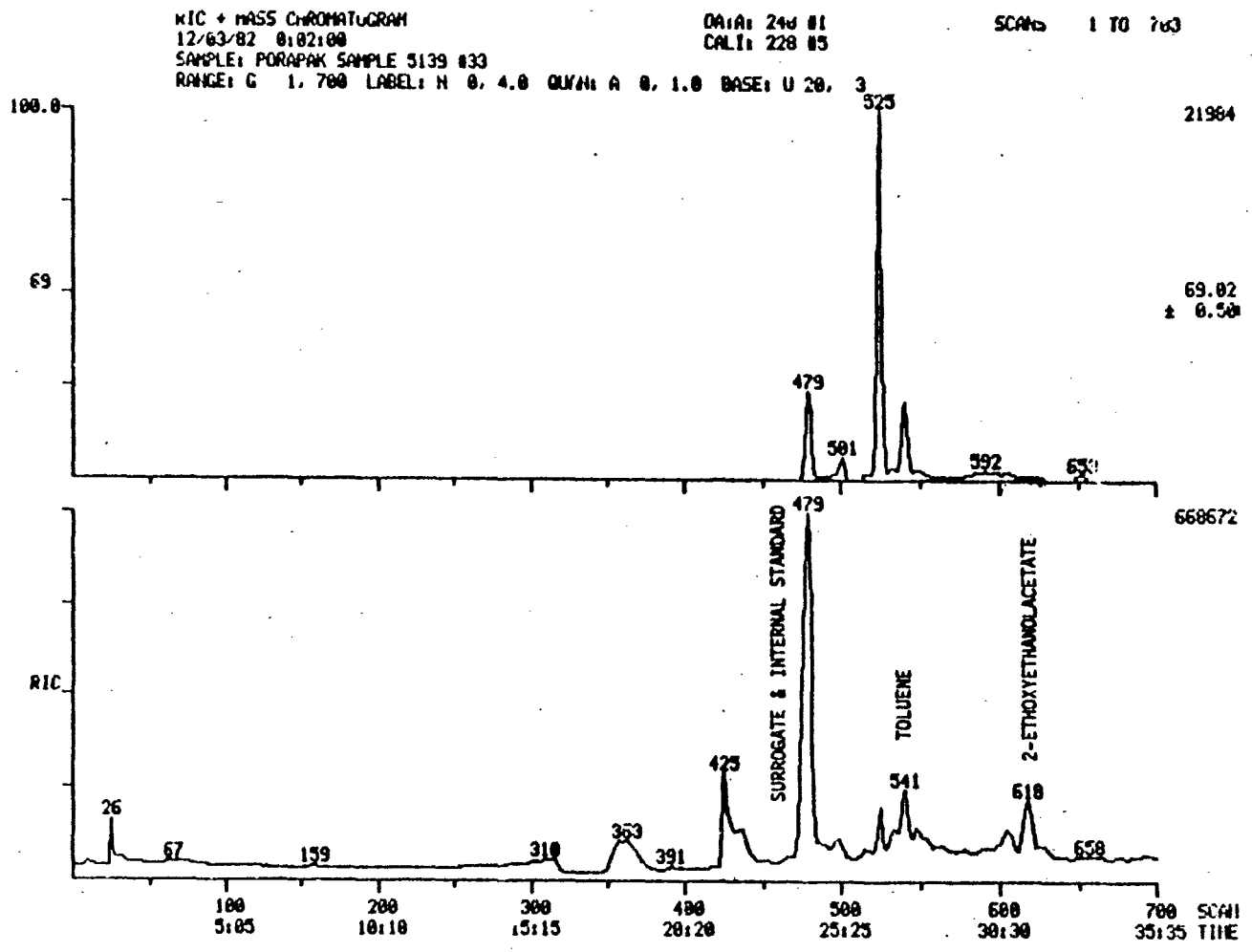


FIGURE 4

INSIDE AIR, 1.0 HR, HIGH HEAT, NO GROMMETS

N-27

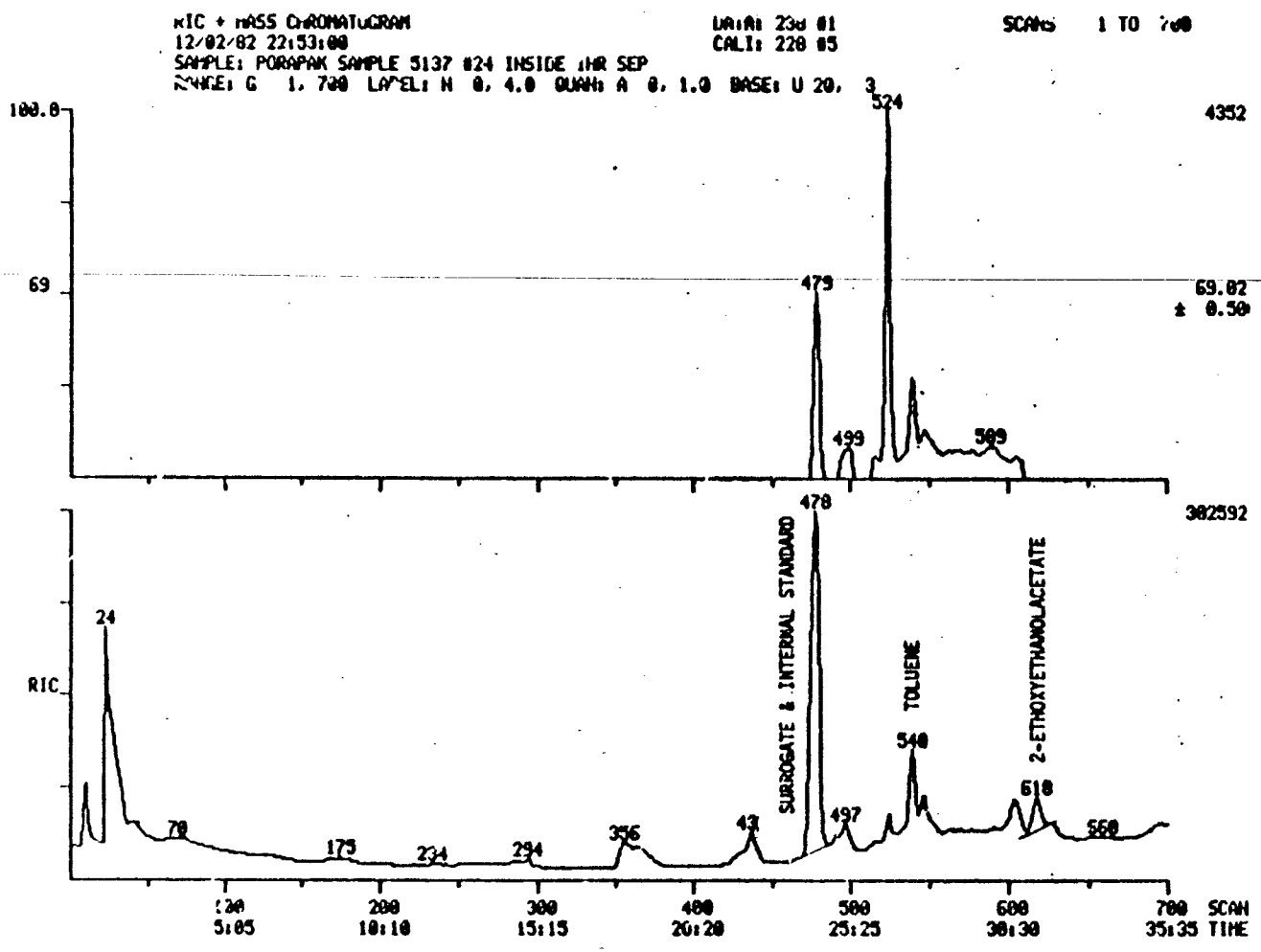


FIGURE 5

INSIDE AIR, 1.0 HR, LOW HEAT

N-22

represent 1.2 mg/m^3 and in the 1.0 hour samples it would equal 0.7 mg/m^3. The detection limit of the method is estimated to be 0.01 mg/m^3 for the volatile materials of interest.

The upper graph is an extracted ion current profile of mass 69 m/z (mass to charge ratio). Ion 69 is the mass fragment CF_3. It is a common fragment of perfluorinated hydrocarbons, and is found to be present in most of the compounds detected by collection of the TFE outgassing products in the experiments conducted on the TFE grommets discussed in Section IV.A. Should fluorinated compounds of molecular weight 131-388 have been present at concentrations of 0.01 mg/m^3 or greater, mass peaks would have probably been detected by the method. However, since no mass peaks are present, other than those also present in the blanks, it is reasonable to conclude that the TFE decomposition products are not detectable due to their individual concentrations being less than 0.01 mg/m^3.

Gravimetric Analysis of TFE Grommets

The TFE grommets in each of the heater/air conditioner units were carefully removed and sent to the laboratory. Each grommet from the units was weighed, and the results were compared to a new set of grommets obtained from the manufacturer of the units; Keco Industries. The results are presented in Table 5. The average weight of the used grommets in both of the units was lower than the new grommets. If the grommets removed from the units initially had the same weight as the new grommets, then a total weight loss can be calculated. An average grommet in unit 801163 lost 0.067 grams of TFE. The total amount of TFE lost in unit 801163 was 1.005 grams. Since TFE is 76 percent fluorine, this corresponds to 760 mg of fluorine that was lost from the grommets. In unit 81014 the average loss was 0.25 grams and the total loss was 3.75 grams. This corresponds to 2.85 grams (2850 mg) of fluorine. The total amount of fluorine lost from both units was 3.61 grams (3610 mg).

In the 19 October 1982 report on the PATRIOT Heater/Air Conditioners a worst case risk analysis was used. In this model we assume that all of the material is released into the shelter at one time, and that there is no dilution of the contaminants. The inside of the shelter is 14.4 m^3. With these assumptions, the predicted concentration of TFE decomposition products is 251 mg/m^3.

There are no officially accepted Threshold Limit Values (TLVs) for decomposition products of TFE. In 1961 The American Conference of Governmental Industrial Hygienists recommended a TLV of 0.05 mg/m^3 as fluoride.[1] This recommendation, however, has not been adopted. TLV's for some inorganic fluorine compounds which are measured by the hydrolyzable fluoride analysis are presented in Table 6.[4] Other authors have reported that polymer fume fever can occur at hydrolyzable fluoride concentrations as low as 0.05 ug/m^3.[3] The worst case risk assessment indicates, therefore, that the concentration of decomposition products could be over 5,000 times higher (251 mg/m^3) than the concentrations which cause symptoms (0.05 ug/m^3).

TABLE 5

GROMMET WEIGHTS, FORT BLISS SAMPLING
10 NOVEMBER 1982

	New Grommets (grams)	Unit 801163 (grams)	Unit 81014 (grams)
	1.433	1.309	1.310
	1.370	1.310	1.242*
	1.397	1.333	1.081*
	1.419	1.303	0.972*
	1.367	1.314	1.032*
	1.393	1.427	1.106*
	1.385	1.308	1.150*
	1.406	1.301	1.079*
	1.408	1.299	1.190*
	1.408	1.299	1.190*
	1.368	1.294	1.118*
	1.404	1.314	1.208*
		1.295	1.198*
		1.345	1.109*
		1.417	1.196*
MEAN	1.394	1.327	1.144
S.D.	0.019	0.042	0.086
N	12	15	15
Total Fluoride Lost	0	1.00	3.75

*Visibly heat damaged.

TABLE 6

TLV's FOR SEVERAL SELECTED FLUORINATED COMPOUNDS

Carbonyl Fluoride	15 mg/m^3
Fluorine	2 mg/m^3
Fluoride dust	2.5 mg/m^3 as F
Hydrogen Fluoride	2 mg/m^3

III. HYDROLYZABLE FLUORIDE ANALYSIS IN PATRIOT SHELTERS AT FORT BLISS AND WHITE SANDS AFTER GROMMET REMOVAL

A. Introduction

Based on the weight loss and obvious damage to TFE grommets the presence of hydrolyzable fluoride in the 3 November 1982 incident at Fort Bliss, MERADCOM decided to remove all TFE grommets. It was decided and concurred by PATRIOT Missile Office to subject all enclosures in use at Fort Bliss, Texas and White Sands, New Mexico to the same test series done on the 3 November 1982 Fort Bliss shelter. The plan was reviewed by VSE/Versar and U.S. AEHA staff in detail prior to beginning the field sampling and testing. Two air sampling pumps were borrowed from AEHA to collect some specialized AEHA sorption tubes as back-up to the standard Porapak N tubes. No indications of detectable organics were found and extra sorption tubes were not analyzed.

B. Field Sampling

Field sampling was conducted on 22 November 1982 at Fort Bliss and on 23 November 1982 at White Sands Missile Range. Seven shelters were sampled while the heater/air conditioners on each shelter were operated in the high heat mode. During all tests, there were no TFE grommets in position and therefore no TFE available to be exposed to the heated portions of any of the heater rods in a heater/air conditioner. Air samples were collected for the following target parameters:

- Hydrogen fluoride
- Acrolein
- Semi-volatile organic compounds
- Volatile organic compounds

Similar to the sampling conducted on 10 November 1982, the M8 chemical agent alarm was used during all sampling activities when air was being monitored in each shelter. The M8 chemical agent alarm was operated by Sgt. Lee of the NBC school located at Fort Bliss. Sgt. Lee traveled with

Versar personnel to White Sands Missile Range to operate the M8 chemical agent alarm during sampling.

The development of the target parameter list was made based upon recommendations from US AEHA and review of analytical results from both previous sampling trips and results from the thermal degradation studies conducted earlier in the project by Versar. The major emphasis for this trip was to quantify air concentrations in each shelter for hydrolyzable fluoride. The use of the M8 chemical agent alarm during this sampling trip was recommended by US AEHA. Versar also collected air samples on a specially prepared organic sorbent tube at each shelter for analysis by US AEHA (sampling tubes were also prepared by US AEHA). These special air samples were submitted to US AEHA upon return from the sampling trip.

B.1 Sampling

All sampling procedures were either recommended or approved EPA and NIOSH methods for the target parameters of interest. As mentioned above, air samples were collected for both specific chemical constituents and general chemical groups using impinger solutions, Porapak sorbent tubes, and charcoal sorbent tubes. The special air sampling tube was collected for US AEHA to perform their organic analysis. The tube consisted of a front section of Tenax GC sorbent material and a back section of Ambersorb sorbent material. The M8 chemical agent alarm was operated in each shelter continuously during sampling. A total summary of samples collected at both Fort Bliss and White Sands Missile Range are presented in Tables 7 and 8.

All sampling activities were conducted for a one hour duration at each shelter described in Tables 7 and 8. All TFE grommets had been removed from all heater/air conditioner units tested prior to sampling activities by MERADCOM personnel.

TABLE 7

SUMMARY OF AIR SAMPLES COLLECTED ON 22 NOVEMBER 1982 AT FORT BLISS FROM VARIOUS SHELTERS EQUIPPED WITH PATRIOT HEATER/AIR CONDITIONER UNITS

	ECS Shelter*	CRG Shelter**	ICC Shelter***	Make-up Air	Total Summary
0.1N NaOH impinger	2	2	2	2	8
1 percent $NaHSO_3$ impinger	2	2	2	2	8
Porapak Tubes	1	1	1	1	4
Charcoal Tubes	1	1	1	1	4
Tenax/Ambersorb Tubes	1	1	1	1	4
M8 Chemical Agent Alarm	1	1	1	-	3
TOTALS	8	8	8	7	31

* Curbside unit was SN 801167; Roadside unit was SN 81001.
** Curbside unit was SN 801198; No roadside unit required on this shelter.
*** Curbside unit was SN 81014; Roadside unit was SN 801163.

TABLE 8

SUMMARY OF AIR SAMPLES COLLECTED ON 23 NOVEMBER 1982 AT WHITE SANDS MISSILE RANGE FROM VARIOUS SHELTERS EQUIPPED WITH PATRIOT HEATER/AIR CONDITIONER UNITS

	CRG Shelter*	ECS Shelter**	ECS Shelter***	ICC Shelter+	Make-up Air	Total Summary
0.1N NaOH impinger	2	2	2	2	2	10
1 percent $NaHSO_3$ impinger	2	2	2	2	2	10
Porapak Tubes	1	1	1	1	1	5
Charcoal Tubes	1	1	1	1	1	5
Tenax/Ambersorb Tubes	1	1	1	1	1	5
M8 Chemical Agent Alarm	1	1	1	1	-	4
TOTALS	8	8	8	8	7	39

* Curbside unit was SN 801173; No roadside unit required on this shelter. Shelter was located at Elephant Mountain.

** Curbside unit was SN 81002; Roadside unit was SN 81004. Shelter was located at Dog Site.

*** Curbside unit was SN 801177; Roadside unit was SN 81003. Shelter was located at LC-38.

\+ Curbside unit was SN 801164; Roadside unit was SN801169. Shelter was located at LC-38.

All samples except the Tenax/Ambersorb tubes were submitted to Versar's analytical laboratory on 24 November 1982 for analysis. The Tenax/Ambersorb tubes were submitted to the US AEHA analytical laboratory on 29 November 1982

During all sampling activities, the M8 chemical agent alarm was operated by Sgt. Lee and at no time was an audible signal heard indicating presence of potential irritant air borne chemicals. Sampling personnel and US Army support personnel were in and out of the shelters during heater operation and no unusual odors were noticed, nor did personnel feel any adverse health effects as a result of being inside the heated shelter.

C. Fort Bliss and White Sands Sampling Trip, 22 and 24 November 1982

In this sampling trip seven different PATRIOT Heater/Air Conditioners were sampled for hydrolyzable fluoride, chloride, acrolein, semi-volatile organic compounds and volatile organic compounds. At Fort Bliss three shelters were sampled; #801167 (curbside) and #81001 (roadside) in the ECS shelter, #81014 (curbside) and #801163 (roadside) in the ICC shelter, and #801198 in the CRG shelter. At White Sands four units were sampled; #81002 (curbside) and #81004 (roadside) in the ECS shelter, #801177 (curbside) and #81003 (roadside) in the ECS shelter, #801164 (curbside) and #801169 (roadside) in the ICC shelter, and #801173 in the CRG shelter. Ambient air samples were collected at both Fort Bliss and White Sands. The TFE grommets were removed from all of the units before sampling.

Hydrolyzable Fluoride

Hydrolyzable fluoride air analyses were performed using NIOSH Method P&CAM 117. The fluoride results are presented in Table 9. No fluoride was detected in the ambient samples, and no fluoride was

TABLE 9

SUMMARY OF AIR SAMPLE CHEMICAL ANALYSIS TAKEN ON 22-23 NOVEMBER 1982 FROM ICC SHELTER EQUIPPED WITH TWO PATRIOT HEATER/AIR CONDITIONER UNITS

Site	Unit #	Hydrolyzable Fluoride Duplicate A	Hydrolyzable Fluoride Duplicate B	Chloride	Acrolein	Semi Volatile Organics*
Ambient, Fort Bliss	----	N.D.	N.D.	N.D.	N.D.	N.D.
ECS, Fort Bliss	801167	2	N.D.	N.D.	N.D.	N.D.
ICC, Fort Bliss	81014	N.D.	N.D.	N.D.	N.D.	N.D.
CRG, Fort Bliss	801198	N.D.	N.D.	N.D.	N.D	N.D.
Ambient, Elephant Mountain (WSMR)	----	N.D.	N.D.	N.D.	N.D.	N.D.
ECS, WSMR	81002	3	3	N.D.	N.D.	N.D.
ECS, WSMR	801177	1	1	N.D.	N.D.	N.D.
ICC, WSMR	801164	N.D.	N.D.	N.D.	N.D.	N.D.
CRG, WSMR	801173	N.D.	N.D.	N.D.	N.D.	N.D.
Method Detection Limit		1	1	180	60	*

Numbers are in ug/m^3.

*No blank corrected peaks larger than 0.53 mg/m^3 toluene eluting after toluene.

detected in four of the units. In the remaining three units very low levels of hydrolyzable fluoride were found. These levels are well below the TLVs for TFE decomposition products.

Chloride

Chloride in air analyses were done using NIOSH Method P&CAM 115. The results are presented in Table 9. No chloride was detected in any of the samples.

Acrolein

Acrolein was analyzed using NIOSH method P&CAM 118. The results are presented in Table 9. No acrolein was found in any of the samples.

Semi-Volatile Organic Compounds

Semi-volatile organic compounds were analyzed using the method previously described. The results are presented in Table 9. No significant amounts of semi-volatile organic compounds were found in the samples.

Volatile Organic Compounds

Volatile organics were determined using the EPA Method 603 as described in Section II of this report. The results are summarized in Table 10. Small amounts of solvent materials were detected in five of the seven units tested. These volatile organic compounds were toluene, xylene, trichloroethane and 2-ethoxyethanolacetate. No acrolein was detected. Also, there was no evidence of fluorinated hydrocarbons at the estimated detection limit of 0.01 mg/m^3. Surrogate recoveries are listed in Table 11.

The GC/MS analysis chromatograms of the seven units are shown in Figures 6 through 13. No volatile organic component peaks are present in the lower RIC graph in equal or greater concentrations than the surrogates or the internal standard.

TABLE 10

VOLATILE ORGANICS SUMMARY

SAMPLE DESCRIPTION	UNIT	COMPOUNDS	CONC. (mg/m^3
ECS, Fort Bliss	801167	Toluene Xylene	0.05 0.06(1)
ECS, Fort Bliss	81014	None Detected	ND
CRG, Fort Bliss	801198	Toluene	0.06
ECS, White Sands Missile Range	81002	Toluene Trichloroethane 2-Ethoxyethanolacetate	0.04 0.02(1) 0.1(1)
ECS, White Sands Missile Range	801177	None Detected	ND
ICC, White Sands Missile Range	801164	Toluene	0.03
CRG, White Sands Missile Range	801173	Toluene	0.02

(1) Estimated concentrated based on internal standard response.

TABLE 11

SURROGATE RECOVERIES

SAMPLE DESCRIPTION	UNIT #	PERCENT RECOVERY ACRYLONITRILE-d3	2-Fluorobenzene-d5
ECS, Fort Bliss	801167	18	100
ECS, Fort Bliss	81014	43	85
CRG, Fort Bliss	801198	54	92
ECS, White Sands Missile Range	81002	105	108
ECS, White Sands Missile Range	801177	62	110
ICC, White Sands Missile Range	801164	0	65
CRG, White Sands	801173	39	96

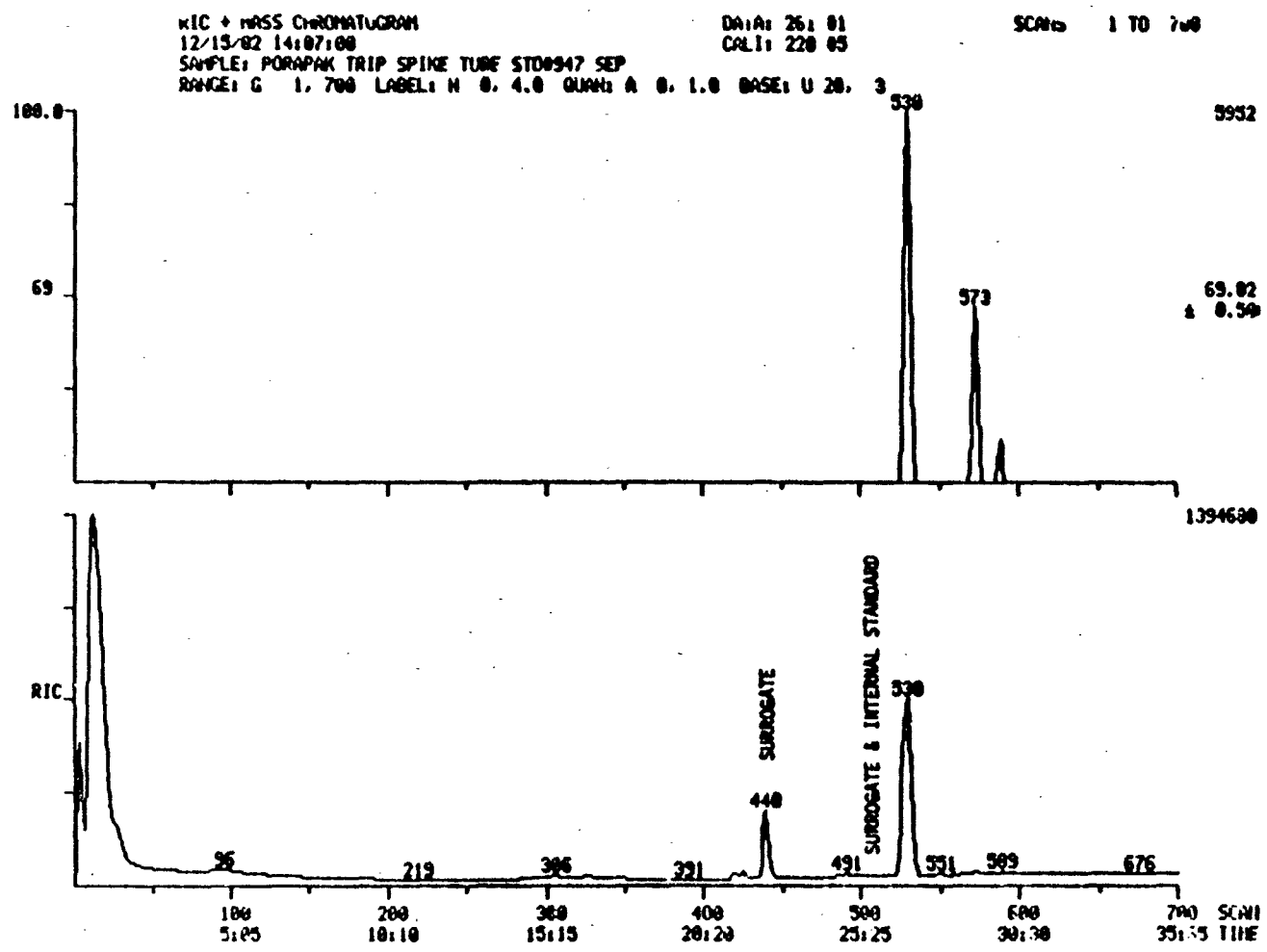


FIGURE 6

SPIKED TRIP BLANK, 22-23 NOVEMBER 1982

N-12

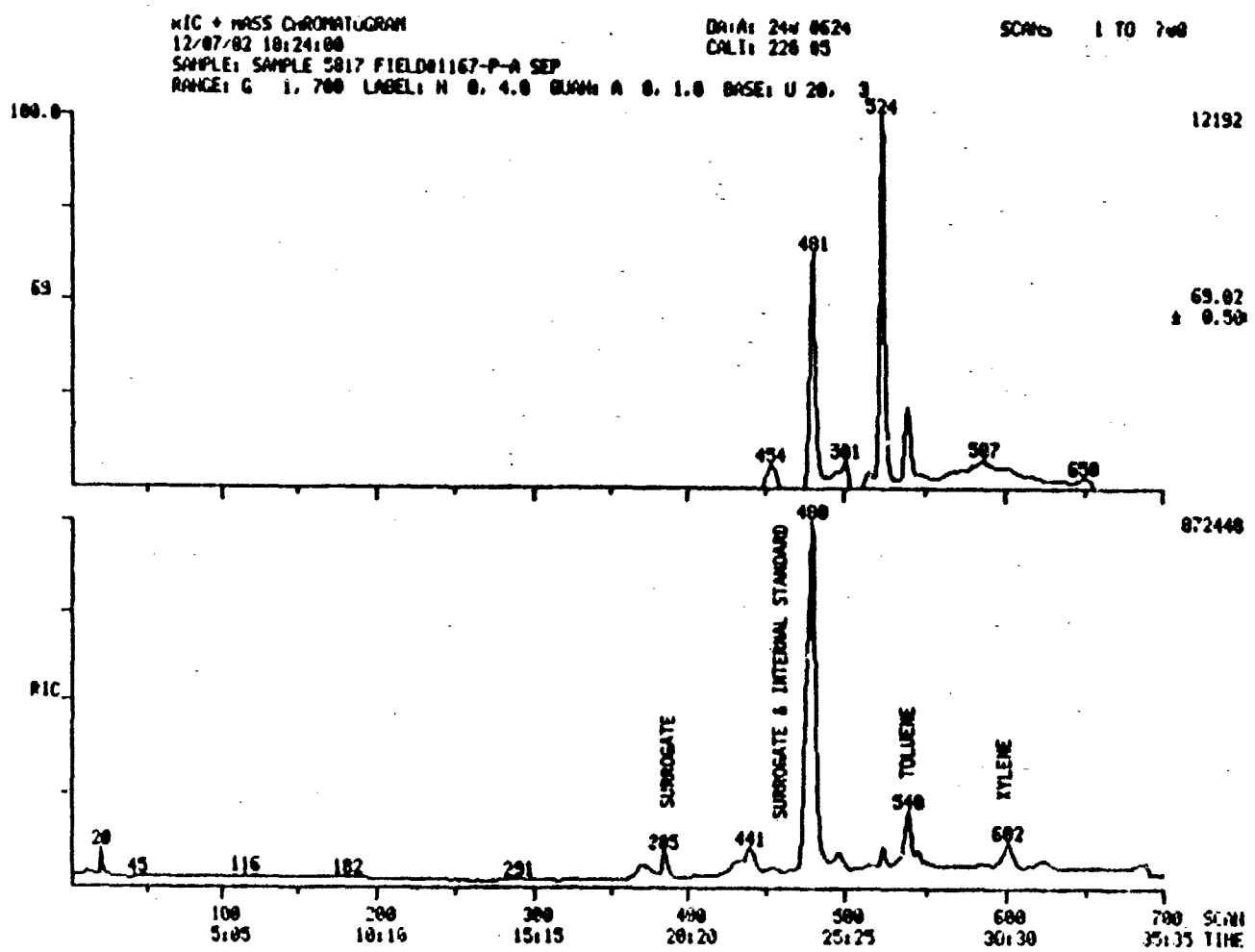


FIGURE 7
INSIDE AIR, ECS, FORT BLISS, TEXAS

N-43

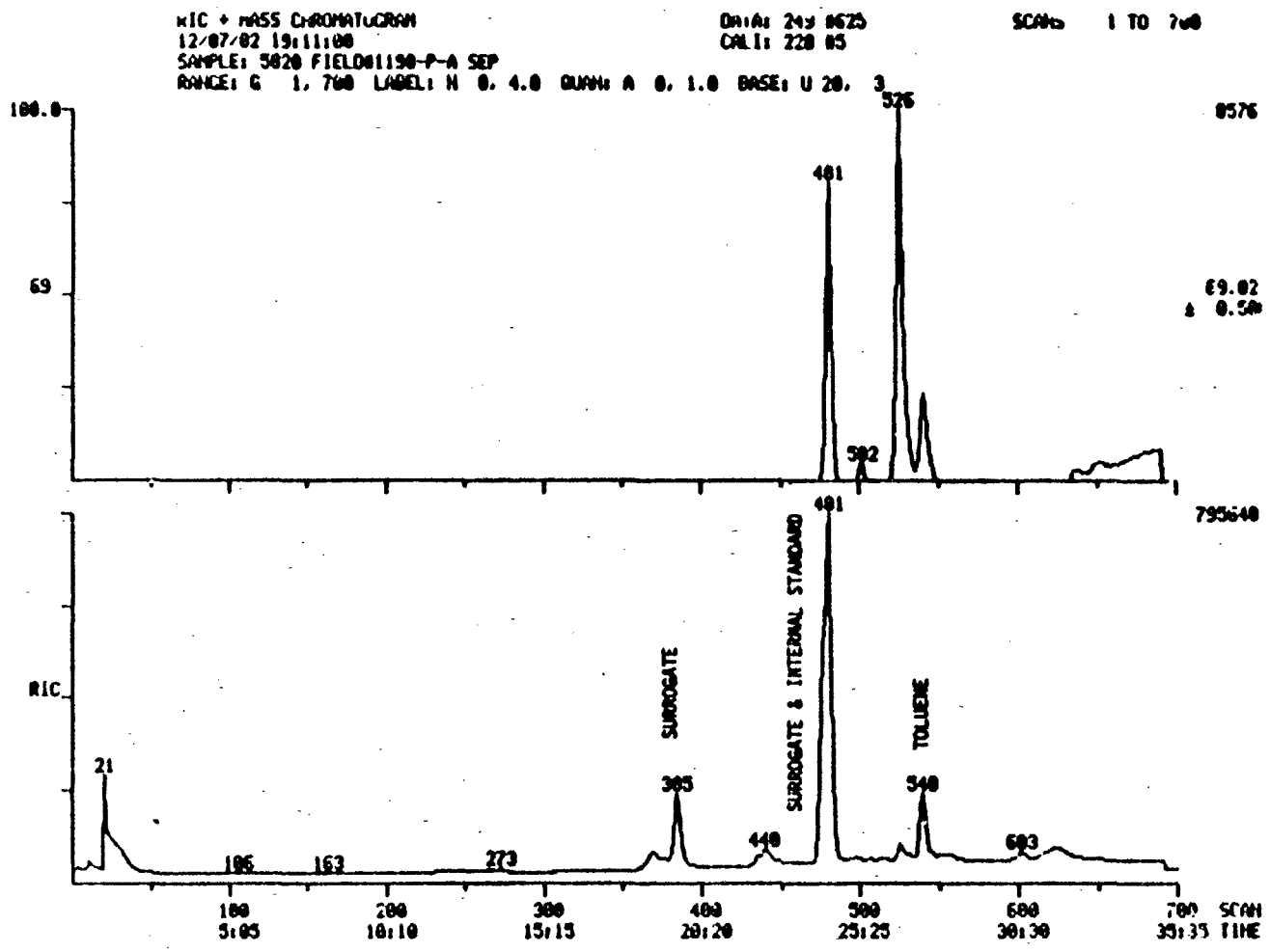


FIGURE 8

INSIDE AIR, CRC, FORT BLISS, TEXAS

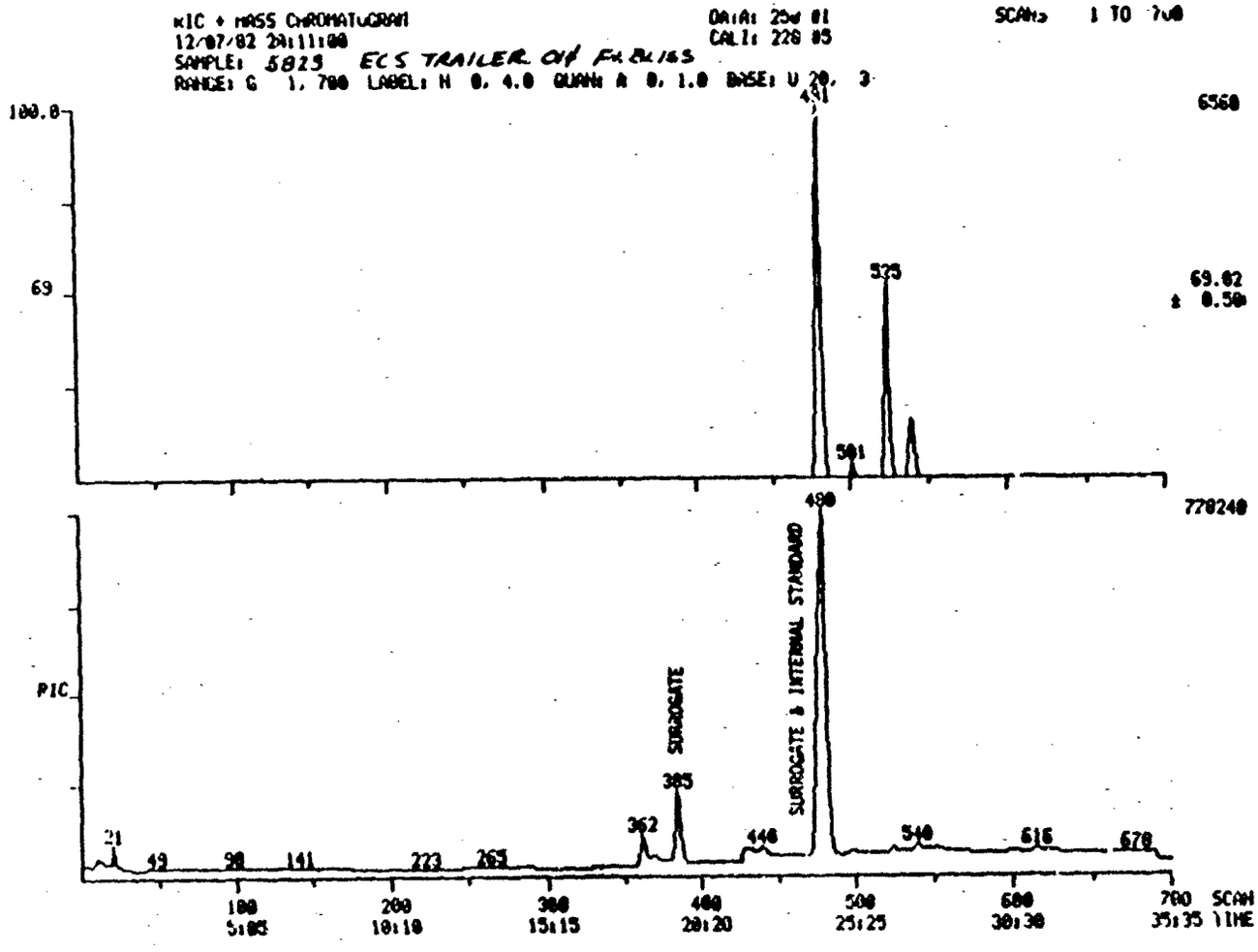


FIGURE 9

INSIDE AIR, ICC, FORT BLISS, TEXAS

N-45

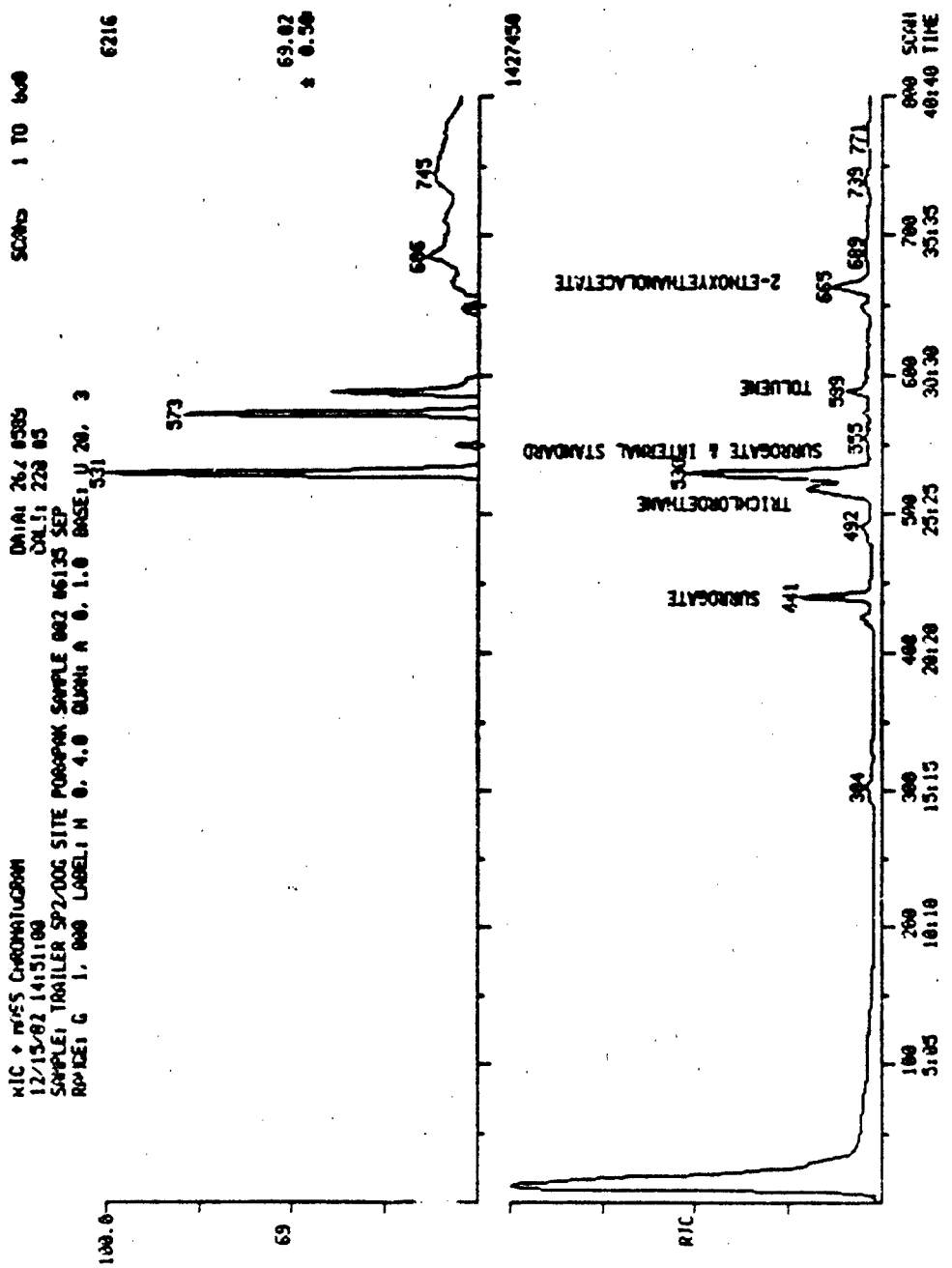


FIGURE 10

INSIDE AIR, ECS, WHITE SANDS MISSILE RANGE

N-16

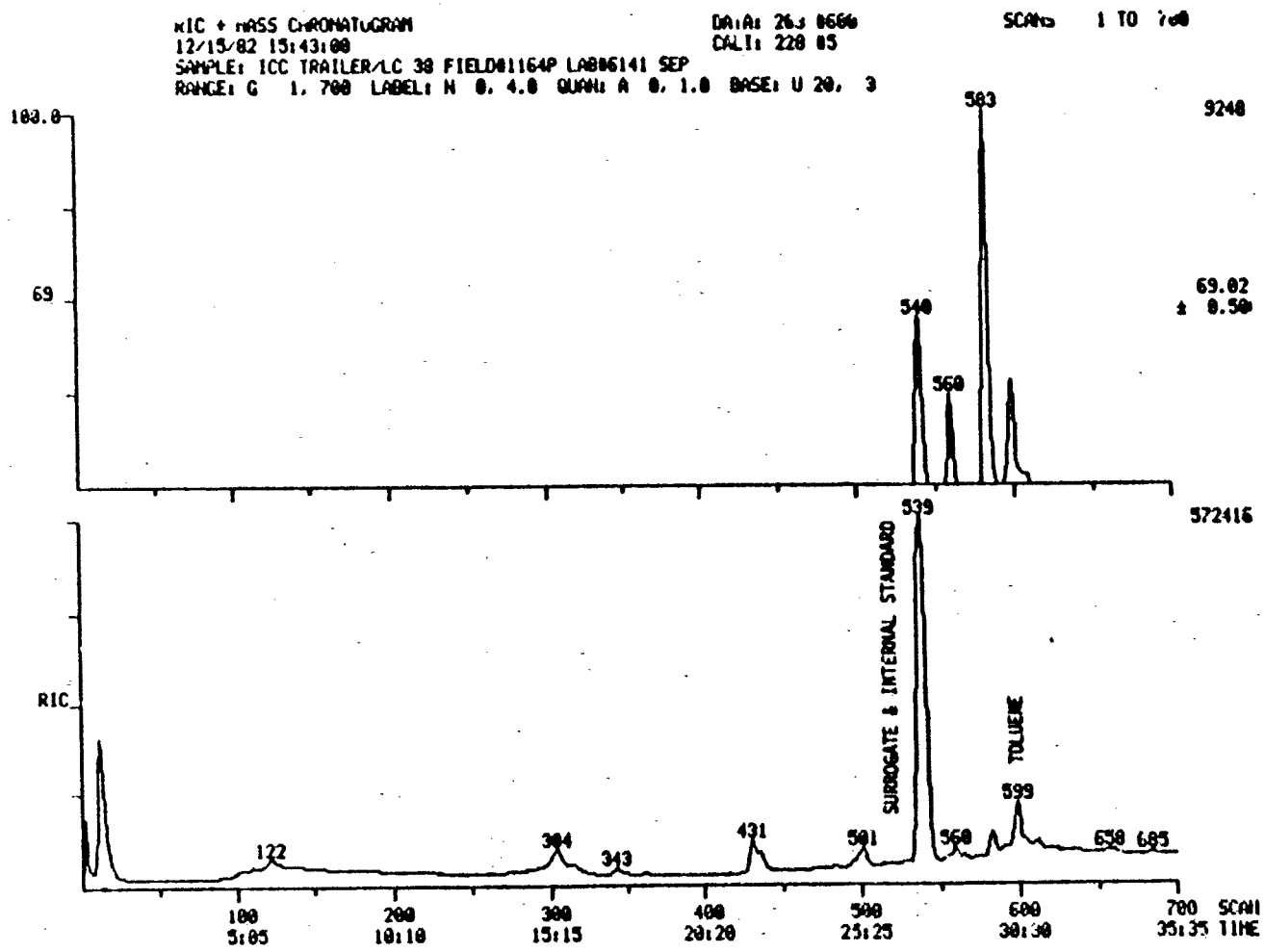


FIGURE 11

INSIDE AIR, ICC, WHITE SANDS MISSILE RANGE

N-47

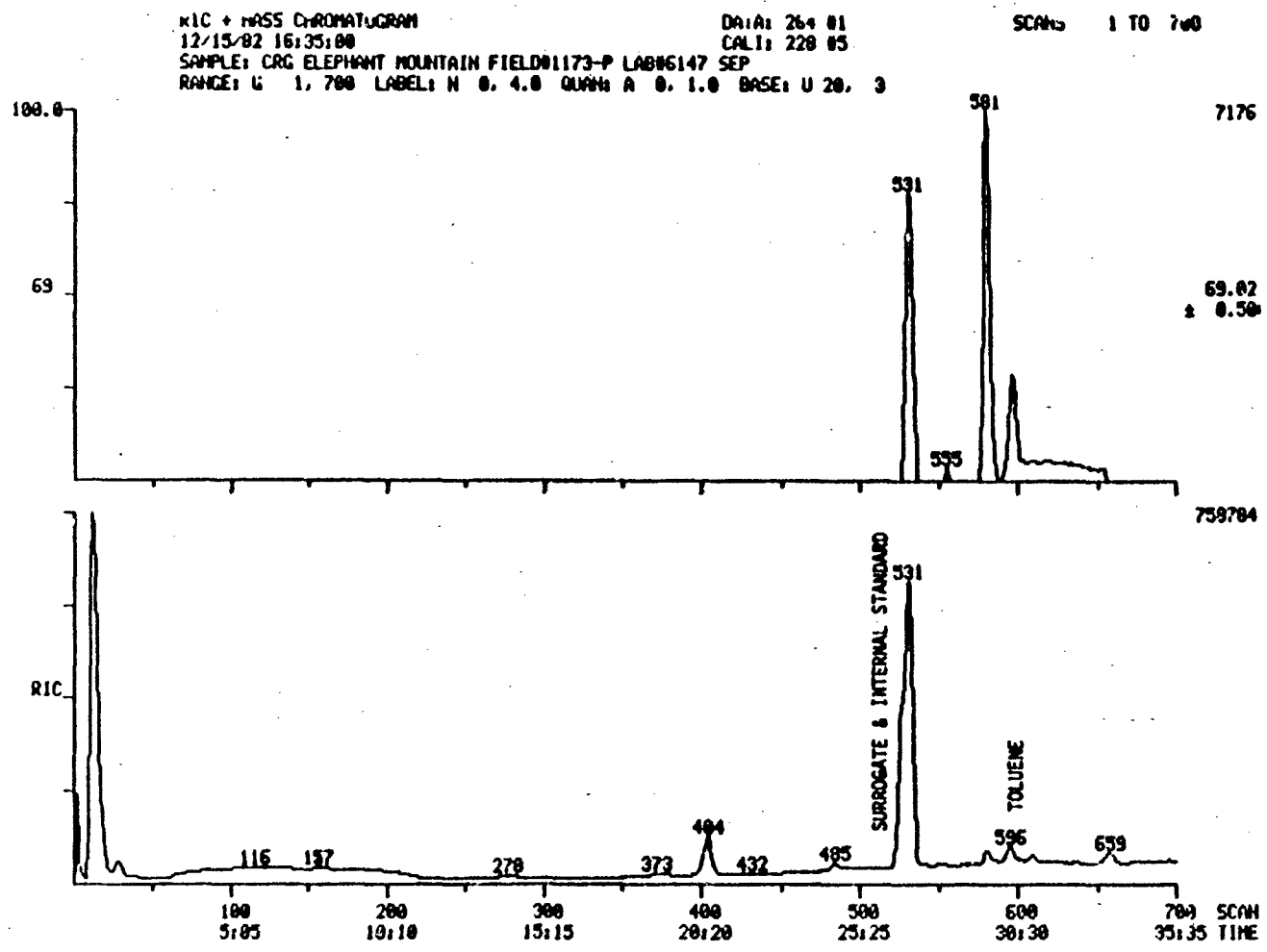


FIGURE 12
INSIDE AIR, CRG, WHITE SANDS MISSILE RANGE

N-43

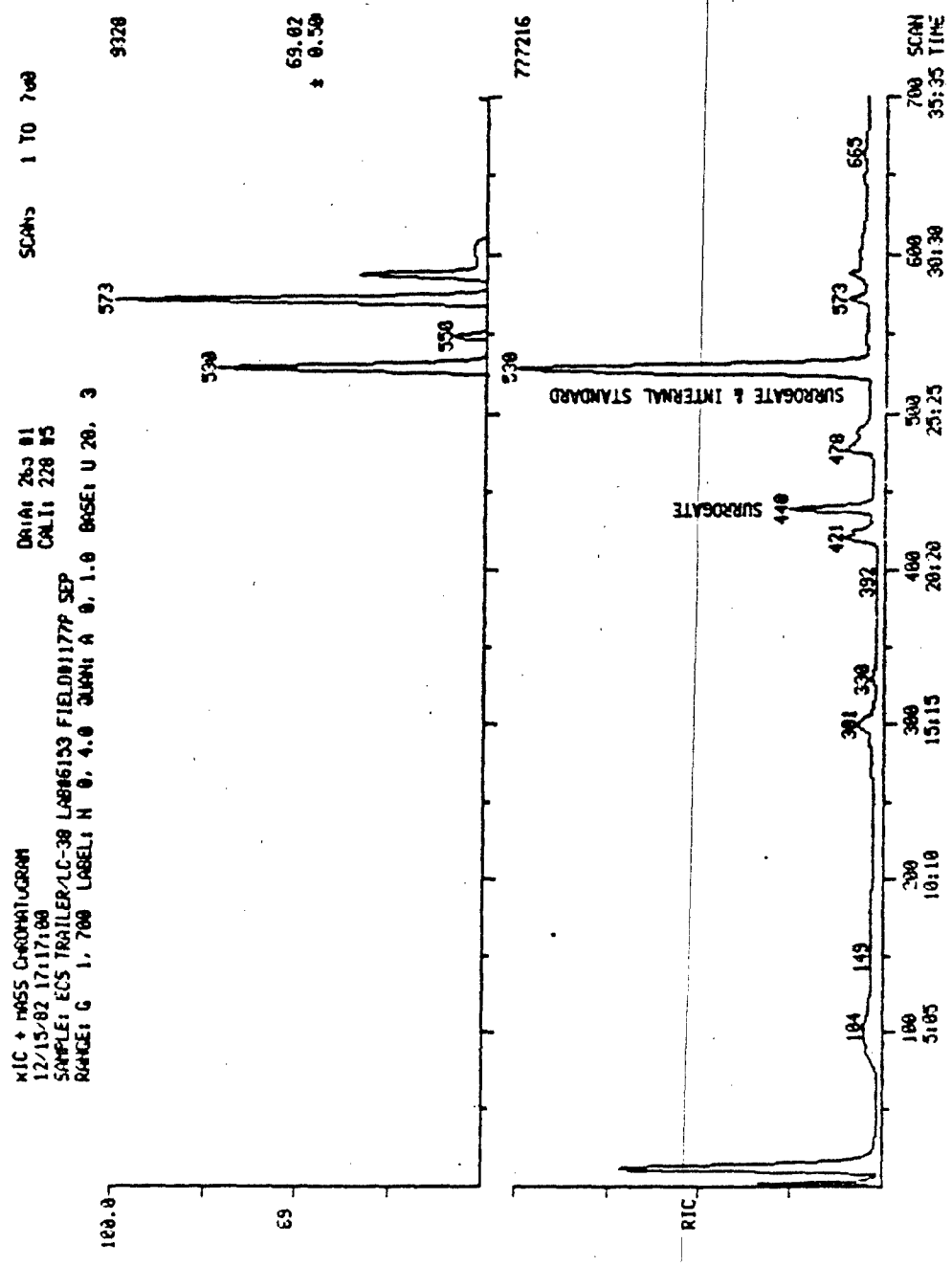


FIGURE 13
INSIDE AIR, ECS, WHITE SANDS MISSILE RANGE

N-49

Also, ion 69 of CF_3 is shown in the upper graph, and no mass peaks are present. This indicates that the concentration of individual component TFE outgas products that are trapped on Porapak N of molecular weight 131 and greater, are of less than 0.01 mg/m^3.

Gravimetric Analysis of Used Grommets

MERADCOM personnel removed the grommets from a number of PATRIOT Heater/Air Conditioners. The grommets from each unit were put in plastic bags and were given to Versar personnel at Fort Bliss. The personnel collecting the grommets did not know that they would be used as samples, so they were removed forcefully and many of them were mechanically damaged. Due to the damage we did a modified gravimetric analysis. The results are presented in Table 12. Two of the columns in Table 12 deserve special attention. Column two is the mean weight of the grommets which were not mechanically damaged. The weight of these grommets can be compared to the weight of new grommets which is 1.394 grams. The smallest average weight loss was 0.031 grams in unit #81003. The largest average weight loss was 0.433 grams in unit #N315 (a research and development unit). A weight loss was observed in every set of grommets. Column four is the number of heat damaged grommets over the total number of grommets examined. Some of the grommets were mechanically damaged during removal, but it was still possible to see whether there had been obvious heat damage on the grommets. Unit #801162 had the least visible damage. Of the 15 recognizable grommets sampled none of them were visibly heat damaged. Unit #N315 had the most visible damage. Of the eight recognizable grommets in the sample, all eight were heat damaged. These results show that the TFE grommets have decomposed in all of the PATRIOT Heater/Air Conditioners sampled. In some cases the decomposition has been fairly minor, while in other cases it has been severe.

TABLE 12

GRAVIMETRIC ANALYSIS OF TFE GROMMETS

Unit #	Mean Weight Undamaged Grommets	Number of Undamaged Grommets	Heat Damaged Grommets Recognizable Grommets
801173	1.303	9	0/11
N336	1.348	8	0/12
81002	1.357	9	0/13
81004	1.325	9	1/13
801184	1.289	6	0/8
N327	1.062	4	4/7
N315	0.961	4	8/8
N314	1.208	10	14/14
N329	1.339	8	1/10
----	1.334	8	0/13
801162	1.306	11	0/15
801172	1.319	11	0/12
801167	1.209	6	3/8
801183	1.323	11	0/13
801198	1.353	14	1/15
801177	1.322	9	1/15
801164	1.257	7	0/13
81003	1.363	7	0/11
81001	1.226	5	14/15
801169	1.301	10	0/11

IV. RECONSTRUCTION OF THE INCIDENT CONDITIONS

A. Phase I - Laboratory Experiments on Decomposition of TFE Grommets

These experiments were intended to determine the major products of the decomposition of TFE grommets in contact with a heater rod from a PATRIOT Heater/Air Conditioner. We also attempted to relate the quantity of the various products found to the weight loss of the grommet. The experimental apparatus is shown in Figure 14. Briefly, the heater rod was connected to a 206 Volt source and the end of the rod was placed about 20 cm inside a 2.5 cm ID glass tube. The end of the glass tube where the heat rod entered was bathed in a stream of purified air. A sampling manifold was connected to the other end. With this configuration the purified air entered the tube, passed over the TFE grommet on the end of the rod, and was pulled into the sampling manifold. The grommets were placed between 0.3 cm and 1.5 cm from the end of the rod.

The air entering the sampling manifold was analyzed for hydrolyzable flouride, acrolein, semi-volatile compounds, and volatile organic compounds in the initial experiments. Later experiments concentrated on hydrolyzable fluoride.

Hydrolyzable Fluoride

The results of the experiments are presented in Table 13. Experiments 1 and 5 were run without TFE grommets on the rod. As expected, no fluoride was produced in these experiments. In experiment 2 the TFE grommet slipped on the rod during heating and got very close to the end of the tube. This probably caused the apparently low fluoride recovery. In all of the other experiments the grommet was held stationary on the rod with stainless steel clips. A number of things are apparent in the data. The grommets lose less weight when they are held 3 mm from the end of the rod than when they are held 8 mm or 15 mm from the

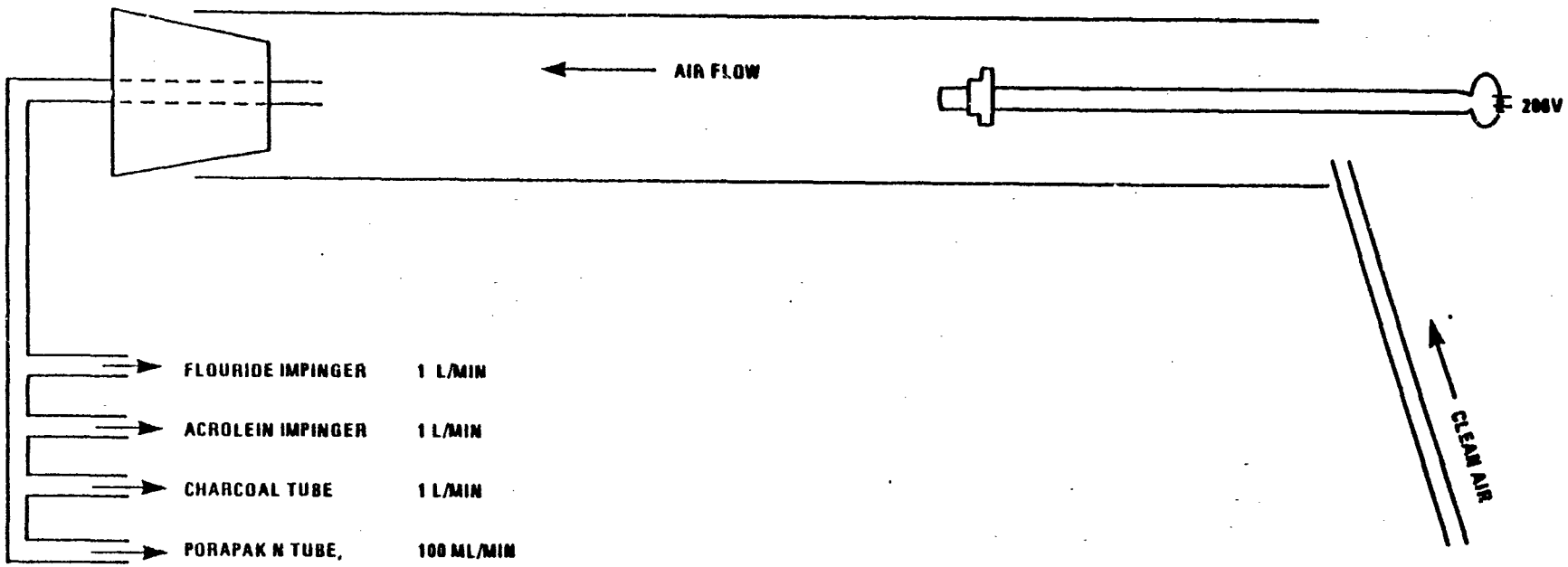


FIGURE 14 EXPERIMENTAL APPARATUS

TABLE 13

RESULTS: DECOMPOSITION EXPERIMENTS

Experiment Number	Grommet Position	Initial Weight g	Final Weight g	Weight Loss g	Hydrolyzable Fluoride Found, mg	Percent Accounted For
1	no grommet	----	----	----	N.D.	----
2	varied	1.373	1.171	0.202	7.8	5.1
3	3 mm	1.396	1.309	0.087	18.5	27.9
4	3 mm	1.395	1.206	0.189	44.3	30.9
5	no grommet	----	----	----	N.D.	----
6	3 mm	1.399	1.396	0.003	0.71	23.7
7	3 mm	1.382	1.362	0.020	6.3	31.3
8	15 mm	1.414	1.181	0.233	48.1	20.6
9	8 mm	1.392	1.294	0.098	32.7	33.4
10	3 mm	1.440	1.392	0.048	14.1	29.4
11	8 mm	1.392	1.082	0.31	107	34.5
12	15 mm	1.404	1.027	0.377	81.8	21.7

end of the rod. This is expected since the grommet is closer to the heated portion of the rod in the latter two positions. The weight loss of the grommet can be converted to a weight loss of fluoride since the TFE grommets are 76 percent fluorine by weight. The percent of fluoride accounted for is the ratio of the hydrolyzable fluoride found to the calculated amount of fluoride lost from the grommet. Excluding experiment 2 where the grommet slipped on the rod, the percent accounted for ranged from 20.6 to 34.5 percent. Given the difficulty of reproducing the exact same contact of the grommet with the rod in each experiment, this is surprisingly consistent. The data shows that a substantial amount of the fluoride lost will consistently show up as hydrolyzable fluoride.

Experiments 10 and 11 were run for 60 minutes and 45 minutes, respectively. During these two experiments samples were taken in 15 minute intervals. There were four 15 minute fluoride samples in Experiment 10, and three samples in experiment 11. The detailed data from these experiments are presented in Table 14. In Experiment 10 the grommet was 3 mm from the end of the rod. The fluoride level in this experiment apparently increased during the first 15 minutes, and reached a slowly decreasing plateau between 15 and 60 minutes. In Experiment 11 where the grommet was 8 mm from the end of the rod the highest fluoride level was observed in the first 15 minutes. The fluoride level then continually decreased. These data are supported by the visual observations of the experiments. In Experiment 10 the grommet slowly heated up and turned from white to a translucent gray color. At about 10 minutes into the experiment the surface touching the rod began to bubble, and this continued for the rest of the experiment. In Experiment 11 the grommet turned from white to translucent gray sooner. White vapors came off the grommet and it was bubbling vigorously during the first 15 minutes. A substantial portion of the grommet had been vaporized during the first 15 minutes. The amount of vapor and the bubbling decreased for

TABLE 14

EXPERIMENTS 10 AND 11
WEIGHT LOSS VERUS TIME

Time	Experiment 10, Hydrolyzable Fluoride Found, mg	Experiment 11, Hydrolyzable Fluoride Found, mg
0-15	2.1	62.6
15-30	4.2	32.4
30-45	4.0	12.0
45-60	3.8	Experiment finished

the rest of the experiment because there was less grommet left in contact with the rod. Most of the grommet in direct contact with the rod was vaporized within the first 30 minutes.

The experiments attempted to reproduce the conditions inside the PATRIOT Heater/Air Conditioner. There were, however, some variables which were not controlled. The air flow over the heater rods in these experiments was much lower than the air flow in the heater/air conditioners. The end of the heater rod, therefore, was probably somewhat hotter in these experiments than in actual use. It is not clear to what extent these results can be extrapolated to the conditions inside PATRIOT Heater/Air Conditioners. The weight loss in an operating unit may not be the same as observed in these experiments. Despite this, the experiments show that the percentage of the fluoride lost that becomes hydrolyzable fluoride is fairly consistent.

Acrolein

No acrolein was detected in any of the experiments. The decomposing TFE grommets do not produce measureable amounts of acrolein.

Semi-Volatile Organic Compounds

Semi-volatile organic compounds were collected on charcoal tubes at a flow rate of 1 liter per minute. The tubes were eluted with 5 ml hexane and analyzed by gas chromatography with electron capture detection. The chromatographic conditions are presented in Table 15. Electron capture detection is more sensitive than flame ionization detection for highly fluorinated compounds. Chromatograms for runs 1, 3, and 8 are presented in Figures 15 to 17. Run 1 is a blank. In runs 3 and 8 some products were detected in the samples. The backup traps did not contain any detectable products. Clearly some organic compounds are formed during the decomposition of the TFE grommets.

TABLE 15

CHROMATOGRAPHIC CONDITIONS

Column:	0.1 percent SP-1000 on 80/100 Carbopack C, 6 ft.
Detector Temperature:	250°C
Injector Temperature:	200°C
Carrier Gas:	Argon/Methane
Flow	30 ml/min
Temperature Progress:	30°C to 150°C at 8°C per minute

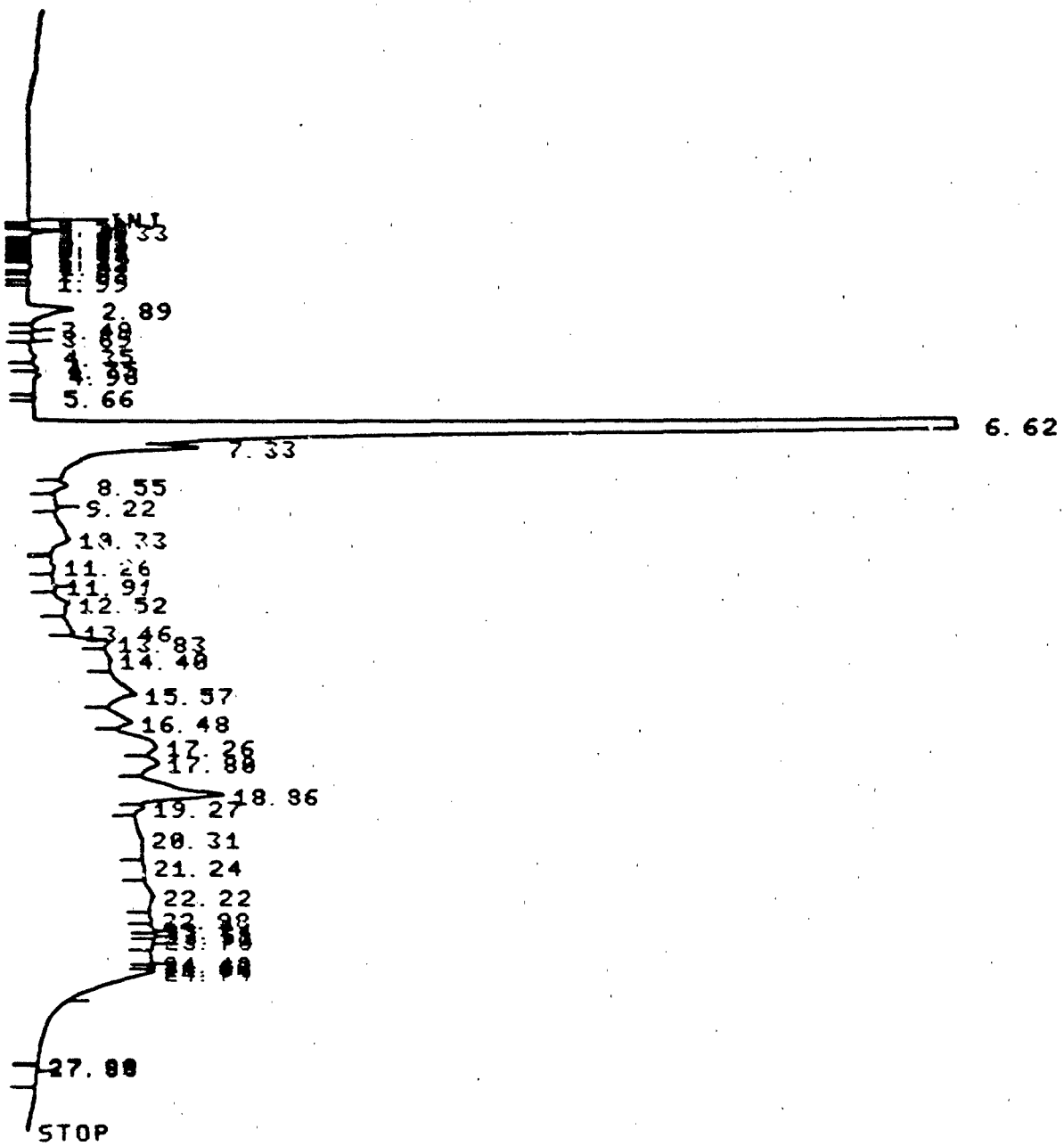


FIGURE 15

RUN 1, BLANK

N-59

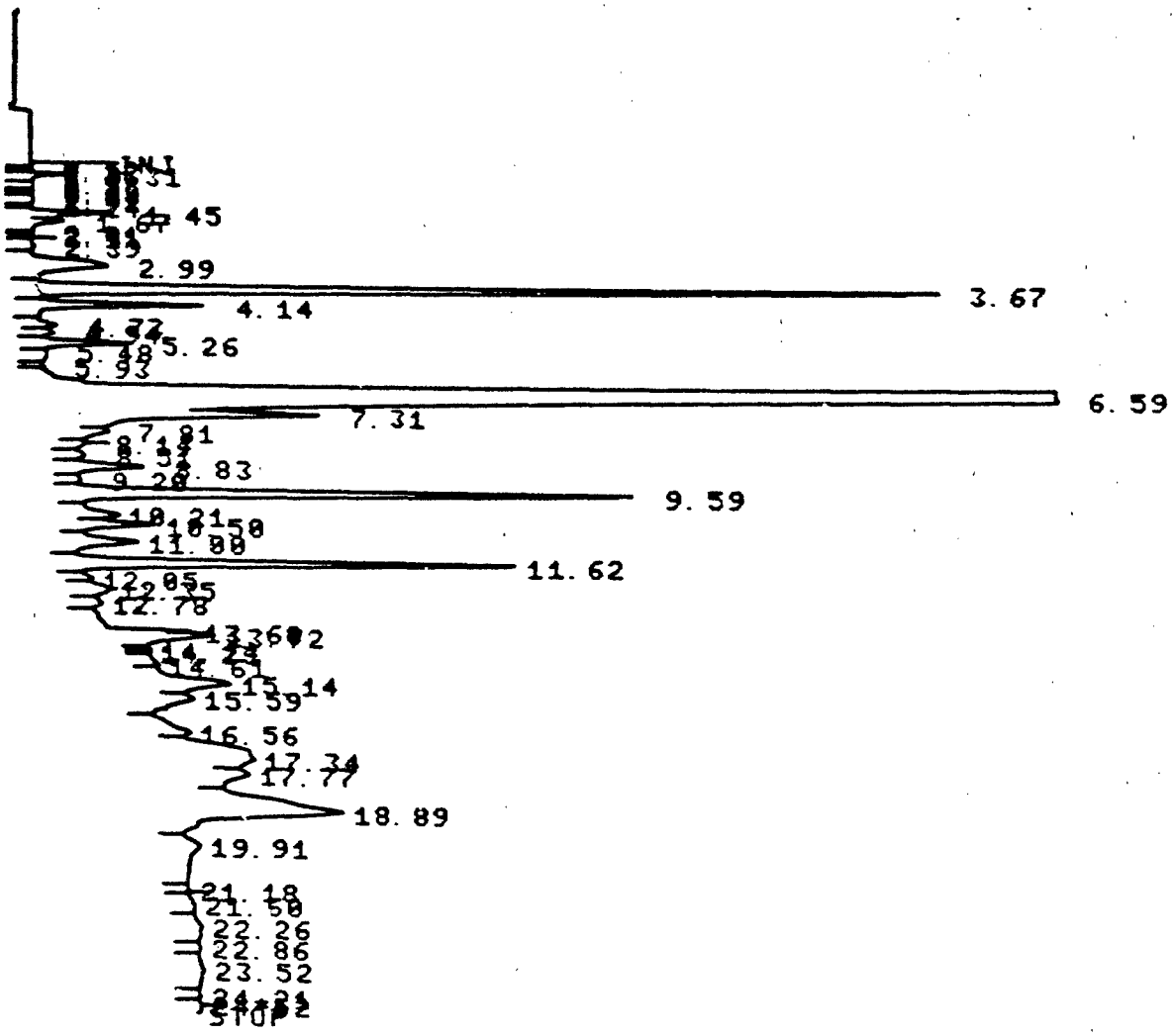


FIGURE 16

RUN 3: WEIGHT LOSS 0.087 g

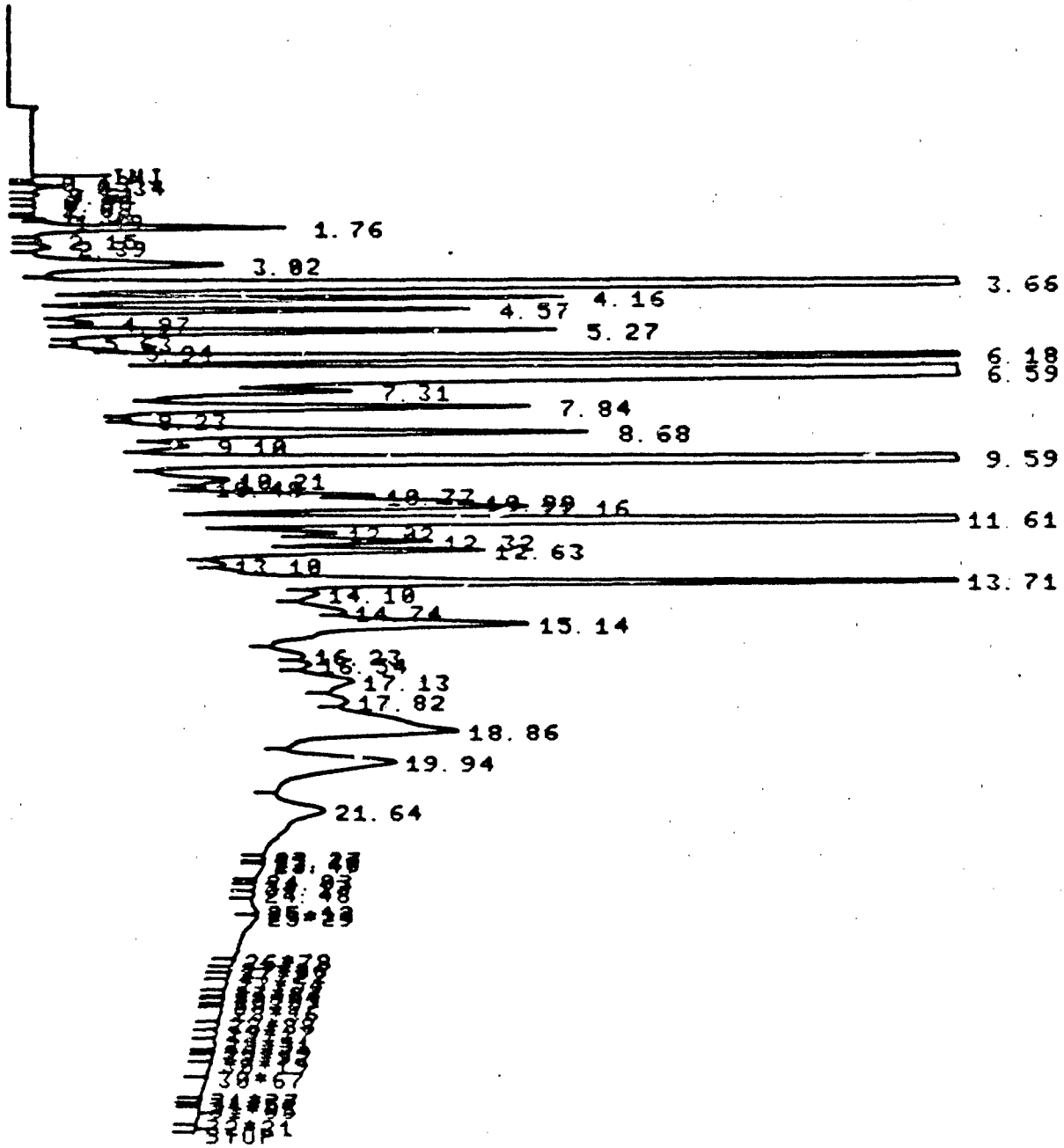


FIGURE 17

RUN 8: WEIGHT LOSS 0.233 g

A number of highly fluorinated compounds were analyzed as standards to determine the response of the compounds on the electron capture detector. The data is presented in Table 16. None of the compounds in the samples could be identified, but they probably have similar structures to the fluorinated standards. We assume, therefore, that the compounds produced during TFE decomposition will have similar responses. If this is the case, the largest peak in Run 8 (Figure), which is 12.6 x 10^6 area counts, corresponds to about 15 mg of the material collected. This is about 6 percent of the total weight loss of TFE. This indicates that some of the organic compounds are produced in fairly large quantities. If the area counts for all of the compounds are summed, the resulting total response corresponds to about 100 mg of organic decomposition products in the extract. This is about 43 percent of the total weight loss of the TFE.

The data from these experiments indicates that fairly large amounts of semi-volatile organic compounds are produced during the decomposition of TFE. However, it is unlikely that these compounds would be detected in actual use. In Experiment 8, the gas stream was so highly concentrated that the front half of the charcoal tube turned white from vaporized TFE. Despite this, the results were only 1000 times greater than the detection limit. Given the large dilution that occurs when the PATRIOT Heater/Air Conditioners are running, the results would probably be below the detection limit in actual use. In contrast to this, the results for hydrolyzable fluoride in Experiment 8 were 2,000,000 times greater than the detection limit. We expect, therefore, that hydrolyzable fluoride will be detectable in the units, but that semi-volatile organic compounds will not.

TABLE 16

DETECTOR RESPONSE FOR HIGHLY FLUORINATED COMPOUNDS

Compounds	Area Counts Per Nanogram Micro-volt/seconds per Nanogram
Perfluorohexane	3200
Perfluorocyclopentane	4360
Perfluoroheptane	4250
Perfluoropentane	260*

*Possible volatilization during preparation of standard. Result may be low.

Volatile Organic Compounds

The volatile organic compounds were determined by collecting the outgassing materials on Porapak N tubes, followed by thermal desorption-gas chromatographic/mass spectrometric (GC/MS) analytical procedures. One experiment was also conducted using a mixed Porapak N/charcoal tube. The volatile compounds were collected on Porapak N tubes at a flow rate of 0.2 liters per minute. The tubes were then connected to the GC/MS and flash heated to 180°C. The volatile materials are thus desorbed from the trap and introduced onto the head of the GC/MS column. The column was held at 45°C for ten minutes during the desorbtion period, with a flow rate of 40 ml/min of purified helium. The column was then programmed to 225°C at 12°C/min and the sample chromatographed into the mass spectrometer. The mass spectrometer was set to scan from 20-450 AMU at three seconds per scan in the electron impact mode.

An initial blank experiment was run to verify that there were no interferences or residual fluorinated and or other TFE decomposition products present on the heater rod or the sampling tubes. No interferences or contamination problems were present. Five experiment burns were conducted and are labeled Run #2, Run #4, Run #15, Porapak Only and Porapak/Charcoal. The fluorinated compounds detected in each experiment are listed in Tables 17-21. The chromatograms for the blank run and the experimental runs are shown in Figures 18-22. The mass chromatograms for some of the expected fluorinated fragments of TFE decomposition products are shown in Figures 23-45. The mass fragments displayed in the graphs are:

Mass-Charge Ratio m/z	Fragment Ion
69	CF_3
100	C_2F_4
131	C_3F_5
181	C_4F_7
219	C_4F_9

Each chromatographic peak containing any of these fragments was identified by library search. In many cases the library algorithm identified several peaks as the same compound. All of the compounds listed in the tables are tentative identifications, and when more than one peak was identified as the same compound, the number of peaks is listed.

Particles

In the TFE decomposition experiments, there was a large quantity of particles produced in addition to the hydrolyzable fluoride and the semi-volatile organic compounds. After each experiment, the inside of the equipment was coated with a fine white powder, apparently vaporized TFE. This vaporized TFE probably accounts for the remainder of the weight loss in the experiments.

Conclusions

These experiments showed that decomposing TFE produces three major classes of products. A large and reproducible fraction of the weight loss from the TFE appears as hydrolyzable fluoride. This appears to be a promising way to monitor the air for the products of decomposing TFE. A second fraction of the weight loss from TFE appears as semi-volatile fluorinated organic compounds. The detection limit for the organic compounds is higher than the detection limit for hydrolyzable fluoride. The organic compound will probably not be useful for monitoring the air for products of decomposing TFE. A third fraction of the weight loss appears as vaporized particles of TFE.

TABLE 17

FLUORINATED COMPOUNDS DETECTED AND TENTATIVELY IDENTIFIED BY LIBRARY SEARCH

COMPOUND	NO. PEAKS	FORMULA	M. WT.
1-Propene, 1,1,2,3,3,3-Hexafluoro-	2	C_3F_6	150
Cyclobutane, Octafluoro	2	C_4F_8	200
Cyclopentane, Octafluoro-1-1-Bis(Trifluoromethyl)-	1	C_7F_{14}	350
Octanoicacid, Pentadeca Fluoro	1	$C_8HO_2F_{15}$	414
Ethane, Hexafluoro-	10	C_2F_6	138
Propane, Octafluoro-	1	C_3F_8	188
Butane, Decafluoro-	3	C_4F_{10}	238
Silane, Difluorodimethyl-	1	$C_2H_6F_2SI$	96
Ethane, 1,1,1-Trifluoro-	1	$C_2H_3F_3$	84
1-Butene, 1,1,2,3,3,4,4,4-Octafluoro-	2	C_4F_8	200
Heptane, Hexadecafluoro-	3	C_7F_{16}	388

TABLE 18

TFE PYROLYSIS EXPERIMENT RUN #4
FLUORINATED COMPOUNDS DETECTED AND TENTATIVELY
IDENTIFIED BY LIBRARY SEARCH

COMPOUNDS	NO. PEAKS	FORMULA	M. WT.
Ethane, Hexafluoro-	4	C_2F_6	138
Heptane, Hexadecafluoro-	5	C_7F_{16}	388
Pentane, Undecafluoro Trifluoromethyl-	1	C_6F_{14}	338
Propene, Hexafluoro-	1	C_3F_6	150
Methane, Dichloro-	1	CH_2Cl_2	84

TABLE 19

TFE PYROLYSIS EXPERIMENT RUN #15
FLUORINATED COMPOUNDS DETECTED AND TENTATIVELY
IDENTIFIED BY LIBRARY SEARCH

COMPOUNDS	NO. PEAKS	FORMULA	M.WT.
1-Propene, 1,1,2,3,3,3-Hexafluoro-	1	C_3F_6	150
Hexane, Tetrodecafluoro-	1	C_6F_{14}	338
Butane, Decafluoro-	2	C_4F_{10}	238
Pentane, Undecafluoro-4-(Trifluoromethyl)-	6	C_6F_{14}	338
Ethane, Hexafluoro-	3	C_2F_6	138
Dodecanoicacid, Tricosafluoro-	1	$C_{12}HO_2F_{23}$	614
Silane, Tetrafluoro-	3	F_4SI	104
Heptane, Hexadecafluoro-	2	C_7F_{16}	388
Diaziridine, Tetrafluoro-	1	CN_2F_4	116
Methane, Trifluoro-	1	CHF_3	70
Aceticacid, Trifluoro-	1	$C_2HO_2F_3$	114
Cyclopentane, Decafluoro-	1	C_5F_{10}	250
Pentane, Dodecafluoro-	1	C_5F_{12}	288
Trioxide, Bis(Trifluoromethyl)-	1	$C_2O_3F_6$	186
Cyclohexane, Dodecafluoro-	1	C_6F_{12}	300
Methanesulfinyl Fluoride,Trifluoro-	1	$COSF_4$	136

TABLE 20

TFE PYROLYSIS EXPERIMENT PORAPAK N ONLY
FLUORINATED COMPOUNDS DETECTED AND TENTATIVELY IDENTIFIED
BY LIBRARY SEARCH

COMPOUNDS	NO. PEAKS	FORMULA	M.WT.
Ethane, Hexafluoro-	3	C_2F_6	138
Trioxide, Bis(Trifluoromethyl)-	1	$C_2O_3F_6$	186
Propane, Octafluoro-	1	C_3F_8	188
Heptane, Hexadecafluoro-	2	C_7F_{16}	388
Propene, Hexafluoro-	1	C_3F_6	150
Pentane, Dodecafluoro-	2	C_5F_{12}	288
Butane, Decafluoro-	1	C_4F_{10}	238
Silane, Tetrafluoro-	1	F_4SI	104
Pentane, Undecafluoro(Trifluoromethyl)-	3	C_6F_{14}	338
Silane, Difluorodimethyl-	1	$C_2H_6F_2SI$	96

TABLE 21

TFE PYROLYSIS EXPERIMENT ON PORAPAK/CHARCOAL
FLUORINATED COMPOUNDS DETECTED AND TENTATIVELY
IDENTIFIED BY LIBRARY SEARCH

COMPOUNDS	NO. PEAKS	FORMULA	M.WT.
Cyclobutane, Octafluoro-	3	C_4F_8	200
Ethene, Tetrafluoro-	2	C_2F_4	100
Ethane, Hexafluoro-	2	C_2F_6	138
Propane, Octofluoro-	1	C_3F_8	188

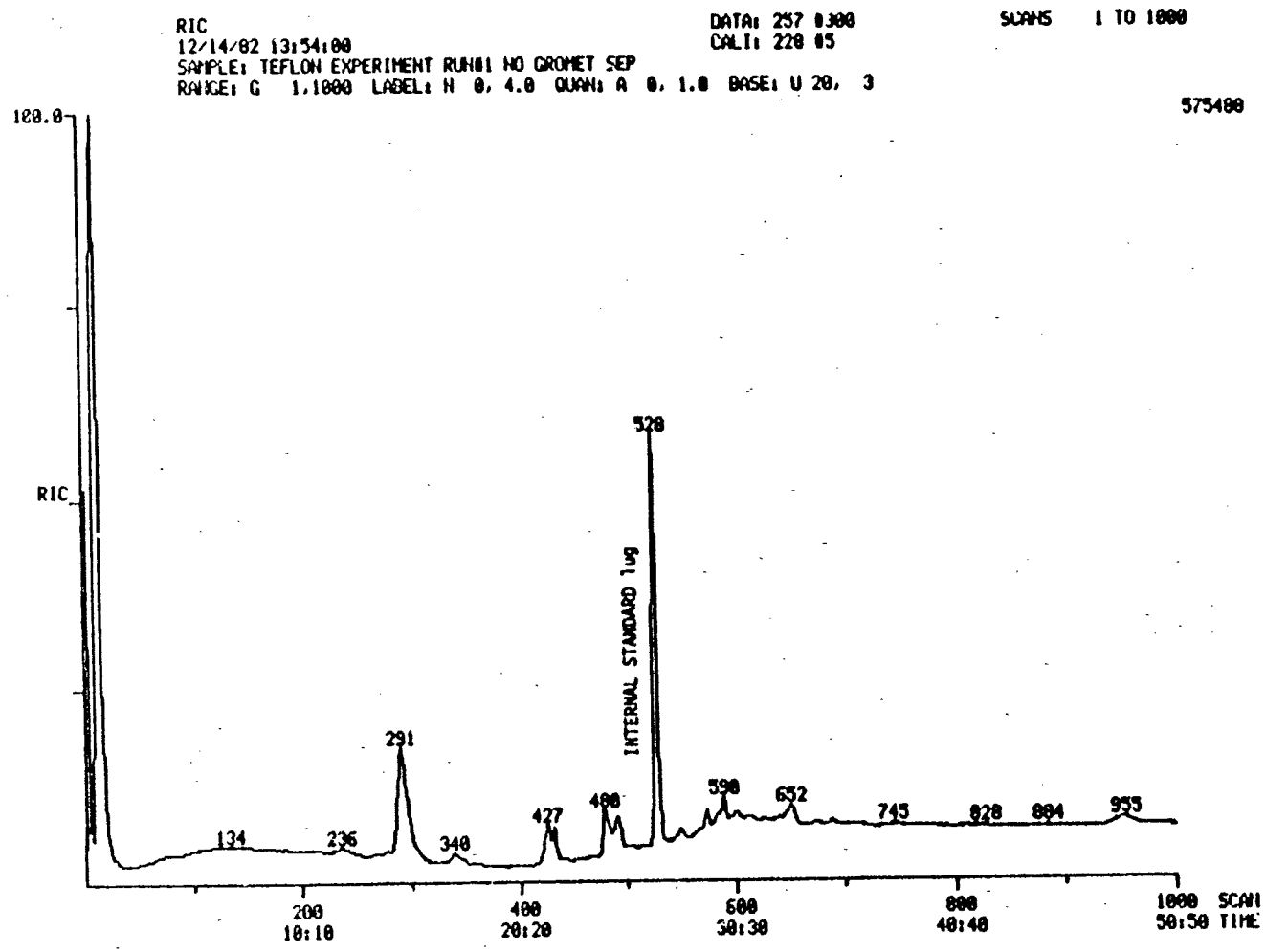


FIGURE 10

BLANK, EXPERIMENT #1, NO GROMMET

N-71

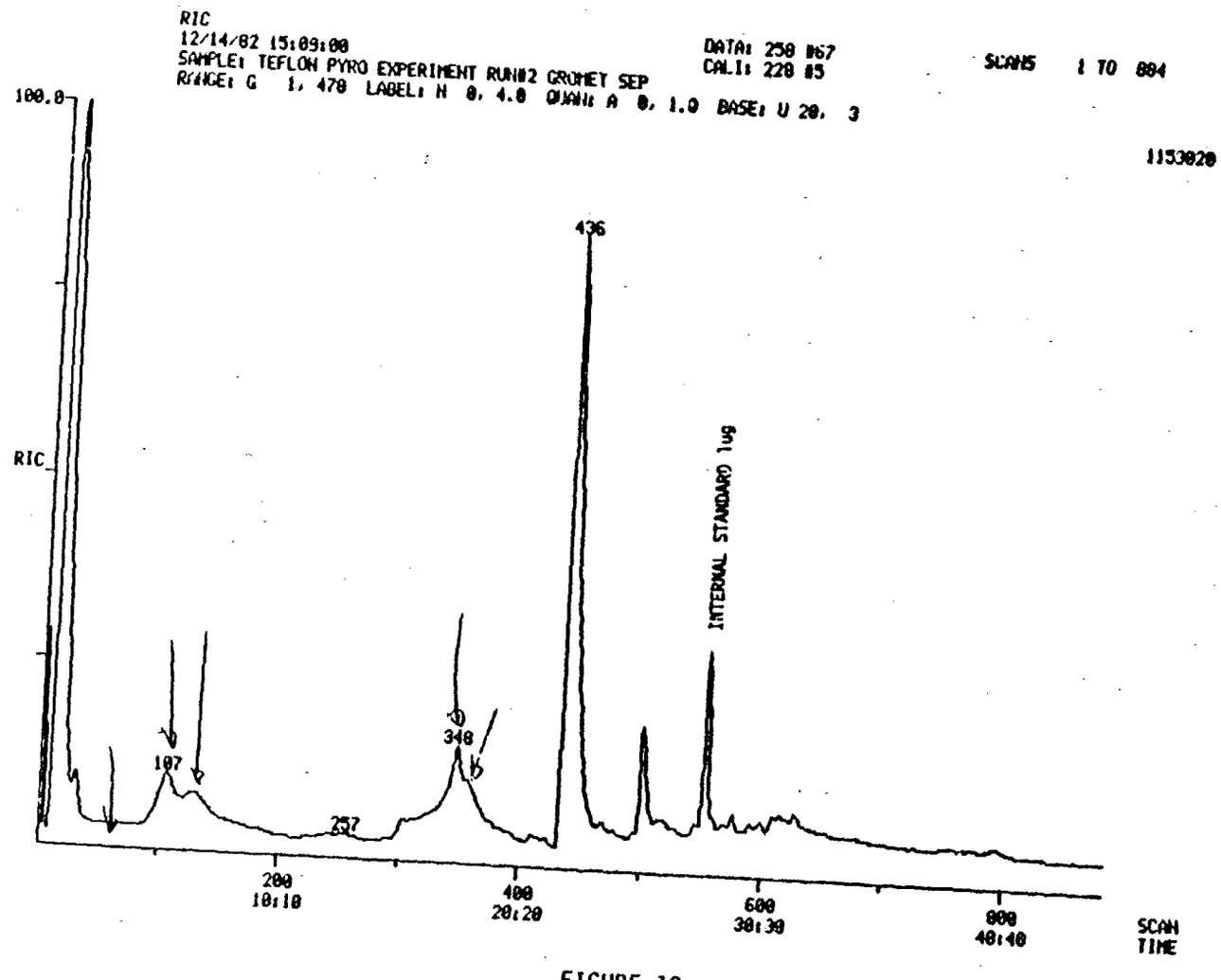


FIGURE 19
RECONSTRUCTED ION CHROMATOGRAM, EXPERIMENT #2

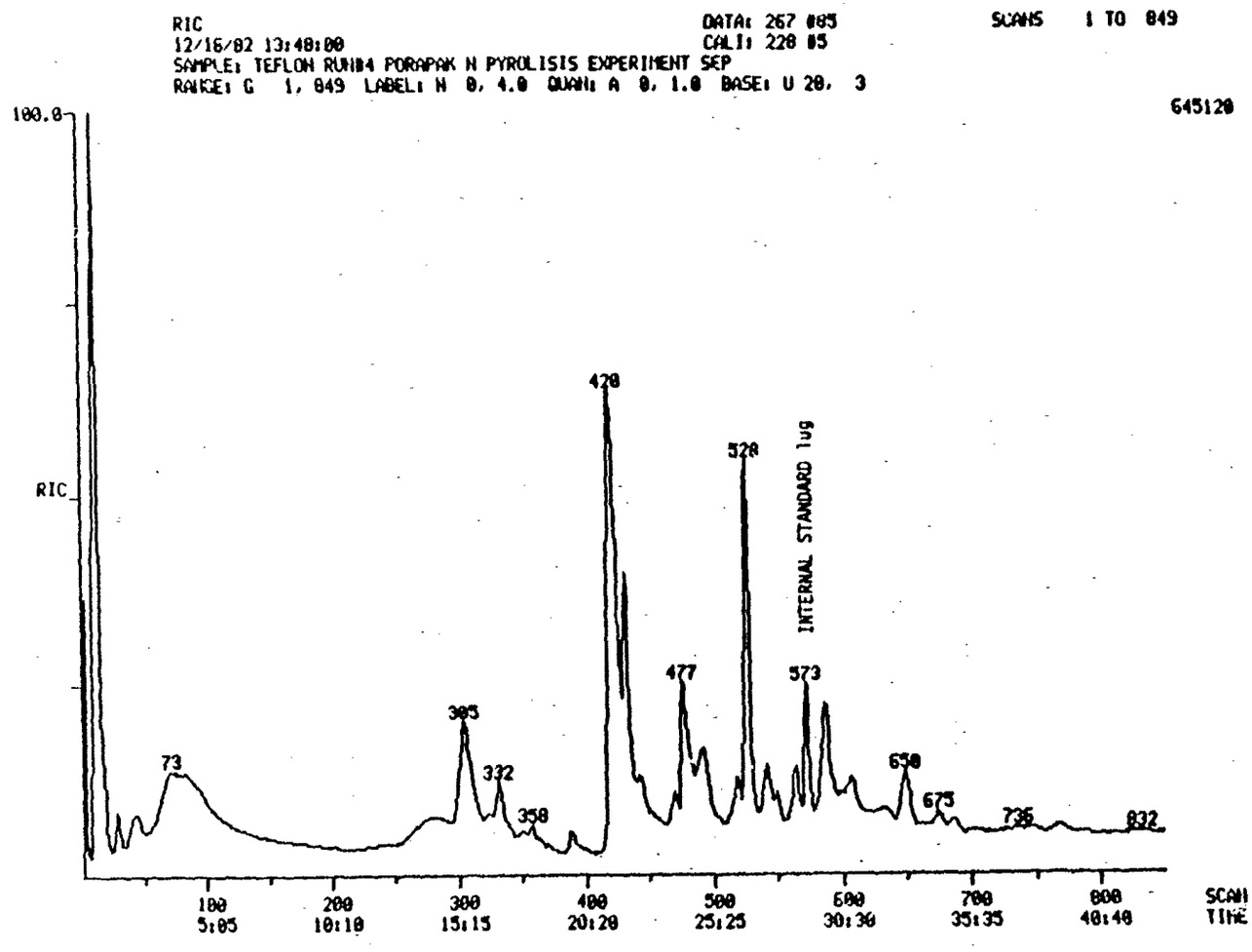


FIGURE 20

RECONSTRUCTED ION CHROMATOGRAM, EXPERIMENT #4

N-13

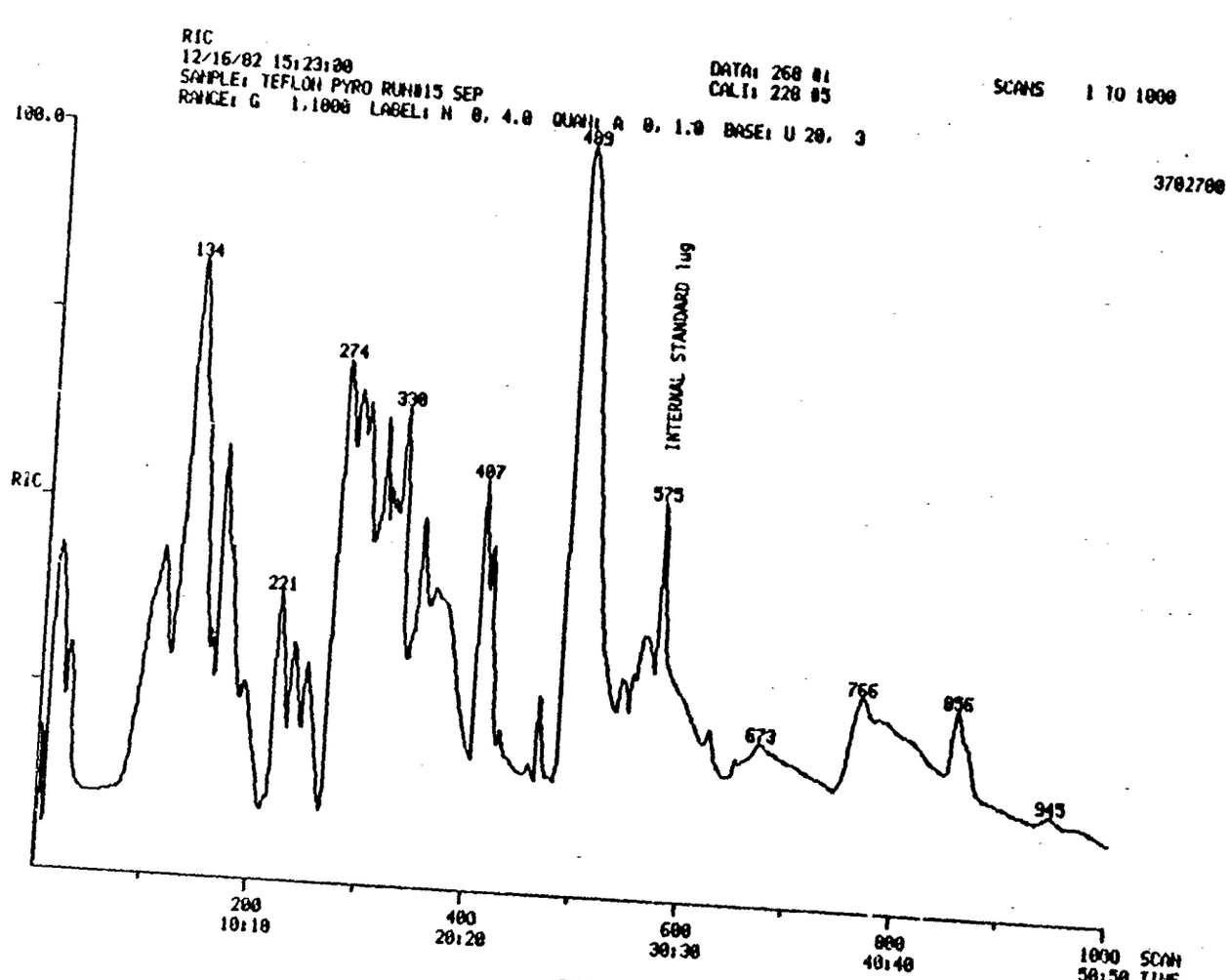


FIGURE 21

RECONSTRUCTED ION CHROMATOGRAM, EXPERIMENT #15

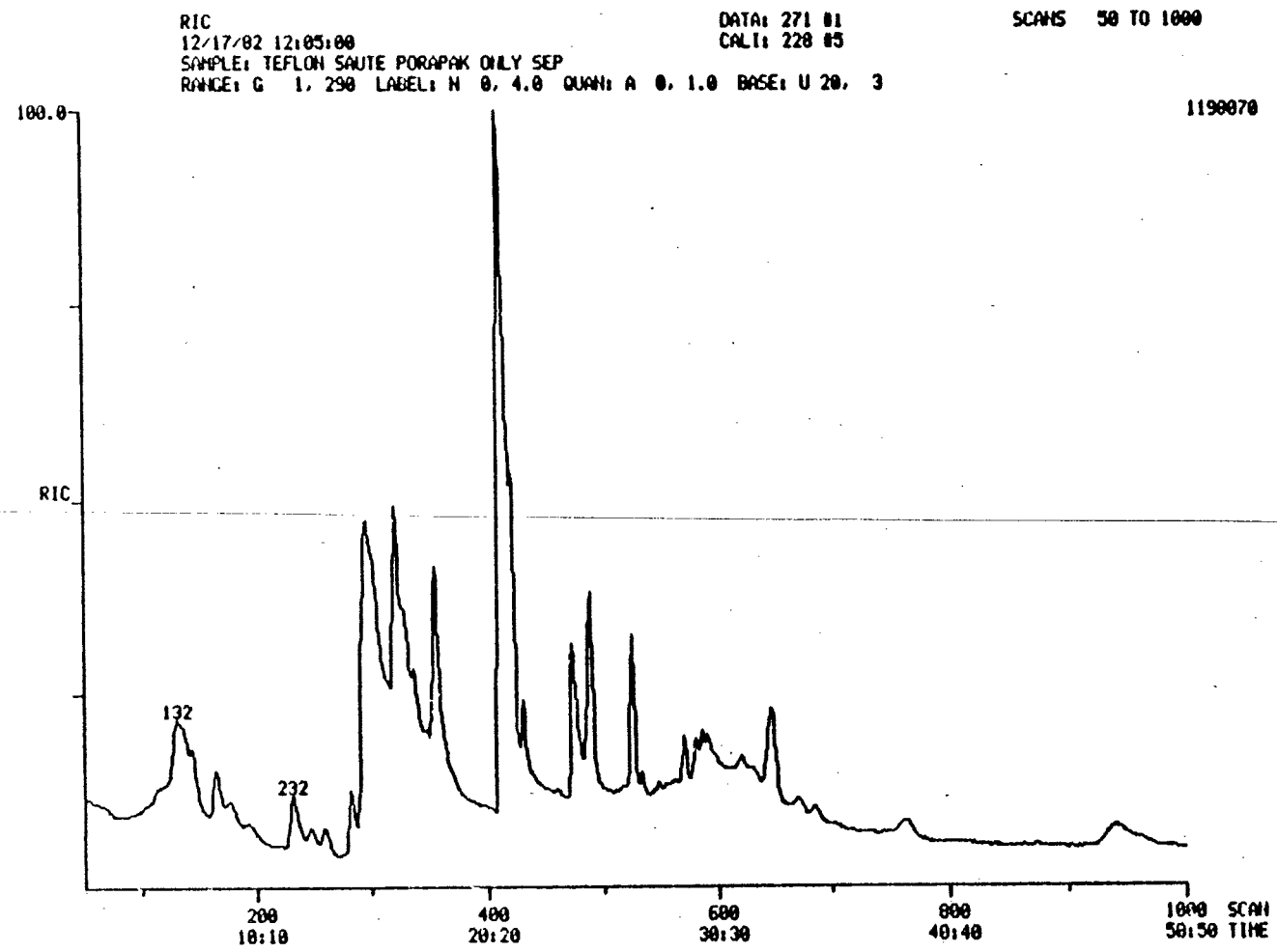


FIGURE 22
RECONSTRUCTED ION CHROMATOGRAM, PORAPAK ONLY

N-75

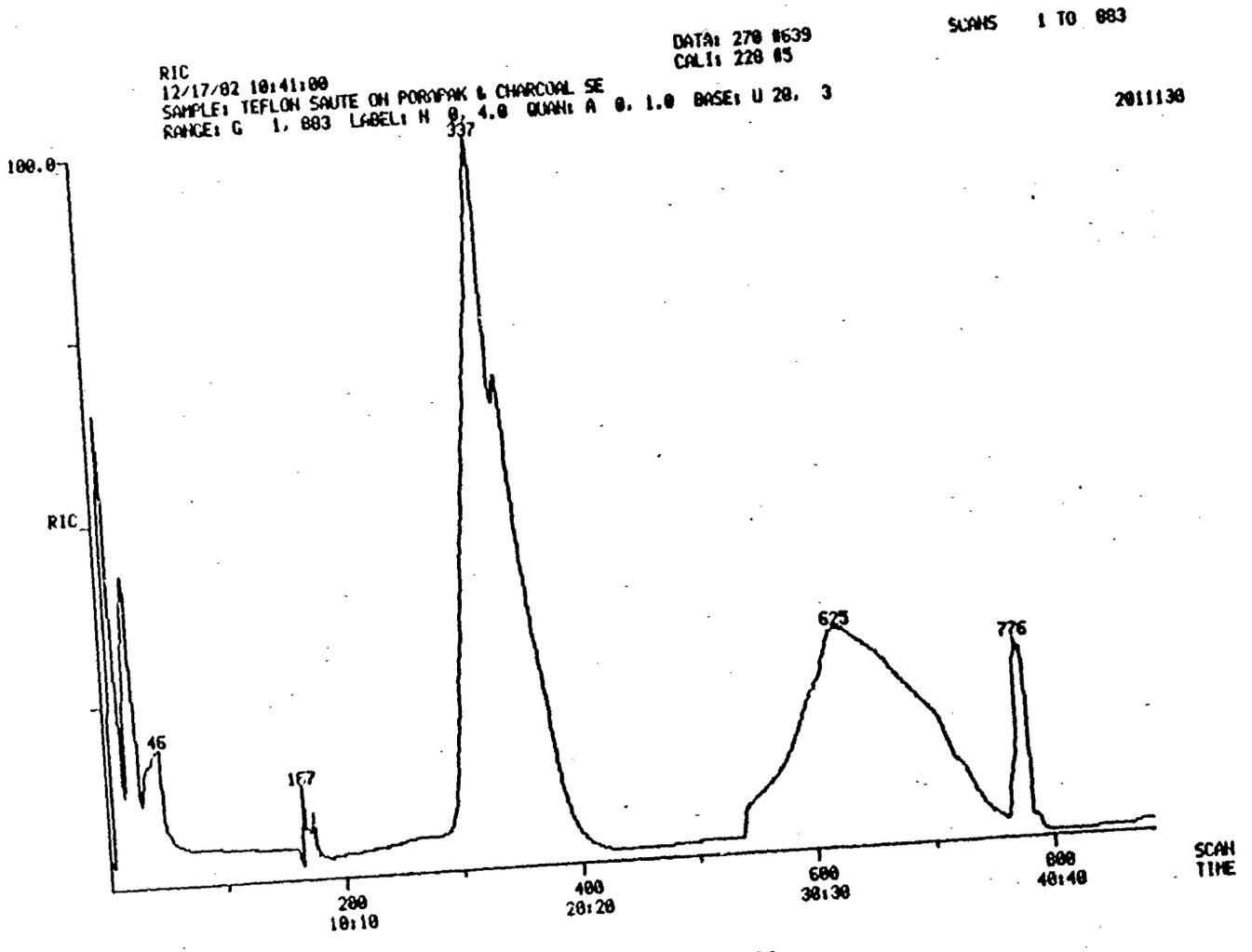


FIGURE 23

RECONSTRUCTED ION CHROMATOGRAM, PORAPAK AND CHARCOAL

N-74

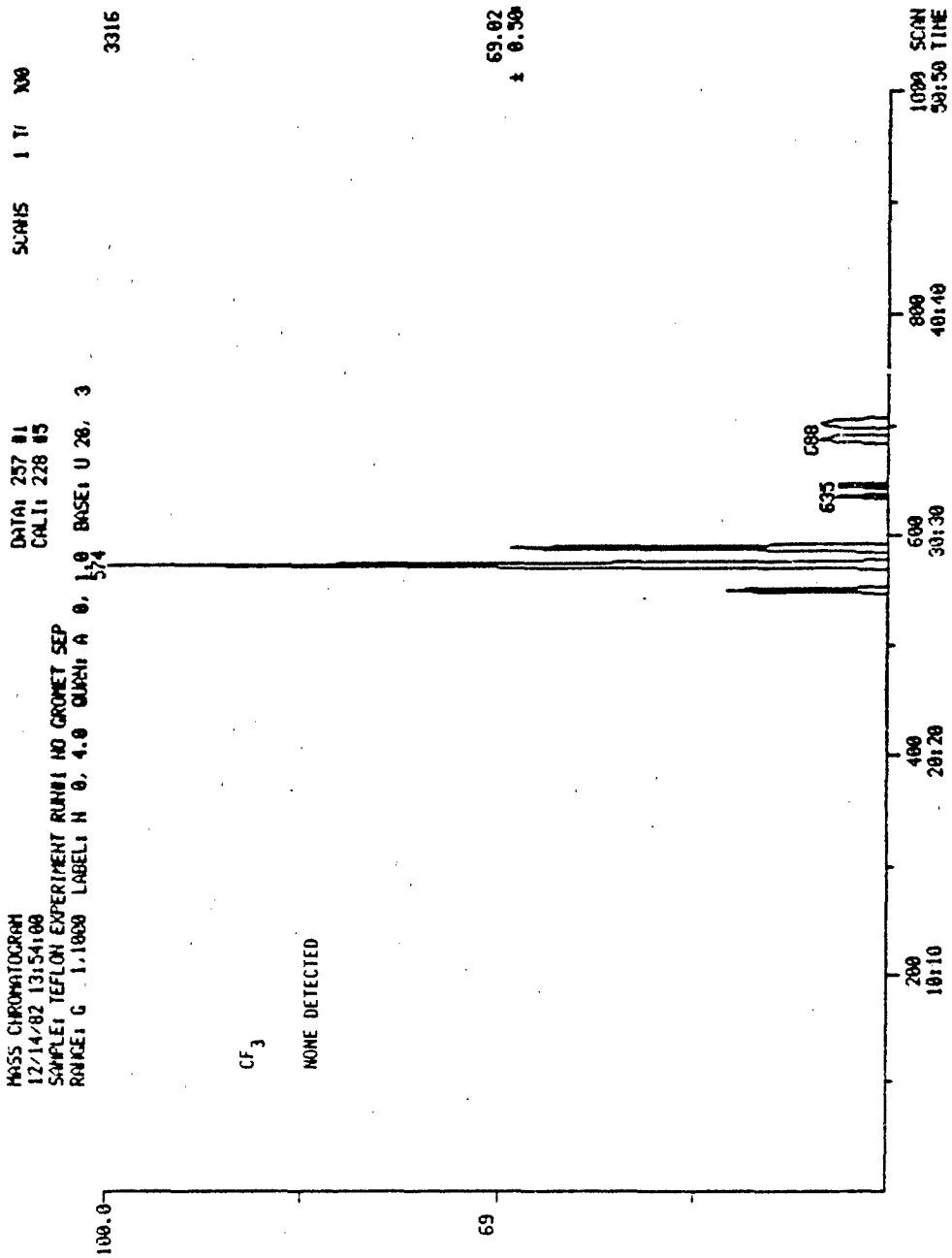


FIGURE 24

MASS CHROMATOGRAM, M/Z = 69, EXPERIMENT #1

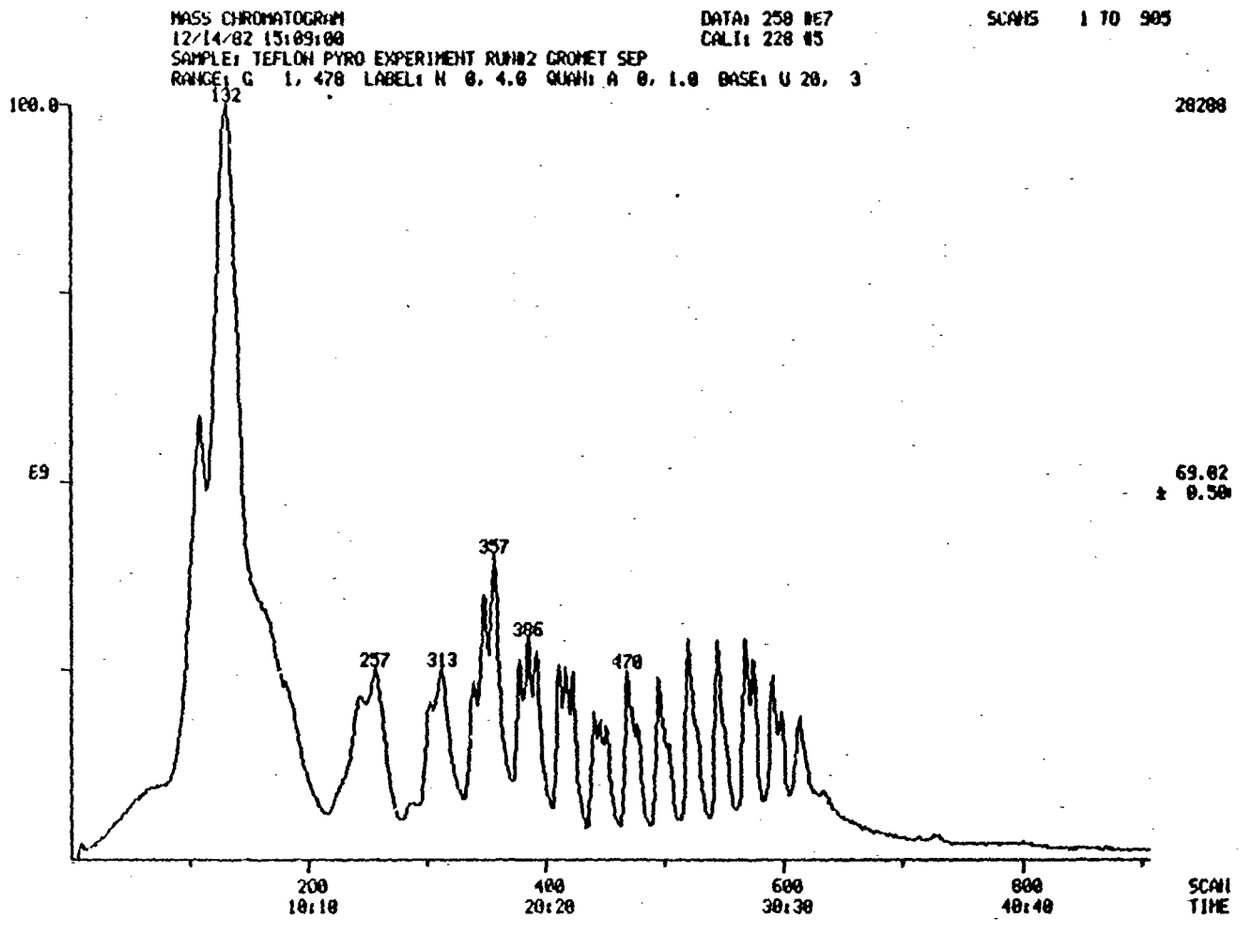


FIGURE 25

MASS CHROMATOGRAM, M/Z = 69, EXPERIMENT #2

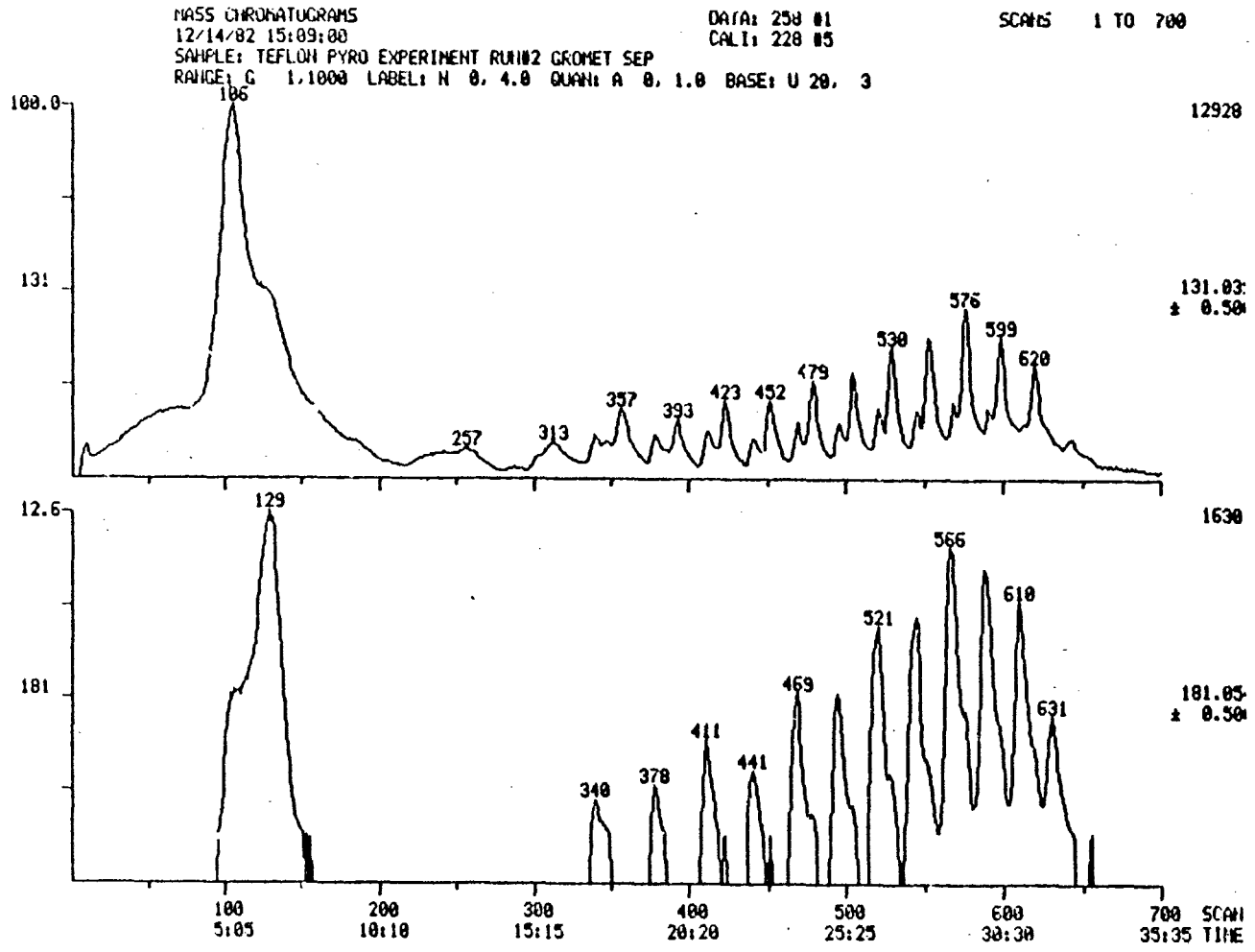


FIGURE 26

MASS CHROMATOGRAM, M/Z = 131 AND 181, EXPERIMENT #2

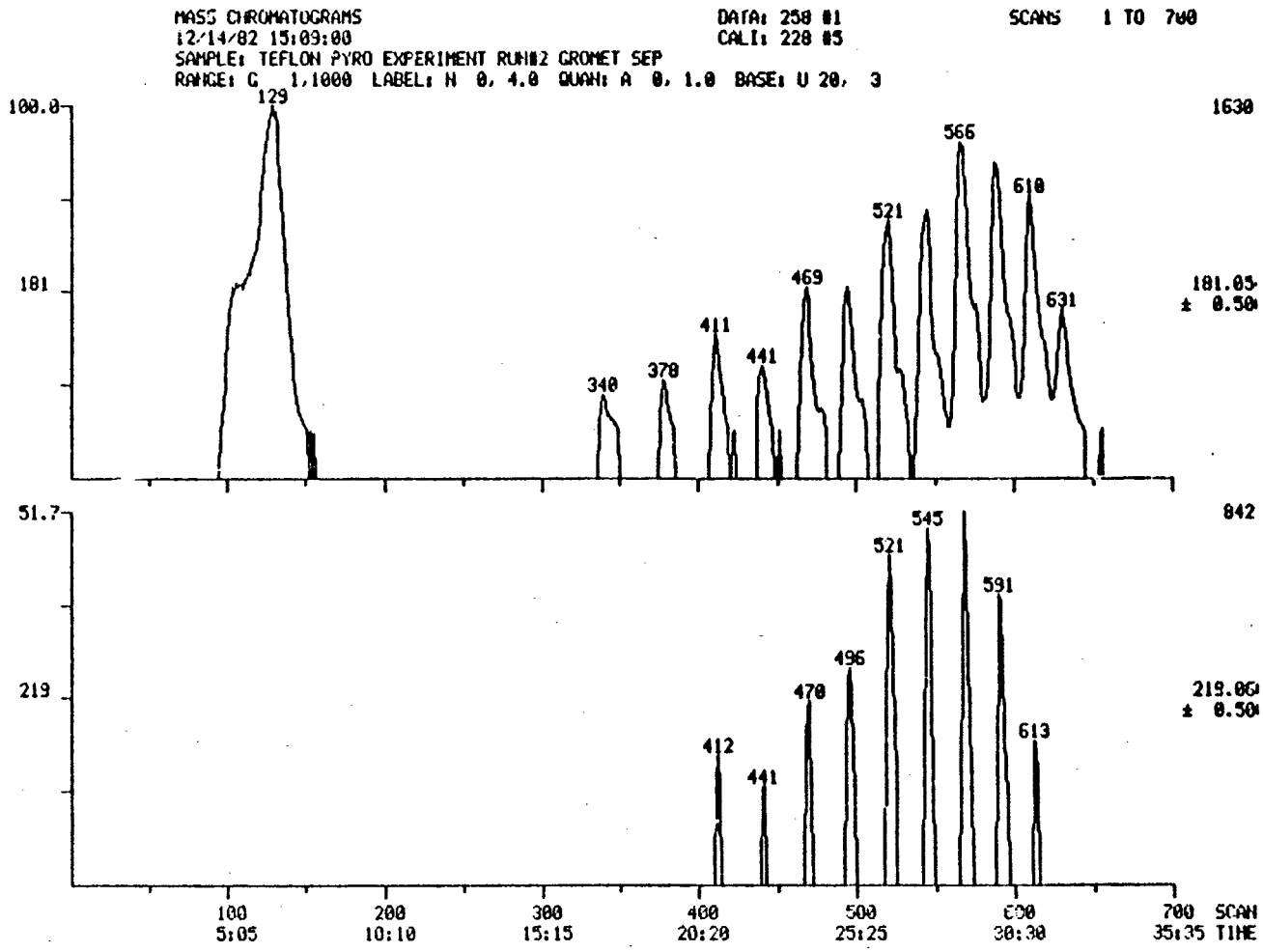


FIGURE 27

MASS CHROMATOGRAM M/Z = 181 AND 219, EXPERIMENT #2

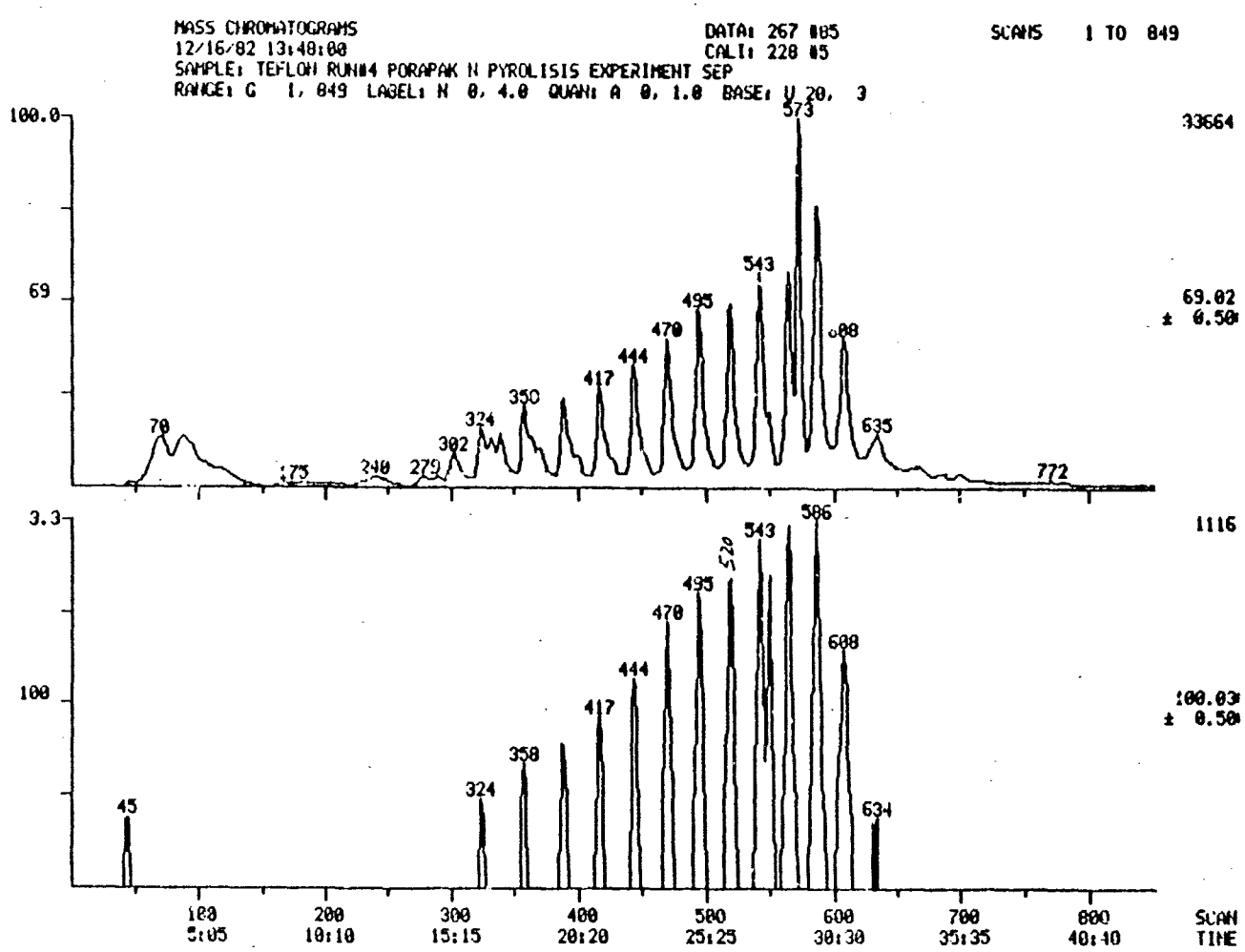


FIGURE 28

MASS CHROMATOGRAM, M/z = 69 AND 100, EXPERIMENT #4

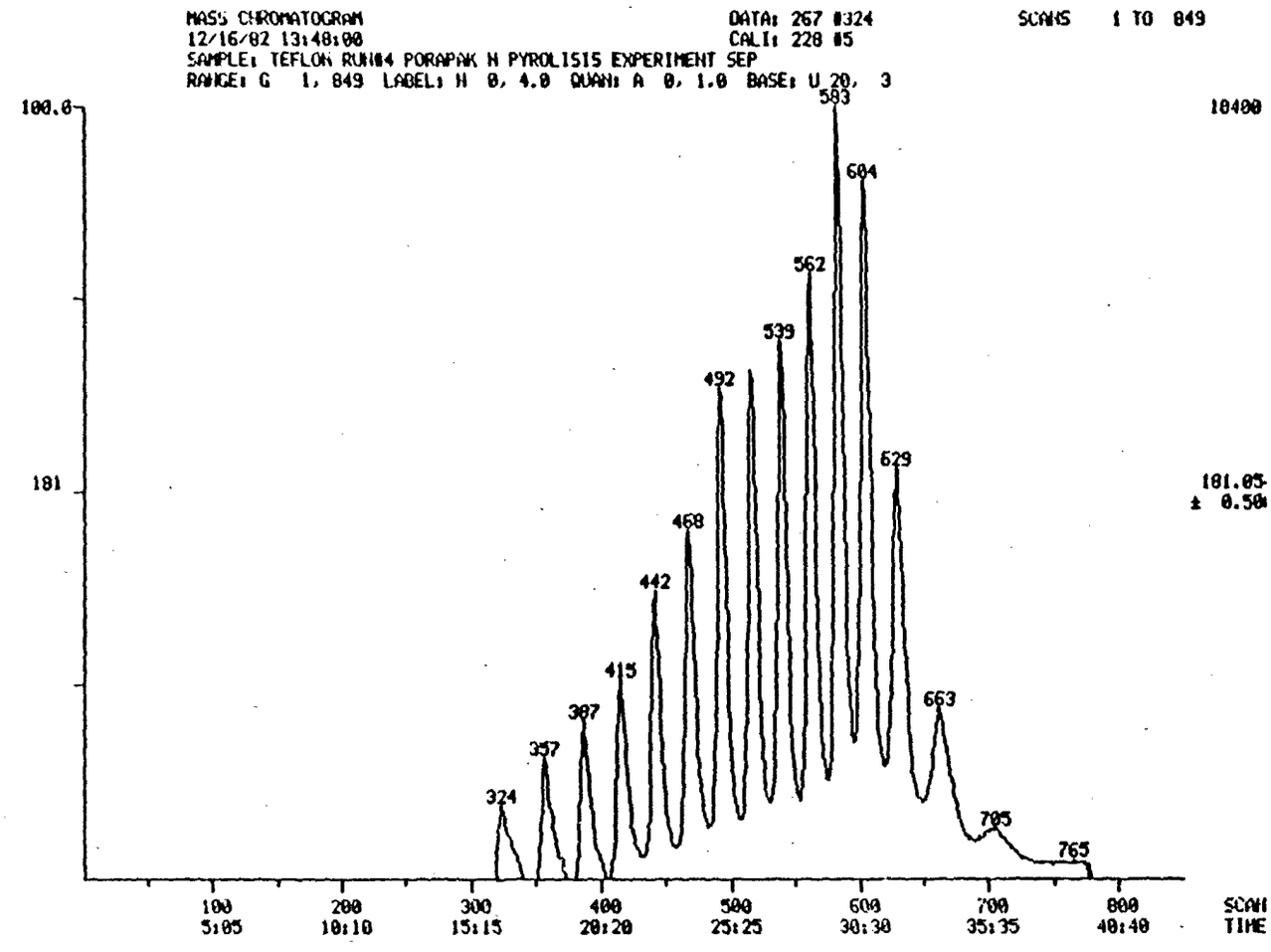


FIGURE 29

MASS CHROMATOGRAM, M/Z = 181, EXPERIMENT #4

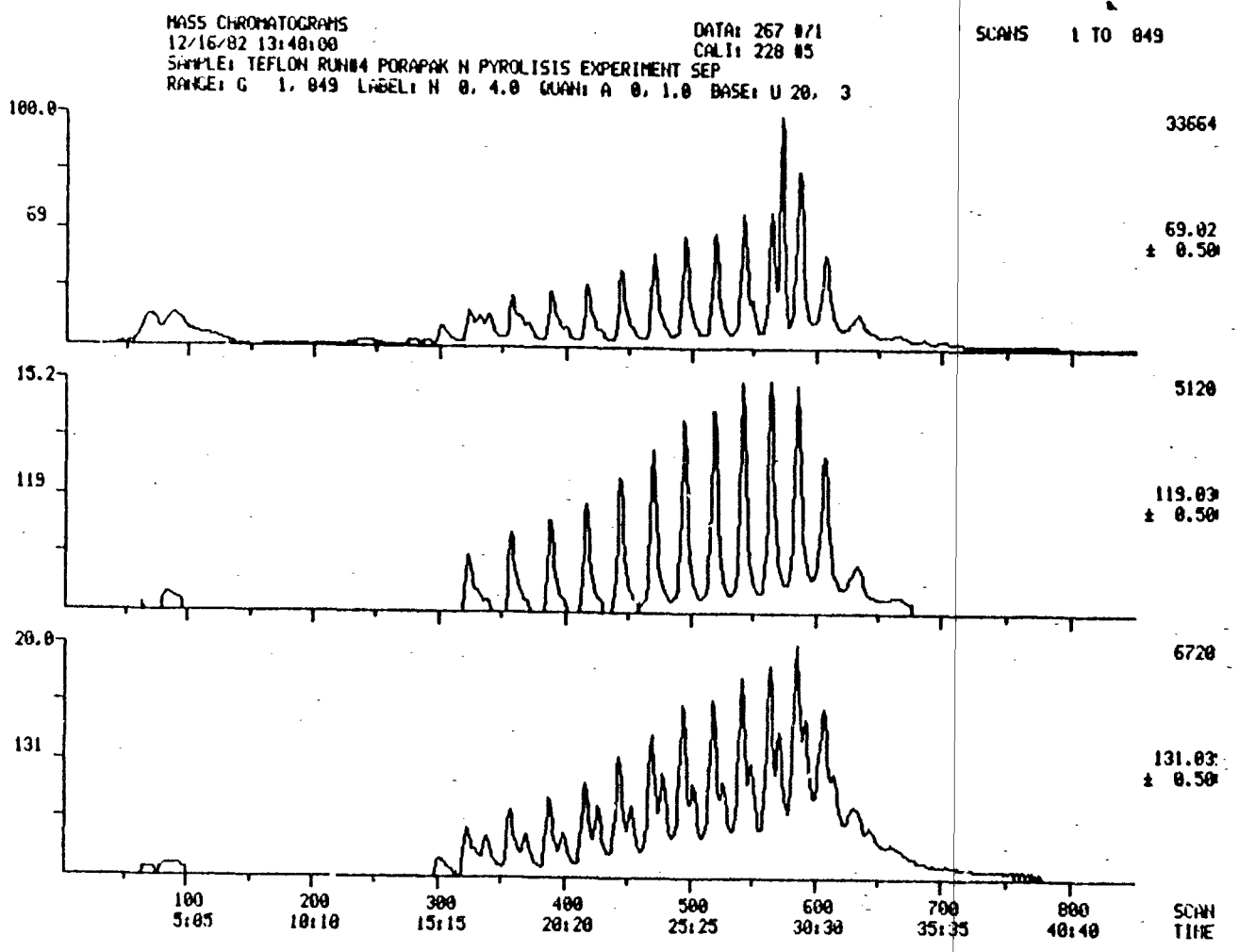


FIGURE 30

MASS CHROMATOGRAM, M/Z = 69, 119, AND 131, EXPERIMENT #4

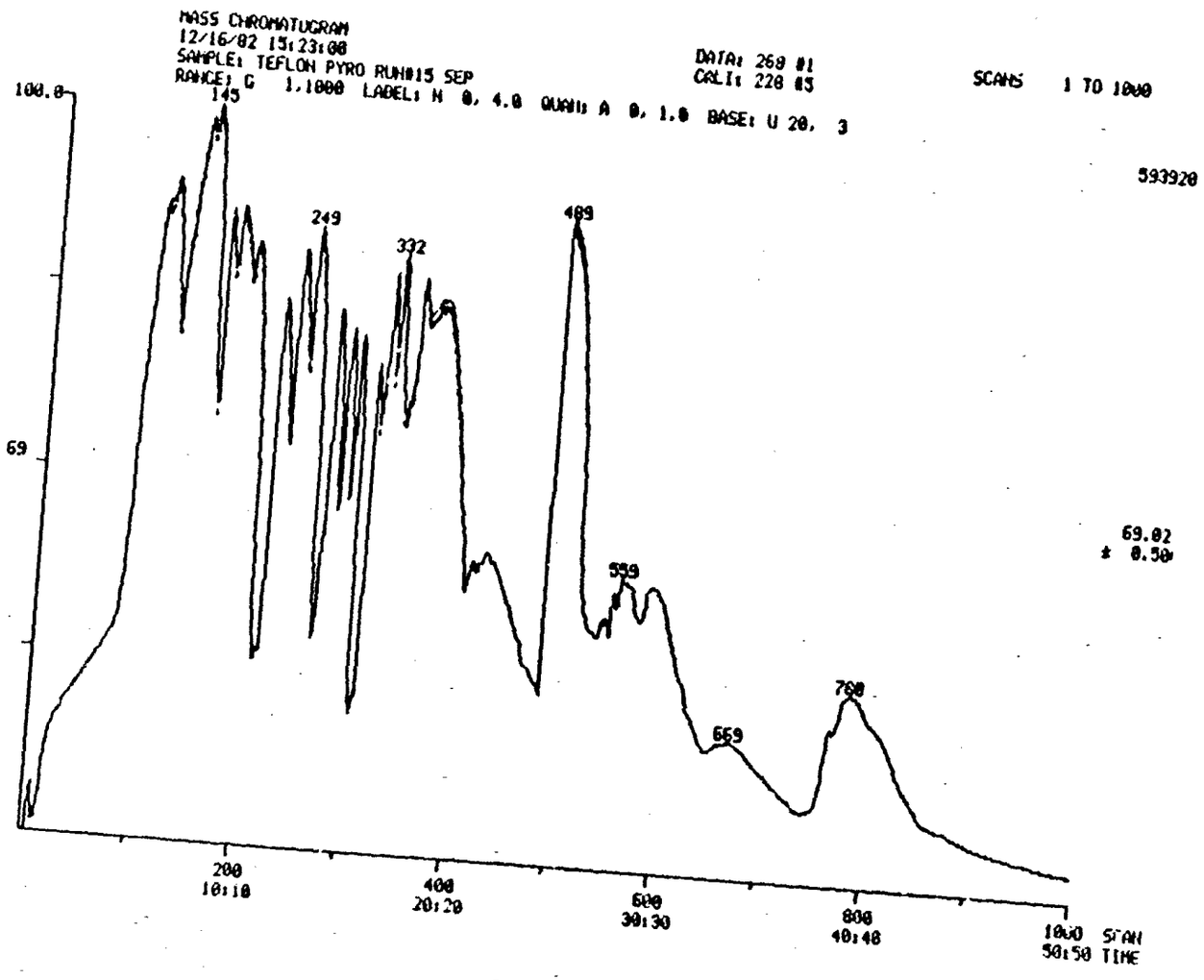


FIGURE 31

MASS CHROMATOGRAM, M/Z = 69, EXPERIMENT #15

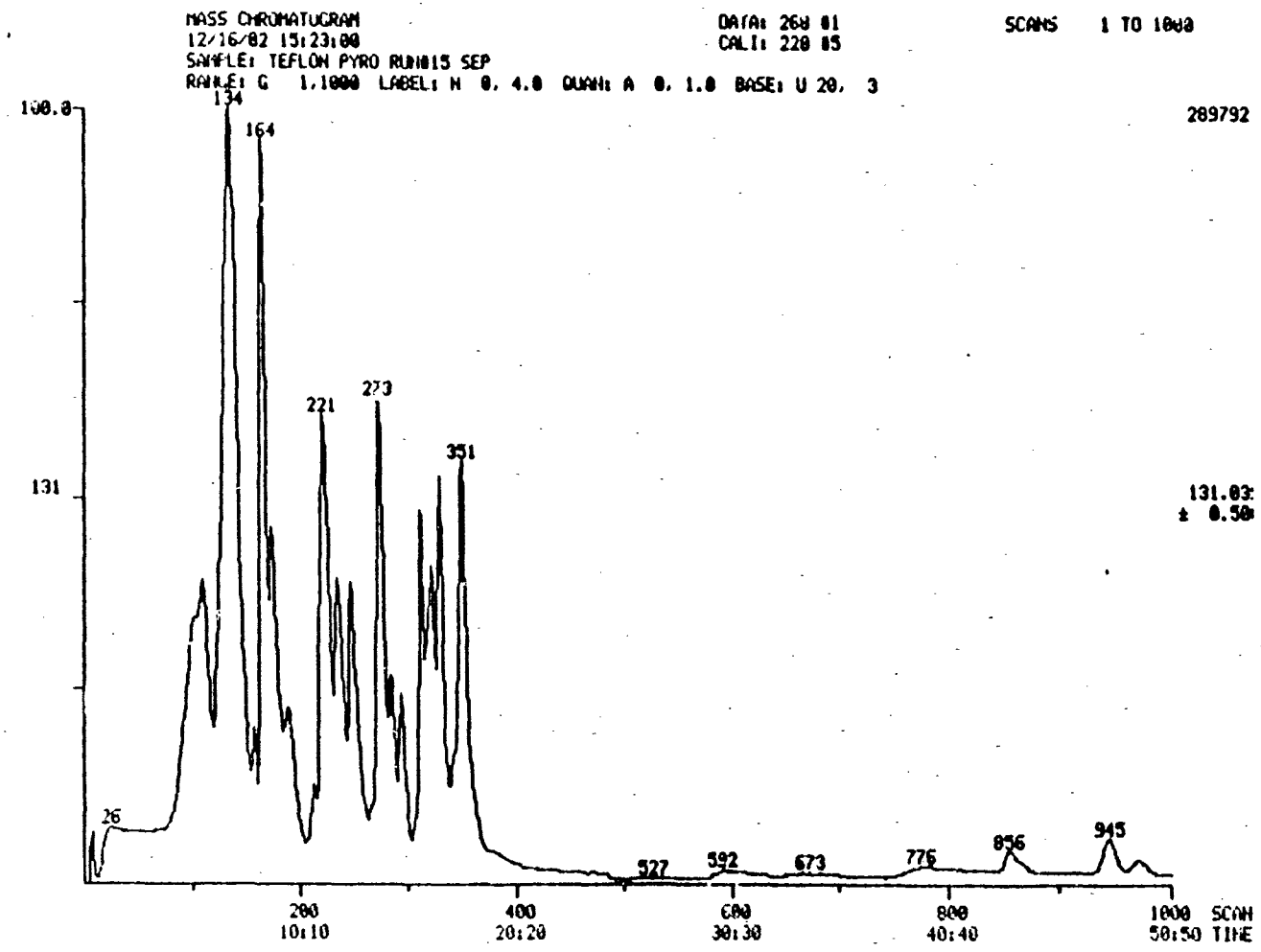


FIGURE 32

MASS CHROMATOGRAM, M/Z = 131, EXPERIMENT #15

N-35

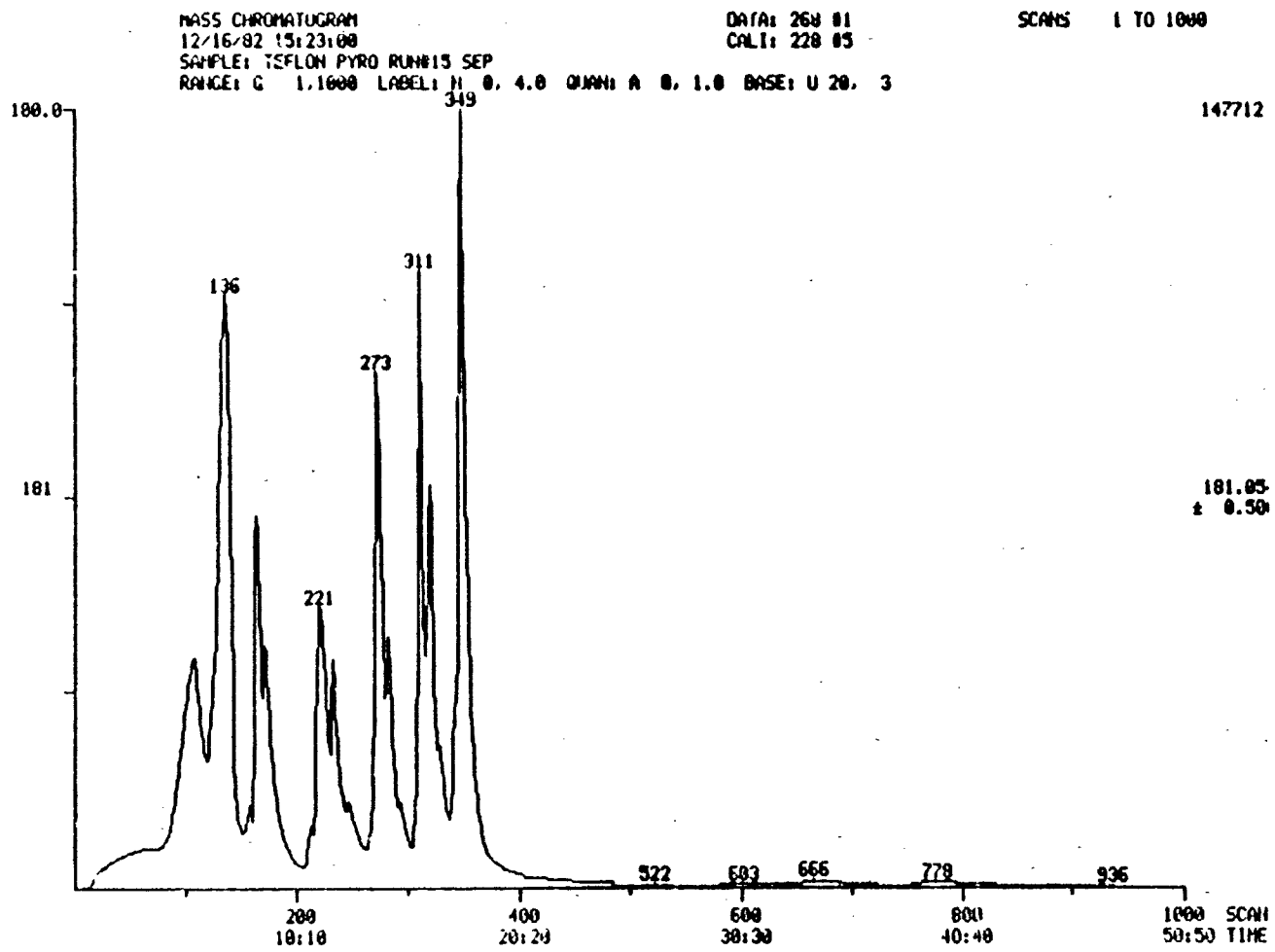


FIGURE 33

MASS CHROMATOGRAM, M/Z = 181, EXPERIMENT #15

N-56

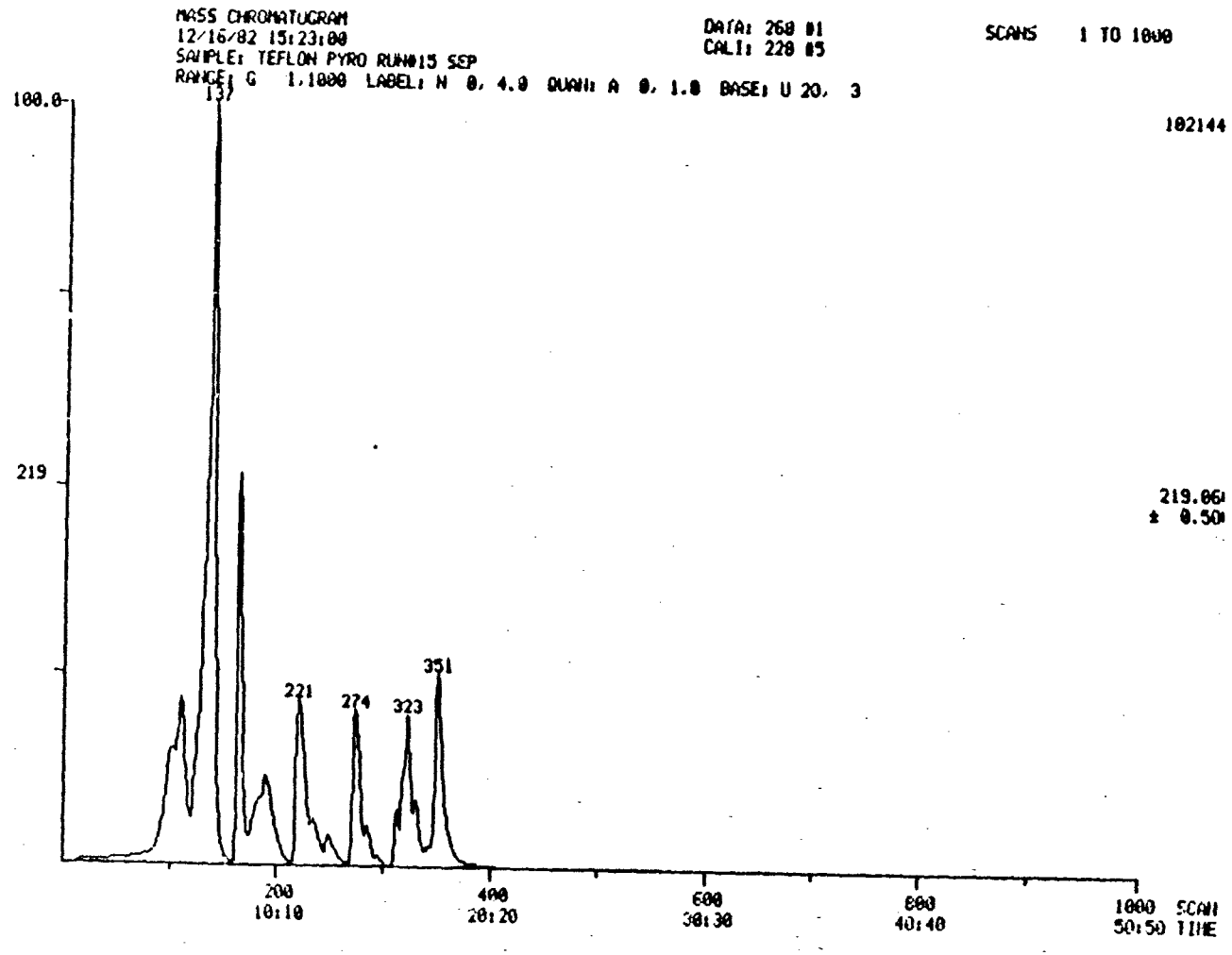


FIGURE 34

MASS CHROMATOGRAM, M/Z = 219, EXPERIMENT #15

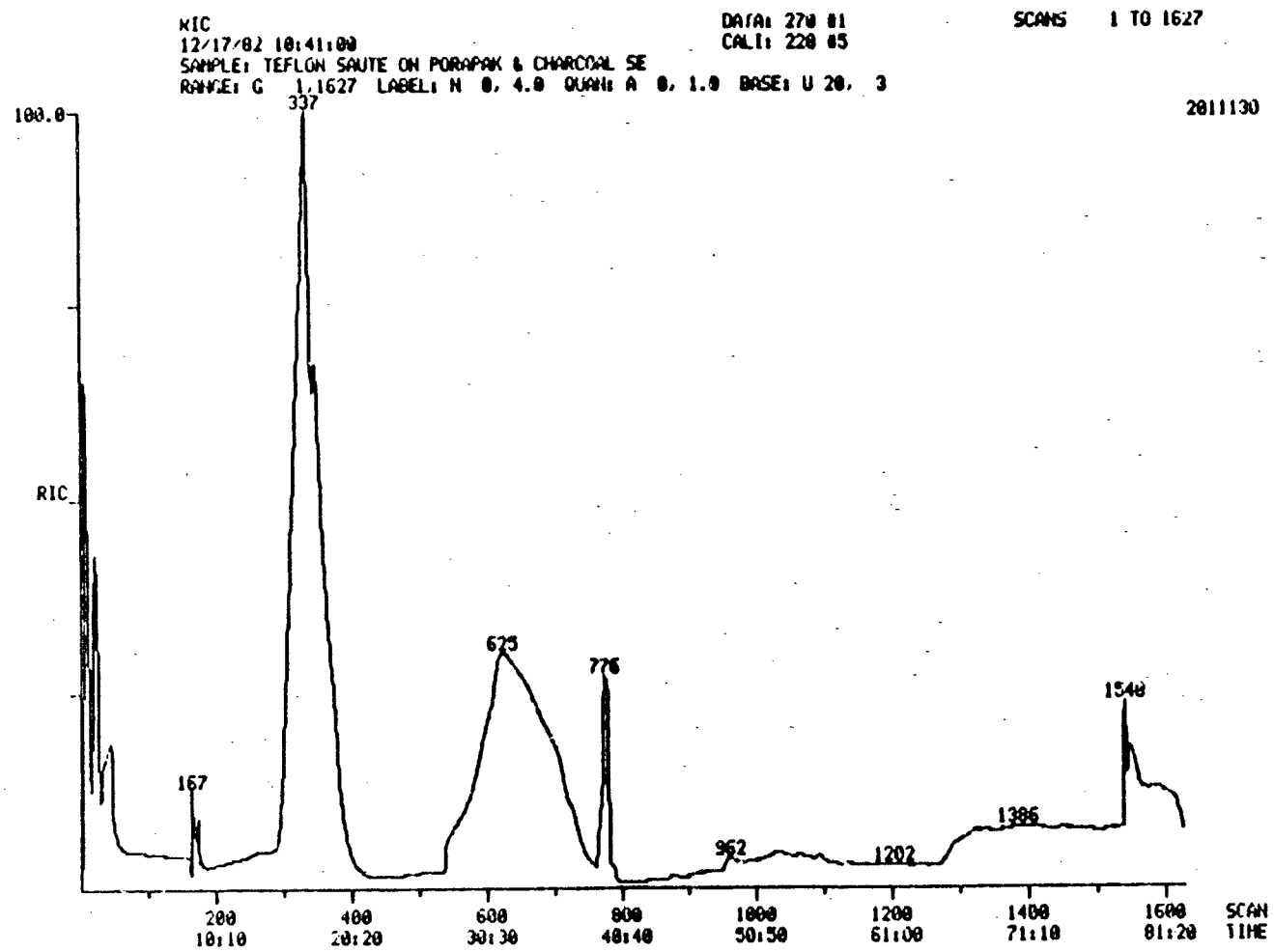


FIGURE 35

RECONSTRUCTED ION CHROMATOGRAM, PORAPAK AND CHARCOAL

N-88

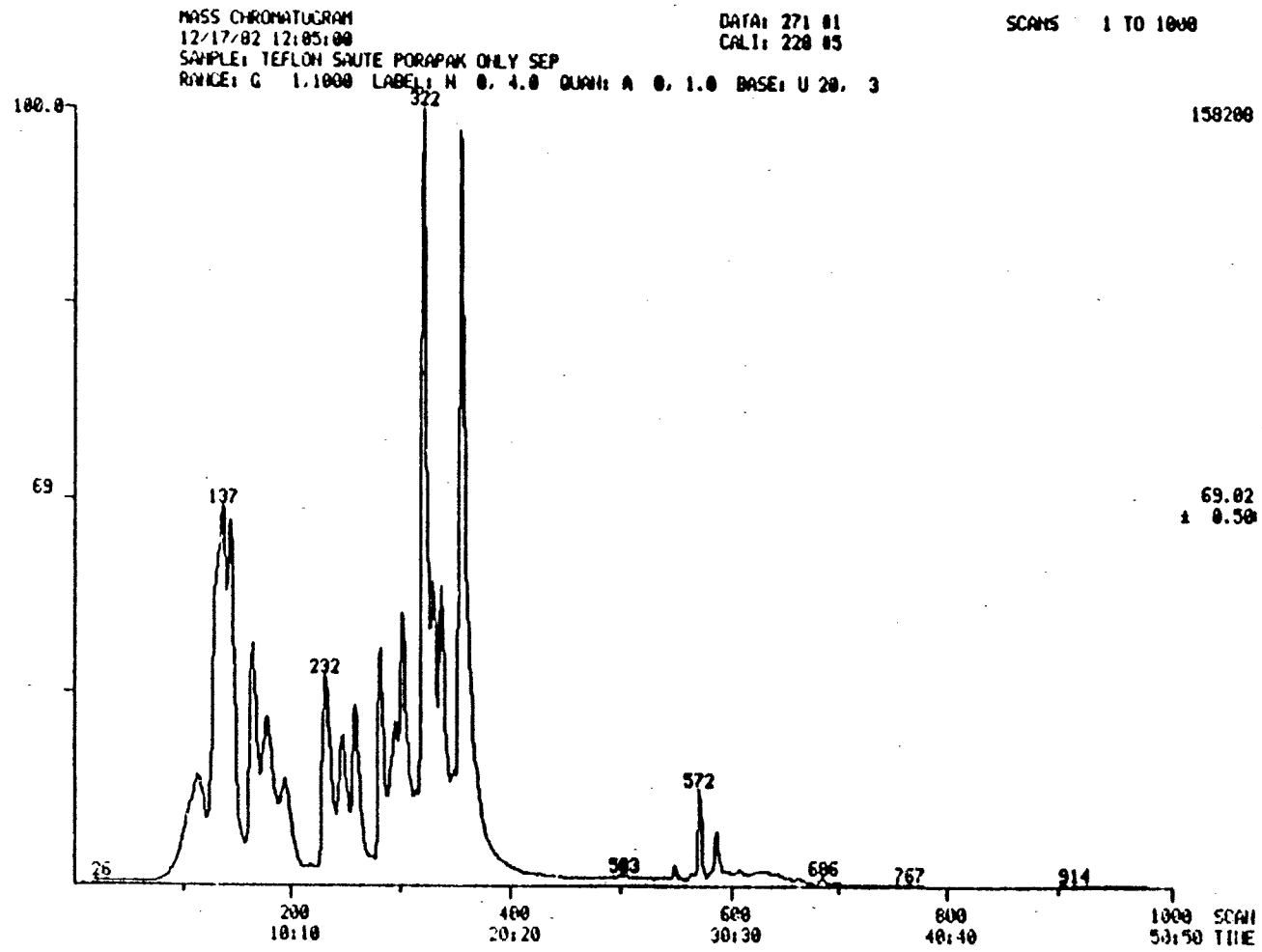


FIGURE 36

MASS CHROMATOGRAM, M/Z = 69, PORAPAK ONLY

N-89

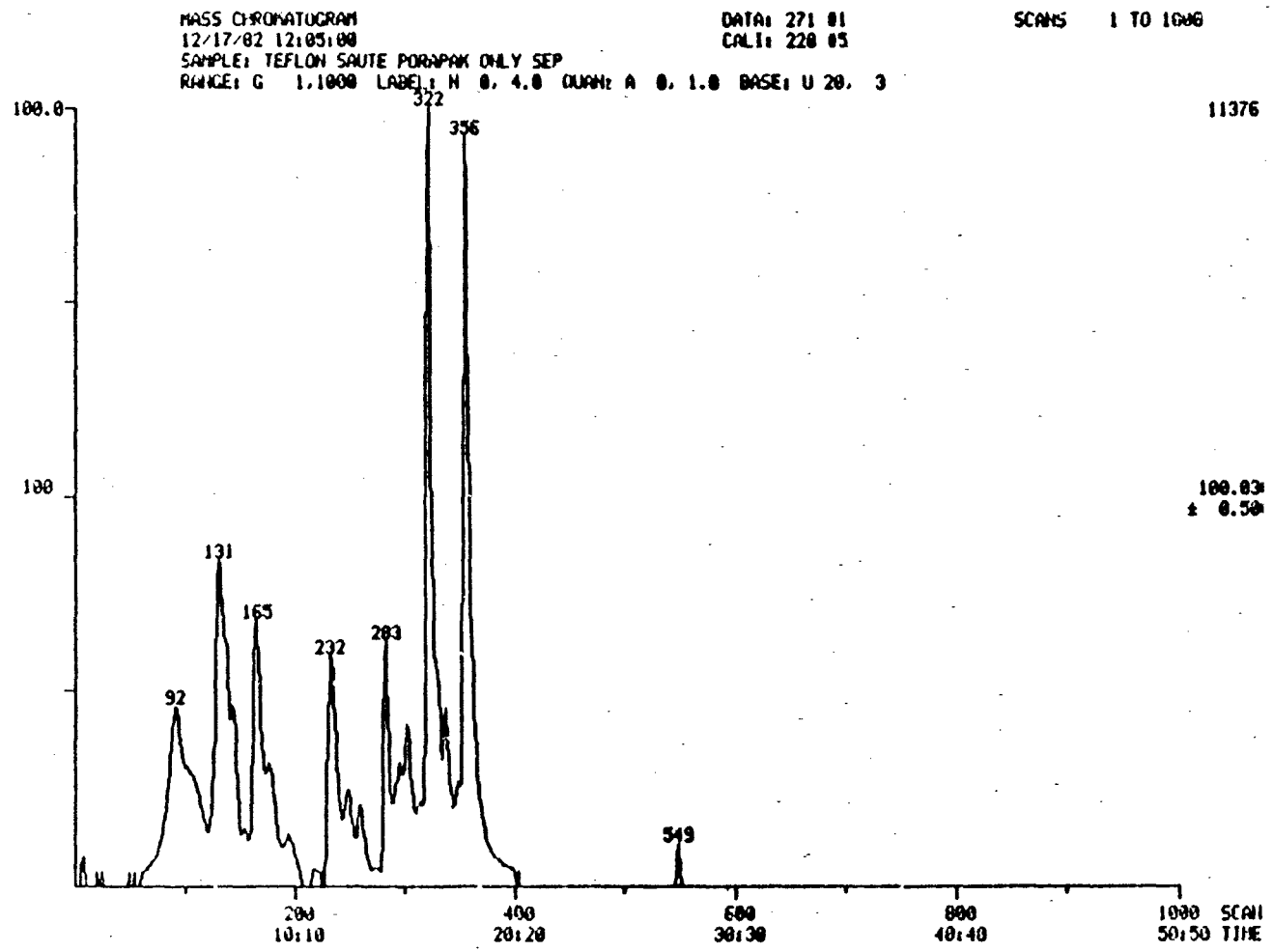


FIGURE 37

MASS CHROMATOGRAM, M/Z = 100, PORAPAK ONLY

N-96

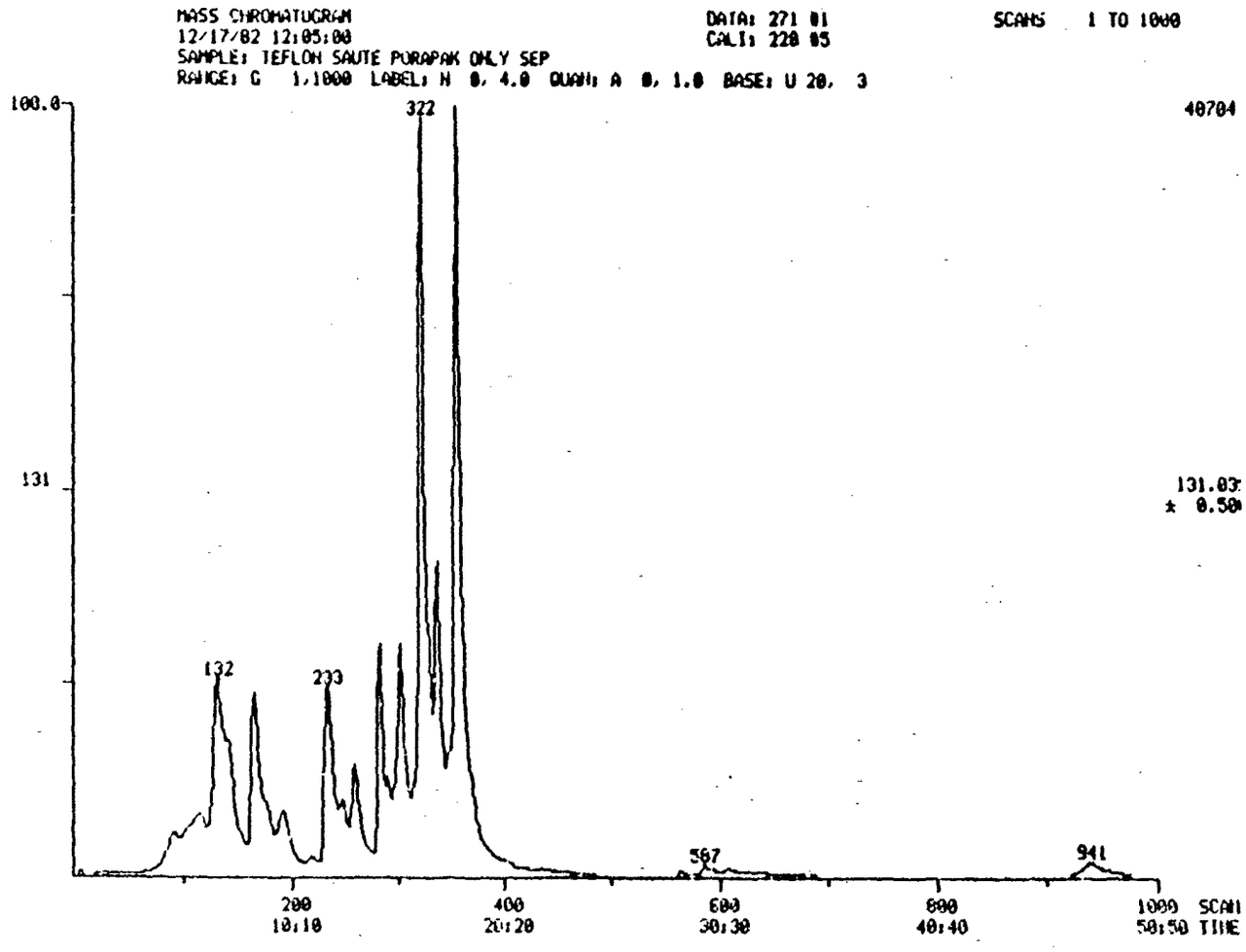
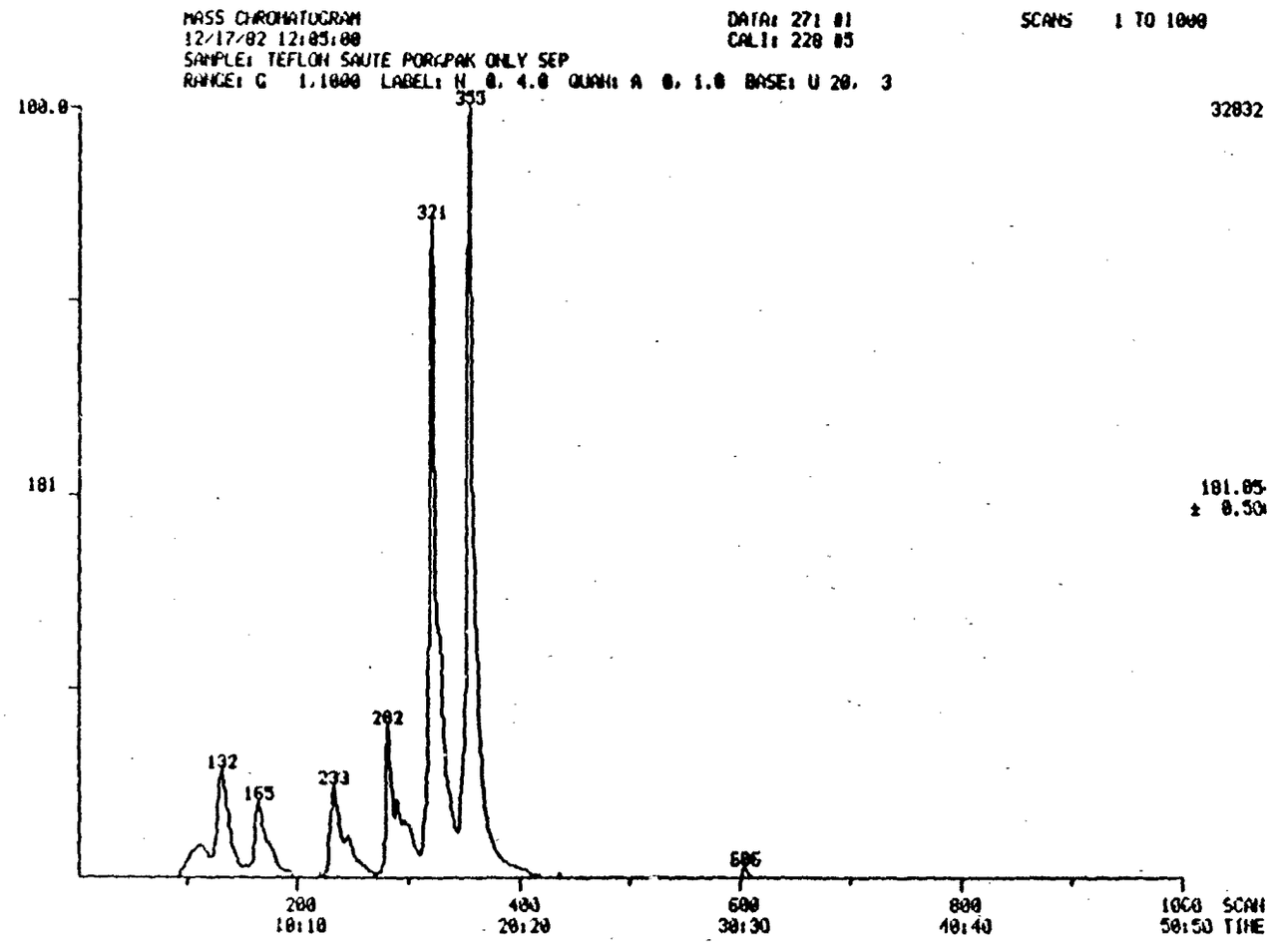


FIGURE 38

MASS CHROMATOGRAM, M/Z = 131, PORAPAK ONLY

N-91



N-92

FIGURE 39

MASS CHROMATOGRAM, M/Z = 181, PORAPAK ONLY

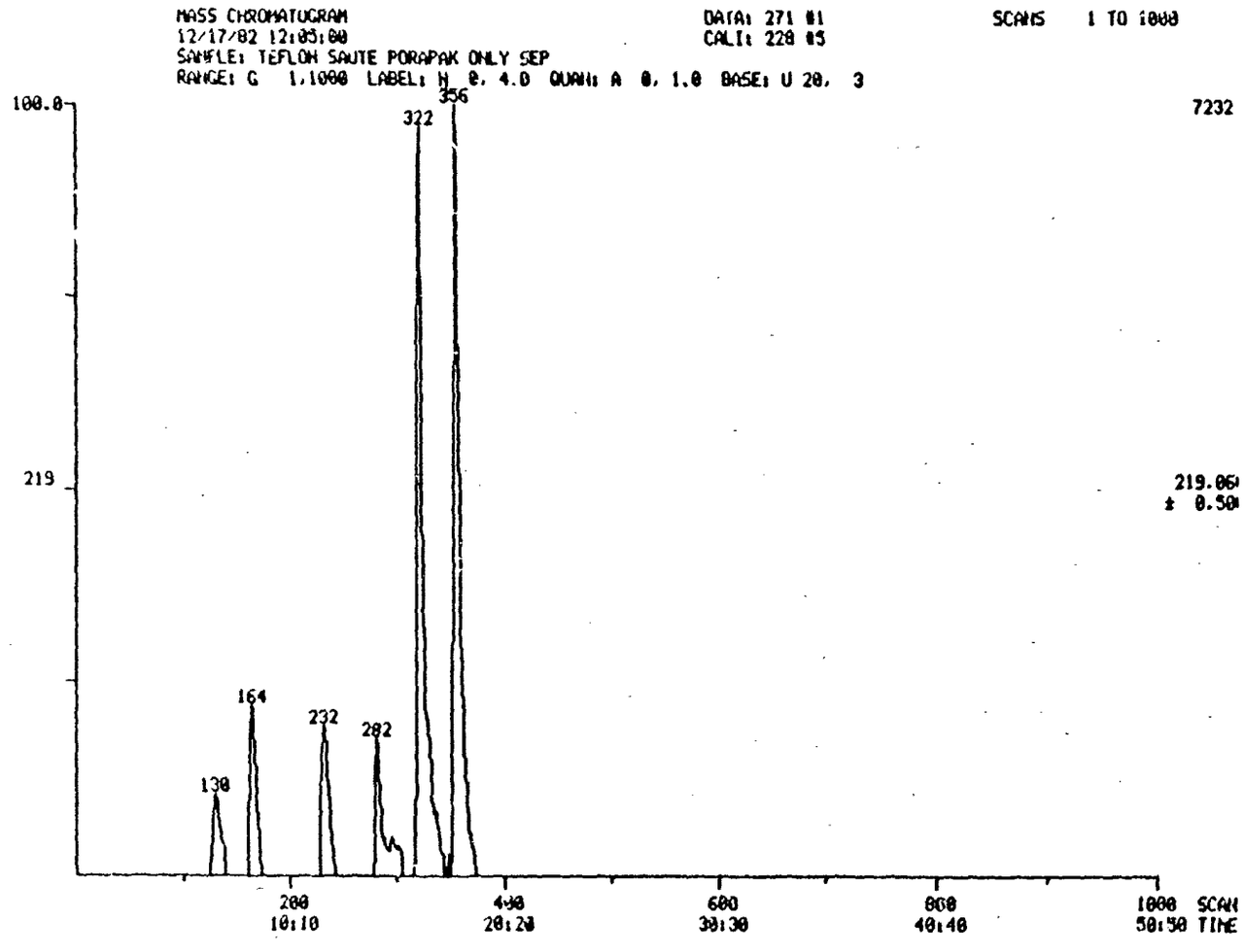
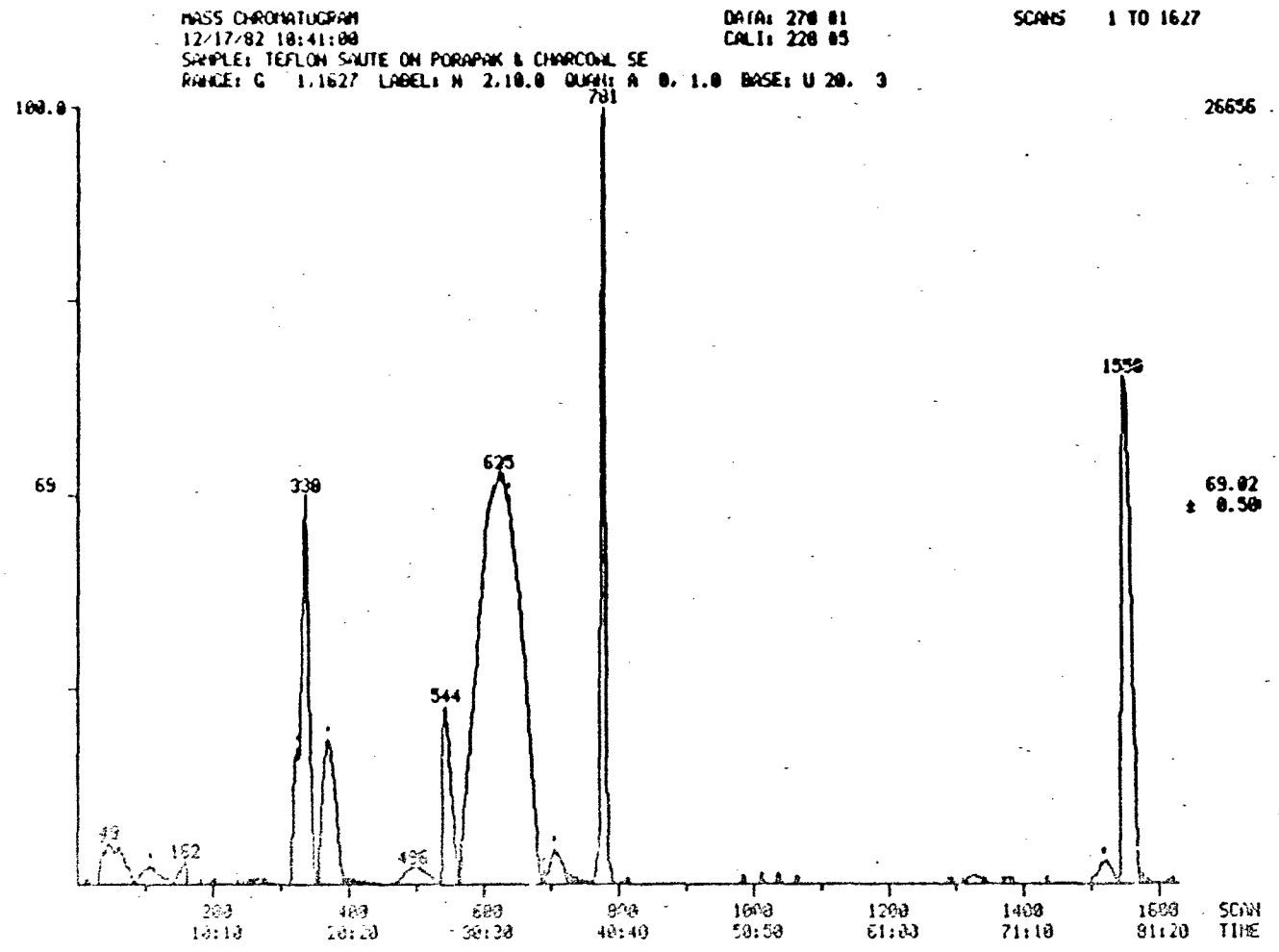


FIGURE 40

MASS CHROMATOGRAM, M/Z = 219, PORAPAK ONLY

N-93



N-93A

FIGURE 41

MASS CHROMATOGRAM, M/Z = 69, PORAPAK AND CHARCOAL

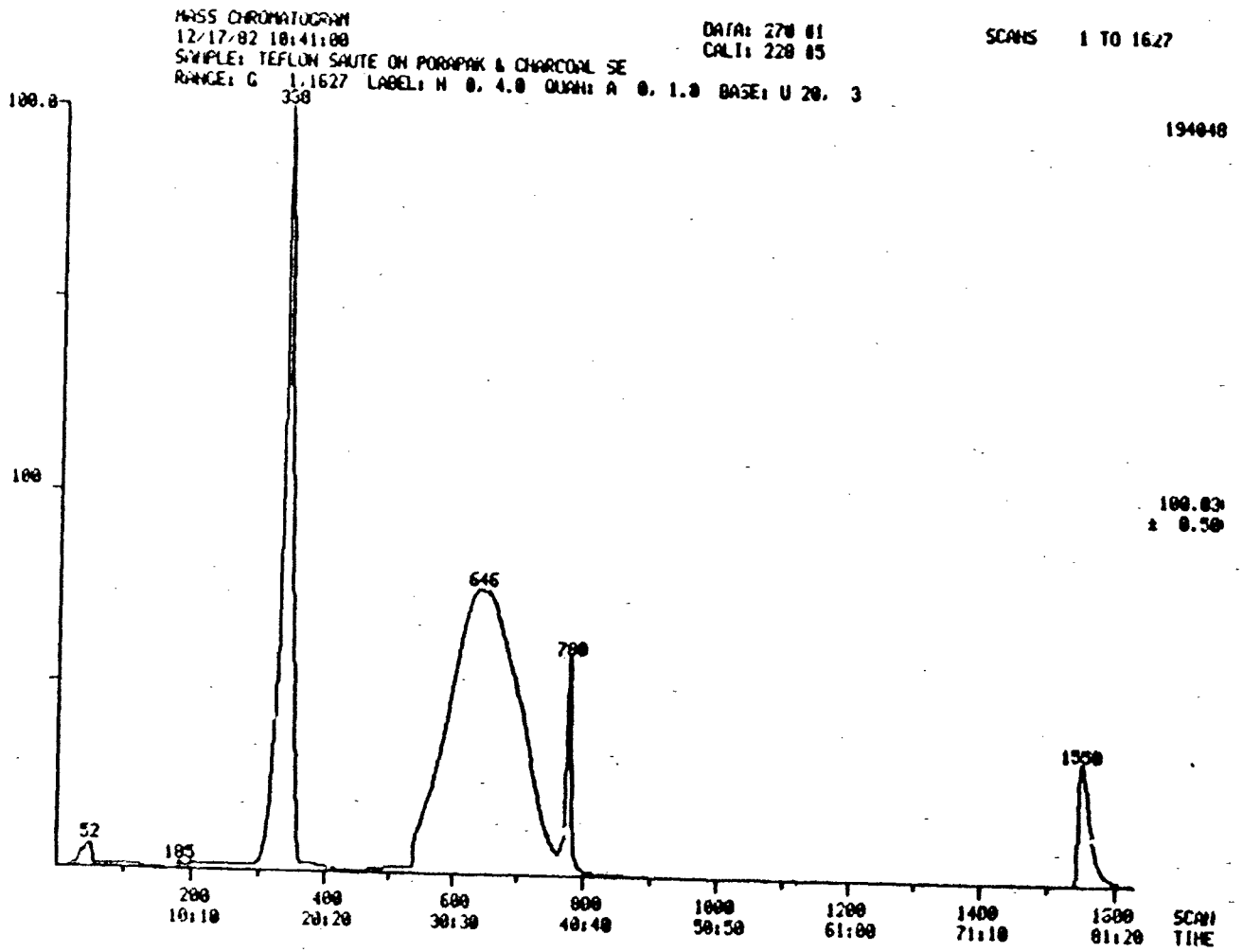
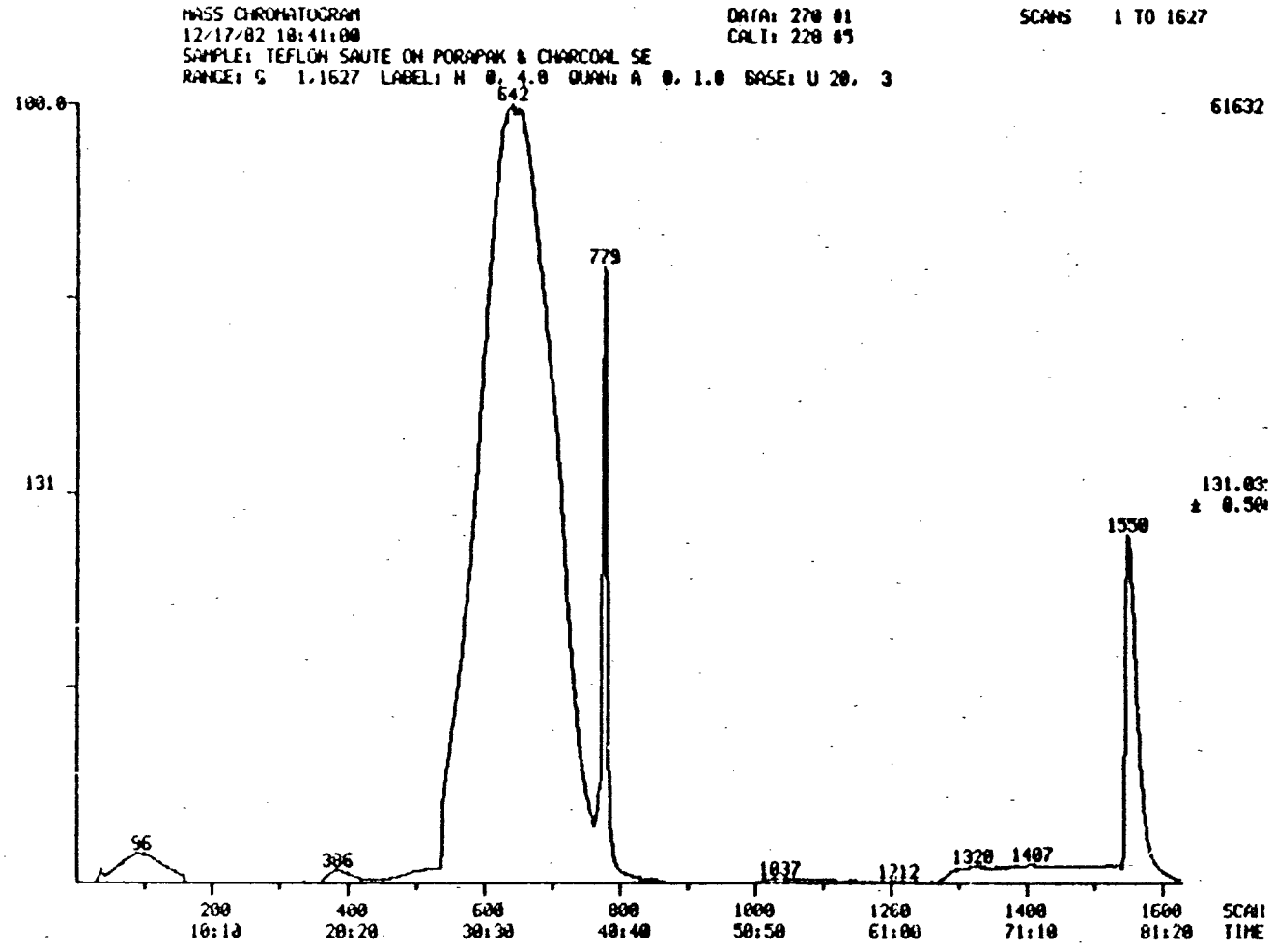


FIGURE 42

MASS CHROMATOGRAM, M/Z = 100, PORAPAK AND CHARCOAL



N-95

FIGURE 43

MASS CHROMATOGRAM, M/Z = 131, PORAPAK AND CHARCOAL

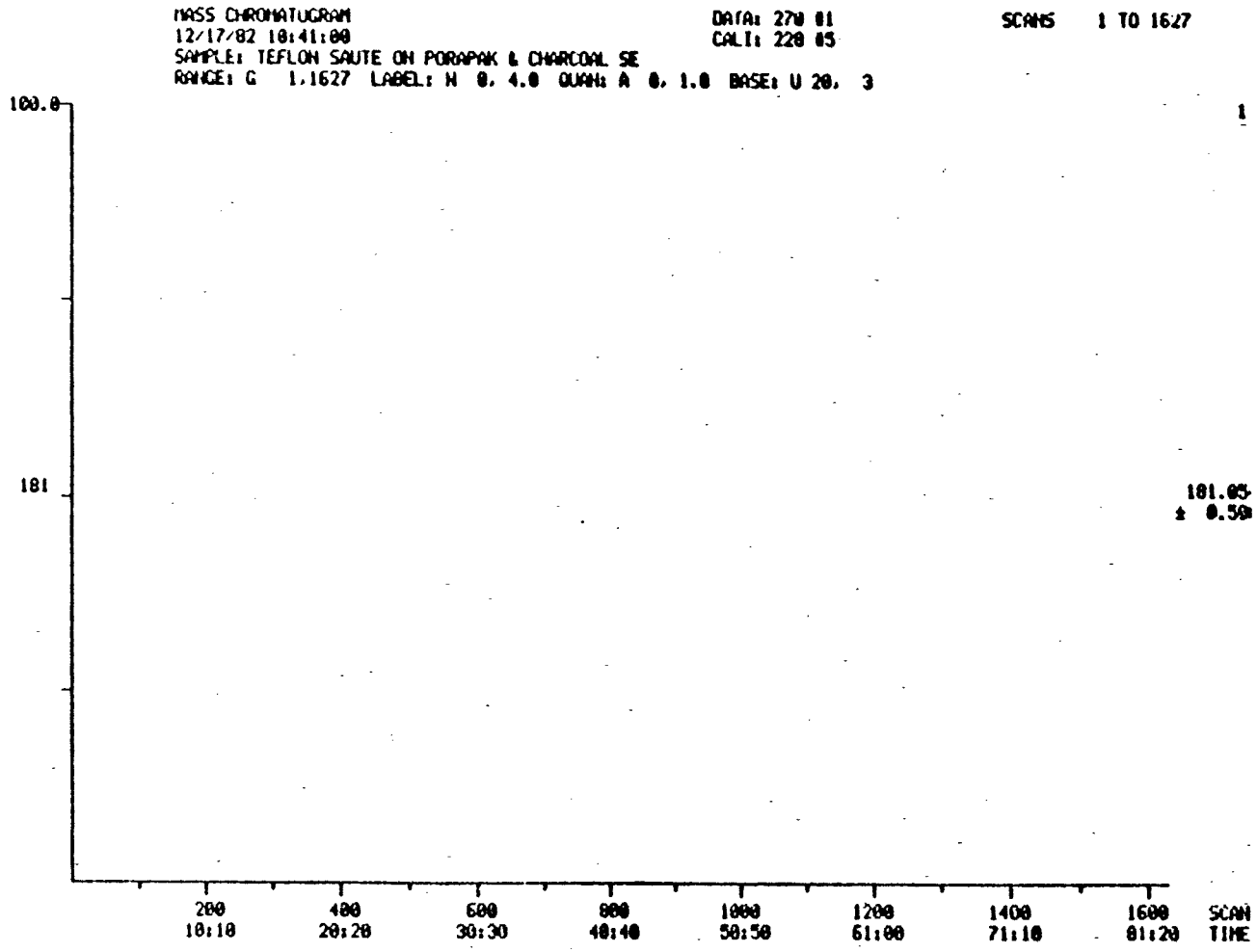


FIGURE 44

MASS CHROMATOGRAM, M/Z = 181, PORAPAK AND CHARCOAL

N-46

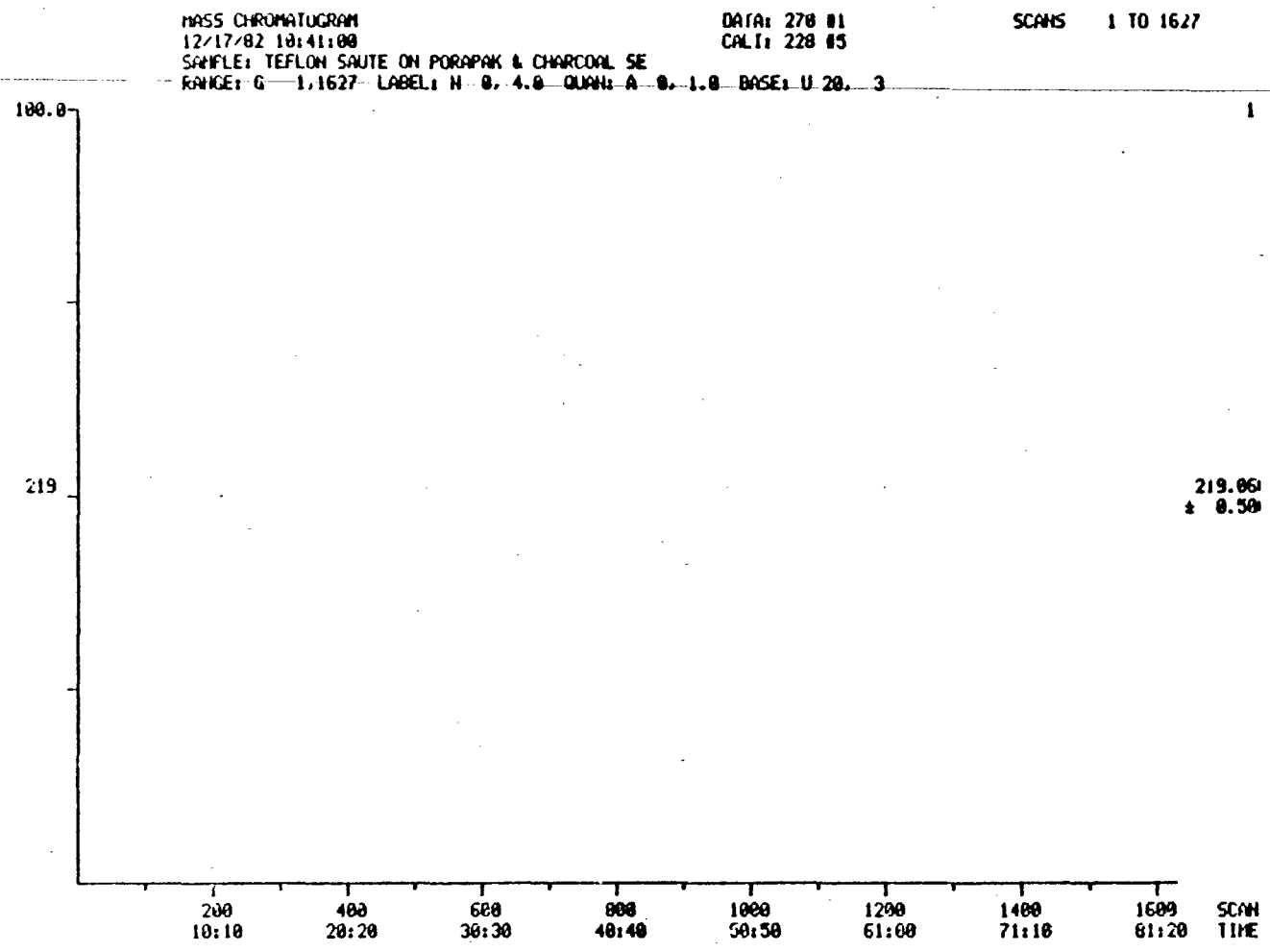


FIGURE 45

MASS CHROMATOGRAM, M/Z = 219, PORAPAK AND CHARCOAL

N-97

B. Phase II - Sampling at VSE Corporation, 18 - 19 December 1982

Samples were collected at VSE Corporation on 18 - 19 December 1982. The samples were taken to the laboratory for analysis for hydrolyzable fluoride, acrolein, semi-volatile organic compounds, and volatile organic compounds.

Field Sampling

The Phase II sampling and analysis activities were developed as a follow-on to Phase I to determine the production of irritant gas from new TFE grommets in a PATRIOT Heater/Air Conditioner. Phase I activities showed that when TFE grommets were heated to a high heat on the end of a heater rod like those from the PATRIOT unit, decomposition products were produced and identified as a complex combination of hydrolyzable and organo-fluorides. The objective of the field sampling was to operate a heater/air conditioner in a high heat mode with new TFE grommets and to collect air samples for several target parameters. Specific air samples were collected for the following parameters.

- Hydrolyzable Fluoride
- Acrolein
- Semi-volatile organic compounds
- Volatile organic compounds

Also during all sampling the M8 chemical agent alarm was exposed to the heated exhaust air stream. The M8 chemical agent alarm was used during these tests to determine if a relationship existed between the alarm signal given by the M8 chemical agent alarm and concentrations of hydrolyzable fluoride detected in the air sample

The sampling test plan was proposed to U.S. AEHA for their approval. U.S. AEHA reviewed the plan and recommended Versar proceed with the planned activities.

The following sampling runs were conducted at VSE on 18 and 19, December 1982:

#0 0.5 hour high heat; no TFE grommets in position; 0.4" H_2O flow restriction.

#1 1.0 hour high heat; new TFE grommets in position; 0.4" H_2O flow restriction.

#2 1.0 hour high heat; new TFE grommets in position; 0.4 to 0.7" H_2O (variable) flow restriction; over temperatures switches were operating which resulted in the heater cycling from high to low to no heat modes.

#3 46 minutes high heat; new TFE grommets in position; 0.7 to 0.78" H_2O (variable) flow restriction; heater fan motor overheated ending test at 46 minutes.

#4 1.0 hour high heat; new TFE grommets in position; 0.74 to 0.78" H_2O (variable) flow restriction.

#5 4.0 hour high heat; new TFE grommets in position 0.74 to 0.84" H_2O (variable) flow restriction.

A summary of the samples collected for each of the sampling runs is presented in Table 22 for 18 December 1982, and Table 23 for 19 December 1982. The M8 chemical agent alarm was operated continuously during all sample collection activities.

During this two day sampling period the M8 chemical agent alarm did produce an audible alarm during several of the above sampling runs. Sampling runs #0 and #1 were performed with the normal 0.4" H_2O pressure differential across the heater and there was no M8 alarm heard. During sampling run #2, the M8 alarmed at +10 minutes with an exhaust temperature of 116°F. The signal lasted for 4 minutes, and stopped. The signal stopped approximately 1 minute after the heater cycled from high heat to low heat. At +46 minutes the heaters cycled to high heat and one minute later the M8 alarm went off at an exhaust temperature of 114°F. The alarm lasted for approximately one minute.

Sampling run #3 lasted for 46 minutes because the fan motor overheated and automatically turned off the unit. The M8 chemical agent alarm was observed continuously from +6 to +36 minutes from an exhaust

TABLE 22

SUMMARY OF AIR SAMPLES COLLECTED ON 18 DECEMBER 1982
AT VSE FROM A PATRIOT HEATER/AIR CONDITIONER UNIT*

	0.5 HR**	1 HR***	1 HR***	1 HR***	1 HR***	TOTAL SUMMARY
0.1 N NaOH impinger	1	3	3	3	3	13
1 percent $NaHSO_3$ impinger	1	3	3	3	3	13
Porapak Tube	1	3	3	3	3	13
Charcoal Tube	2	6	6	6	6	26
M8 Chemical Agent Alarm	1	1	1	1	1	5
TOTALS	6	16	16	16	16	70

* Unit tested was SN 81013.
** No TFE grommets were in position on the heater rods during this test.
*** Before each one hour test new TFE grommets were placed into position on the heater rods; samples were collected for periods of 15, 30, and 60 minutes for each sample type. M8 chemical agent alarm was operating continuously.

TABLE 23

SUMMARY OF AIR SAMPLES COLLECTED ON 19 DECEMBER 1982
AT VSE FROM A PATRIOT HEATER/AIR CONDITIONER UNIT*

	1st HR**	2nd HR***	3rd HR***	4th HR***	TOTAL SUMMARY
0.1 N NaOH impinger	10	4	4	4	22
Porapak Tube	5	2	2	2	11
Charcoal Tube	10	4	4	4	22
M8 Chemical Agent Alarm	1	1	1	1	4
TOTALS	26	11	11	11	59

* Unit tested was SN 81013; new TFE grommets in position.

** During this hour, samples were collected for periods starting at 0-10 minutes, 10-20 minutes, 20-30 minutes, 30-45 minutes, and 45-60 minutes for a total of five sample sets. M8 chemical agent alarm was operated continuously.

*** During the second, third, and fourth hours, samples were collected the first 30 minutes and the second 30 minutes for a total of two sample sets each hour. M8 chemical agent alarm was operating continuously.

temperature of 115°F to an exhaust temperature of 152°F at +36 minutes. The unit was operated at a higher temperature at this point attempting to create the conditions that would cause the alarm to respond. There was no more M8 alarm heard during this sampling run.

During sampling run #4, the M8 alarm began at +5 minutes with an exhaust temperature of 115°F and continued to alarm for the remainder of the 60 minutes. Exhaust temperatures observed during the period the M8 alarmed ranged from a low of 115°F to a high of 147°F.

Sampling run #5 was conducted on 19 December 1982, and its duration was four hours. The M8 alarm was heard on and off during the first three hours, but none in the last hour. At the three hour point the heater fan motor overheated and shut down the system and testing. The unit cooled down and was restarted, but no M8 alarm was heard in the last hour. The M8 chemical agent alarm briefly alarmed at +15 minutes and an exhaust temperature of 117°F. M8 chemical agent alarm was heard continuously from +25 minutes to +65 minutes with exhaust temperatures ranging from 119 to 130°F. In the remaining 115 minutes, the M8 chemical agent alarm was only occassionly heard. During this period the temperature slowly increased from 130 to 147°F.

The summary of the M8 chemical agent alarm results exhibit that new TFE grommets in a heater operated at temperatures near 115°F with some flow restriction may create an irritant that causes the M8 chemical agent alarm to respond. As the TFE grommets continue to be exposed to the heater rods, it takes a much higher temperature in the heater to cause the M8 to respond, indicating that less surface on each TFE grommet is exposed to the heat.

Hydrolyzable Fluoride

There were serious problems with the hydrolyzable fluoride results. Some blanks appeared to be contaminated, and the reproducibility between duplicate samples was greater than 100 times

poorer than laboratory results. Although some hydrolyzable fluoride was found in the exit air from the heater/air conditioners, no conclusions could be drawn from the data. The data could not be used and a second sampling for just hydrolyzable fluoride was planned. Fluoride analysis was done on site and extensive blanks were taken to assure that there was no contamination. These results are discussed below in Fluoride Analysis at VSE 8 January 1983.

Acrolein

No acrolein was found in any of the samples taken.

Semi-Volatile Organic Compounds

Semi-volatile organic compounds were analyzed using the procedure presented in Section IV.A. Briefly, the charcoal tubes were desrobed with 5 ml of n-hexane and analyzed by electron capture gas chromatography. Three peaks consistently showed up in the samples taken at VSE. They were present in the ambient air, and in the discharge air from the heater/air conditioner. They were not present in the blanks. The amount of the three compounds found was proportional to the total amount of sample taken, and it had nothing to do with the operating conditions of the heater/air conditioner. The compounds are apparently low level contaminants in the ambient air at VSE.

Field Sampling at VSE, 8 January 1983

The field sampling activities conducted at VSE's Alexandria facility on 8 January 1983 were developed to ensure reproducible results could be obtained from the fluoride analysis. The PATRIOT heater/air conditioner was operated in a "controlled" high heat mode with fluoride samples and M8 chemical agent alarm being collected from the heated exhaust air at the same location (approximately eight feet from the face of the heater). The "controlled" high heat mode required that both

over-temperature switches be wired out which resulted in high heat operation during all sampling. A constant pressure differential across the heater rods was maintained by restricting the intake air flow to achieve a pressure differential of 0.64 to 0.72" water. Four sampling runs were performed at high heat: one without TFE grommets and three with new TFE grommets placed in position before each run. All activities were carefully documented so that the individual sampling runs could be duplicated and to assist Versar in the determination of a relationship between hydrolyzable fluoride levels and the initiation of the M8 chemical agent alarm.

The following sampling runs were conducted at VSE on 8 January 1983:

- 0.5 hour high heat; no TFE grommets in position; 0.64" H_2O flow restriction.
- 1.0 hour high heat; new TFE grommets in position; 0.67" H_2O flow restriction.
- 2.0 hour high heat; new TFE grommets in position; 0.72" H_2O flow restriction.
- 2.0 hour high heat; new TFE grommets in position; 0.72" H_2O flow restriction.

A summary of all hydrolyzable fluoride samples collected is provided in Table 24. The M8 chemical agent alarm was operated continuously during all sample collection activities.

During the sample collection activities, sampling personnel recorded the periods when the M8 chemical agent alarm was heard. The first sampling run which was 0.5 hour long without TFE grommets did not stimulate the M8 chemical agent alarm which was the expected result. The first 1.0 hour run at high heat with new TFE grommets in position also did not create an M8 alarm. This run was stopped at 1.0 hour because of the lack of the M8 alarm as well as some problems encounted in creating

TABLE 24

SUMMARY OF AIR SAMPLES COLLECTED ON 8 JANUARY 1983
AT VSE FROM A PATRIOT HEATER/AIR CONDITIONER UNIT*

	0.5 HR	1st 1.0 HR**	1st 2.0 HR***	2nd 2.0 HR***	TOTAL SUMMARY
0.1 N NaOH	3	17	23	23	66
M8 Chemical Agent Alarm	1	1	1	1	4
TOTALS	4	18	24	24	70

* Unit tested was SN 81013.

** Prior to heater operation, new TFE grommets in position. Samples collected in triplicate for periods from 0-10 minutes, 10-20 minutes, 20-30 minutes, 30-45 minutes, and 45-60 minutes. Samples collected in duplicate for a period from 0-60 minutes. Sampling run stopped before completion because on-site analytical analysis determined that problems among triplicate samples were encountered. M8 chemical agent alarm was operated continuously.

*** Prior to heater operation for each set, new TFE grommets in position. Samples collected in triplicate for periods from 0-10 minutes, 10-20 minutes, 20-30 minutes, 30-45 minutes, 45-60 minutes, 60-90 minutes and 90-120 minutes. Samples collected in duplicate for a period from 0-60 minutes. M8 chemical agent alarm was operating continuously.

good triplicate fluoride results. It was also observed at +15 minutes that the M8 chemical agent alarm may have been started incorrectly not allowing sample air to be pumped through the alarm. At this time it was restarted correctly, however, no alarm was heard.

The sampling set-up was modified slightly so that all air samples were drawn from the same point, and the flow was restricted to 0.72" H_2O before the first full 2.0 hour run was begun. During this sampling run, M8 chemical agent alarm was heard for a period of eight minutes from +5 to +13 minutes with an exhaust temperature ranging from 132 to 139°F. After +13 minutes, no M8 alarm was heard for the remaining 107 minutes. The next section will describe the analytical results for hydrolyzable fluoride.

A second 2.0 hour run was made to duplicate the above experiment. With new TFE grommets in position and the heater in high heat mode, the sampling equipment and M8 chemical agent alarm were started. The M8 alarm was heard from +7 to +13 minutes with an exhaust temperature of 132 to 139°F. The M8 alarm was also heard from +23 to +30 minutes with exhaust temperatures at 141°F. No M8 alarm was heard during the last 90 minutes. The next section describes the fluoride analysis conducted at VSE on 8 January 1983.

Fluoride Analysis at VSE, 8 January 1983

Fluoride analysis was done on site at VSE during the sampling on 8 January 1983. Versar collected 66 fluoride samples, and analyzed 64. Sixty-seven blank samples and three samples of ambient air were also collected. The ambient air samples and 12 of the blanks were analyzed at VSE. None of the ambient air samples had detectable levels of fluoride, and only one of the blanks had detectable levels of fluoride. The level in this one blank corresponded to 18 ug/m^3. Since most of the airborne fluoride results were much higher than this, the low level in this one blank is not a cause for concern.

We attempted to analyze the fluoride samples very quickly. The results obtained on site would indicate whether any changes in the sampling procedures were necessary. For many samples, the electrode was not allowed to equilibrate long enough because of the short analysis time. The results presented here were confirmed with laboratory analysis.

The results of the fluoride analysis are presented in Table 25. In Experiment 1, where the samples were taken about two inches away from each other in the air stream, there was an unacceptable amount of variability in the triplicate samples (i.e., 20, 38 and 110). Furthermore, the sample taken from 0 to 60 minutes was lower than the samples taken at any time in the 60 minute run. These implausible results indicated that the experiments should be repeated and they were.

In Experiments 2 and 3 the sampling locations were much closer to each other. This resulted in an apparent improvement in the reproducibility between the triplicate samples. There was still a significant amount of variation in some sets, but it was reduced from the first experiment.

Figures 46 and 47 show a plot of the fluoride concentration versus time for the duplicate experiments. The fluoride concentrations are the averages of three determinations.The results from all three experiments show that the fluoride concentration reaches a maximum between 10 and 20 minutes of operation. The concentration then slowly falls off for the rest of the experiment. An apparent effect level in each figure of 50 ug/m^3. Dwiggins, Wiggins and Dwyer[3] have reported levels of hydrolyzable fluoride concentrations in the range of 50 to 1000 ug/m^3 in areas where illness occured.

TABLE 25

FLUORIDE RESULTS

Conditioning	Time	Triplicate Air Concentrations ug/m^3			Average
Without Grommets	0-30	5	4	6	5
Grommets					
Expt. 1	0-10	20	38	110	56
	10-20	250	250	spilled	250
	20-30	60	70	70	67
	30-45	60	32	31	41
	45-60	50	33	47	43
	0-60	12	4	---	8
Expt. 2	0-10	200	140	180	173
	10-20	180	220	140	180
	20-30	108	88	100	99
	30-45	70	120	80	90
	45-60	40	52	100	64
	60-90	60	53	38	50
	90-120	48	43	27	39
	0-60	110	110	---	110
Expt. 3	0-10	115	120	83	106
	10-20	115	230	210	185
	20-30	68	115	138	107
	30-45	110	57	120	98
	45-60	31	63	57	50
	60-90	40	60	65	55
	90-120	31	22	33	29
	0-60	NA	NA	---	NA

NA = Not analyzed in field.
--- = Not collected.

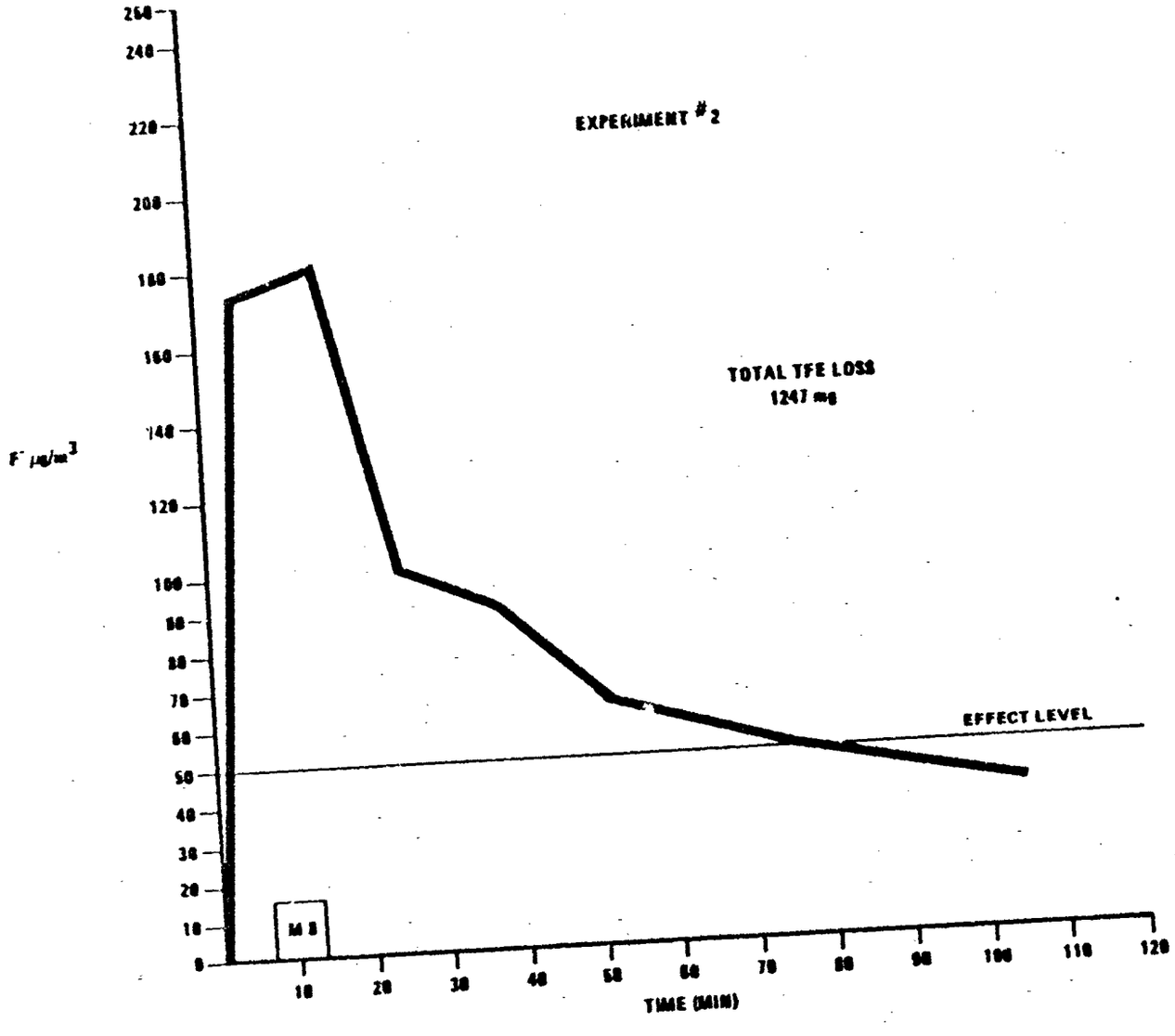


FIGURE 46 FLOURIDE CONCENTRATION VS. TIME

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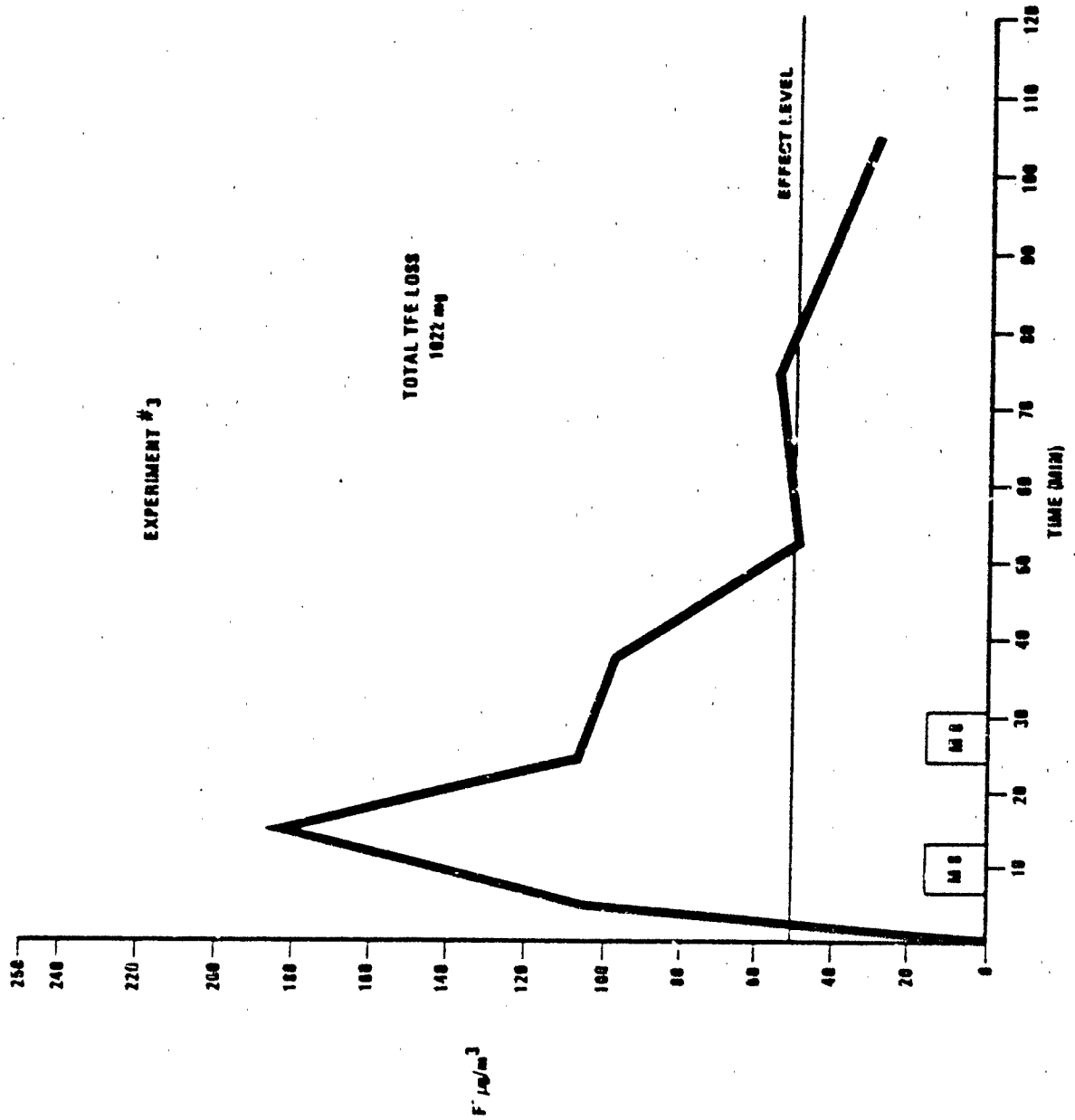

FIGURE 47 FLOURIDE CONCENTRATION VS. TIME

N-110

Using the fluoride results and the air flow rate during the sampling a total amount of hydrolyzable fluoride can be calculated. For example, during the first ten minutes of Experiment 1, the average fluoride concentration was 56 ug/m^3. During this time the discharge rate from the heater/air conditioner was 250 cfm, which is 23.2 m^3/min. The total amount of hydrolyzable fluoride lost during the first ten minutes was, therefore:

$$56\ ug/m^3 \times 23.2\ m^3/min \times 10\ min = 13{,}000\ ug = 13\ mg$$

This procedure can be repeated for every sampling period, and the results can be summed over the duration of the experiment. This analysis shows that 116 mg of hydrolyzable fluoride was released during Experiment 1. During Experiment 2, 220 mg were released, and during Experiment 3, 202 mg were released.

After each experiment the grommets were removed. They were taken to the laboratory and weighed. The total weight loss of the grommets in each of the units was, therefore, obtained. In Experiment 1, 795 mg of TFE were lost, in experiment 2, 1247 mg of TFE were lost, and in Experiment 3, 1022 mg of TFE were lost. The results are presented in Table 26, along with the total amount of hydrolyzable fluoride released during each of the experiments. The table also presents the percentage of the fluorine lost from the grommets which appears as hydrolyzable fluoride. Given the variability of the air stream, the results are remarkably consistent. Between 19.2 and 26.0 percent of the fluoride lost appears as hydrolyzable fluoride.

C. Phase III - Shelter Investigation, Sampling Conducted at Fort Bliss, Texas 20 - 21 January 1983

Activities conducted previous to this sampling trip to Fort Bliss, Texas indicated that decomposition products were observed when TFE grommets were exposed to high heat conditions. The major decomposition

TABLE 26

PERCENT CONVERSION OF TFE TO HYDROLYZABLE FLUORIDE

Experiment	TFE Lost	Fluorine Lost	Hydrolyzable Fluoride Found	Percent Fluoride Accounted for
1	795 mg	604 mg	116 mg	19.2
2	1247 mg	948 mg	220 mg	23.2
3	1022 mg	778 mg	202 mg	26.0

products were measured as hydrolyzable fluoride using a NIOSH approved sampling and analysis methodology. Previous to this Phase III investigation, Phase I was conducted at Versar's laboratory to determine the decomposition products of TFE grommets and which sampling and analytical methods would be applicable to provide the necessary information to direct proposed activities in Phases II and III. The results of Phase I provided sufficient information to perform the Phase II bench study on a free standing heater/air conditioner at VSE's facility. During Phase II, Versar monitored for the decomposition products of TFE using the sampling and analysis method specifically developed for hydrolyzable fluoride along with the use of the M8 chemical agent alarm. A complete description of the Phase I and II activities is provided in Sections IV.A and B.

The objective of the Phase III field investigation conducted Fort Bliss in an ICC shelter was the following:

- Determine air movement in the shelter under several operating conditions and proper heater/air conditioner operation with respect to high and low heat modes.

- Perform on-site analytical determinations of hydrolyzable fluoride concentration in the ICC shelter and provide a relationship between hydrolyzable fluoride levels and the real-time monitor, M8 chemical agent alarm.

- Attempt to duplicate shelter conditions and heater operation similar to those reported by Raytheon Corporation in April 1982 when original incident occurred, and by Fort Bliss personnel when the November incidents occurred.

Sampling

Versar's sampling and analytical personnel arrived at Fort Bliss, Texas at 0800, 20 January 1983 and were taken to Abernathy park where an ICC shelter was made available for our testing for the next two days (the ICC shelter is configured similarily to a CRG shelter; the ICC shelter has two PATRIOT Heater/Air Conditioners rather than one as in the CRG). A physical inspection of the ICC shelter was made as follows:

PATRIOT Heater/Air Conditioners

- SN 80104 (curbside) - no TFE grommets in position; inside of heater box appeared in good condition and no aluminum shielding missing or damage to black foam; and tygon drain tubing on fresh make-up air side burnt.

- SN 801163 (roadside) - no TFE grommets in position; no other inspection performed because heater was not to be operated in a heating mode during tests.

- Inside ICC shelter, dimensions were taken of exhaust and return air ducts and a traverse was set-up on each to perform air velocity determinations. Shelter has an internal "air conditioned" volume of approximately 8 cubic meters (280 cubic feet). The dust filter on the return air duct was dirty; however, all other physical features appeared similar to the previous inspection in November 1982.

Sampling activities were begun on 20 January 1983 at 1000 and completed by 1230 on 21 January 1983. Air samples for hydrolyzable fluoride were collected and the M8 chemical agent alarm was operated during all phases of heater operation. Versar collected 67 air samples and 68 blank samples which were analyzed on-site, and determined air velocities during each testing phase. The two M8 chemical agent alarms were operated by Sgt. Lee of the Fort Bliss NBC school. The following tests were conducted:

Test #1: Curbside unit high heat; roadside unit off; make-up air open; no TFE grommets; duration - 60 minutes.

Test #2: Curbside unit high heat; roadside unit off; make-up air open; new TFE grommets (set #1); duration - 120 minutes.

Test #3: Curbside unit high heat; roadside unit off; make-up air open; no TFE grommets; duration - 60 minutes.

Test #4: Curbside unit high heat; roadside unit off; make-up air closed; new TFE grommets (set #2); duration - 120 minutes.

Test #5: Curbside unit high heat; roadside unit low heat; no heater rods on; make-up air open; new TFE grommets (set #3); duration - 90 minutes.

Test #6: Repeat of Test #5, but with new TFE grommets (set #4).

Test #7: Curbside unit high heat; roadside unit low heat; no heater rods on; make-up air open; no grommets; duration - 30 minutes.

A discussion of the hydrolyzable fluoride results and air flow data will be presented in the next section. The two M8 chemical agent alarms were operated continuously during all testing. The M8s alarmed during Tests #5 and #6 only. These two tests were conducted with the ICC shelter in an operating mode that is similar to the way the shelter should be operated under normal field conditions. During Test #5, the M8s sounded from +9 minutes to +19 minutes with exhaust temperature from 106°F to 114°F. At +19 minutes, the heater cycled to low heat and the alarms ceased. During Test #6, the M8s began alarming at +8 minutes and continued to +32 minutes. The exhaust temperatures ranged fro 108°F to 128°F. At the high temperatue of 128°F and +32 minutes, the heater cycled to low heat and the M8s stopped alarming. During both tests, after the heaters cycled to the low heat mode, the M8 chemical agent alarm was not heard again. A further discussion of the results will be presented in the next section.

Results of Sampling at Fort Bliss, Texas 17 - 18 January 1983

Samples were collected in an ICC shelter at Fort Bliss, Texas. They were analyzed on-site for hydrolyzable fluoride using NIOSH Method P&CAM 117. The temperature in the shelter, the air flow in the shelter, and the weight loss of the TFE grommets were also measured. Finally, we tested the M8 chemical agent alarm to see if it could detect the products of decomposing TFE at low enough concentrations.

Air Flow Results

Air flows in the shelters were measured with a hot wire anemometer. The results are presented in Table 27. The exhaust and return flows were measured at six points across the appropriate ducts. The results in Table 27 are the averages of multiple determinations. The make-up air was measured at the opening of the fresh air intake duct. The results indicate that there is some other source of fresh air to the heater/air conditioners. That is, the sum of the return air and the make-up air flows is less than the exhaust flow. Additional fresh air could possibly enter the heater/air conditioner through two locations. First, the CB filter leads to the fresh air intake. If the filer was on or if it was leaking, extra fresh air could enter which would not be reflected in the measurements. Second, leaks can occur at the point where the heater/air conditioners are attached to the front of the shelter. According to Robert Sherfy (VSE), there is a foam rubber gasket at this connection which could possibly leak. Make-up air flows are much lower than expected, while the flows for the exhaust air and the return air are close to the expected values. Table 27 also includes a calculated make-up air flow. This flow is the difference between the exhaust air flow and the return air flow. In order to define the discrepancy, more detailed air flow measurements need to be made. For the purpose of this work the calculated make-up air values will be used.

Grommet Weight Loss

Before the grommets were taken to Fort Bliss, Texas they were weighed individually and placed in separate containers. After use in the heater/air conditioners, they were again put in separate containers and taken back to the laboratory to be weighed. The weight loss of the four sets of grommets used in presented in Table 28. These four sets of grommets were used in Experiments 2, 4, 5, and 6.

TABLE 27

AIR FLOW RESULTS (cfm)

	Exhaust	Return	Make-up	Calculated Make-up
Experiment #2	574	270	50	324
Experiment #4	486	317	Closed	169
Experiment #5 (2 units operating)	920	552	60	369
Per Unit	460	276	60	184
Experiment #6 (2 units operating)	918	505	65	413
Per Unit	459	252.5	65	206.5

TABLE 28

WEIGHT LOSS

Experiment #2	980 mg
Experiment #4	430 mg
Experiment #5	1725 mg
Experiment #6	2468 mg

Fluoride Results

The data from the fluoride analyses are presented in Tables 29 through 34. In every sampling period three replicate samples were collected. All three results, and the average of the three results are presented in the tables. One sample in every twenty was randomly selected as a quality control sample. One portion of this sample was analyzed as usual, one portion was analyzed as a duplicated, and one portion was spiked with a known amount of fluoride and analyzed. All of the duplicate analyses were identical. The spiked samples gave between 74 percent and 86 percent recovery of fluoride. A blank was analyzed with every sample. Most of the blanks and all of the samples of air outside the shelter had non-detectable amounts of fluoride. In a few experiments some blanks had detectable fluoride, but the amount of fluoride in the blanks was always at least five times lower than the sample with the lowest concentration. The low levels of fluoride in a few of the blanks are, therefore, not a cause for concern. Table 29 through 34 also include the total weight loss of the TFE grommets, the conditions of the experiments, and the duration of the experiments.

The heater/air conditioners did not have TFE grommets installed during Experiments 1 and 3. As expected, the hydrolyzable fluoride levels in these experiments were extremely low. In Experiments 2, 4, 5, and 6, the heater/air conditioners did have TFE grommets installed. In these experiments, every sample collected contained hydrolyzable fluoride. The maximum concentration of hydrolyzable fluoride was always found during the first thirty minutes of operation. The maximum fluoride concentration found in each of the experments is presented in Table 35. Table 35 also includes the weight loss of the grommets and the conditions of the experiments. The maximum fluoride levels for the experiments range from 48 ug/m^3 to 448 ug/m^3. As previously mentioned, other publications[3] indicate that decomposing TFE may cause symptoms of

TABLE 29

FLUORIDE RESULTS, TEST #1, NO GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	ND	ND	ND	ND
30-60	ND	ND	ND	ND
0-60	ND	ND	ND	ND

All Blanks had ND.

Detection Limit - 2 ug/m^3.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 30

FLUORIDE RESULTS, TEST #2, WITH GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	60	60	66	62
30-60	16	12	12	13
0-60	64	45	81	63
60-120	8	7	7	7

All Blanks had ND.

Detection Limit - 2 ug/m^3.

Grommet weight loss - 980 mg.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 31

FLUORIDE RESULTS, TEST #3, NO GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	6	6	8	7
30-60	ND	ND	ND	ND

All Blanks had ND.

Detection Limit - 2 ug/m^3.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 32

FLUORIDE RESULTS, TEST #4, WITH GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	51	44	48	48
30-60	31	18	18	22
0-60	40	43	53	47
60-120	15	15	13	14

All Blanks had ND.

Detection Limit - 2 ug/m^3.

Grommet weight loss - 430 mg.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 33

FLUORIDE RESULTS, TEST #5, WITH GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	287	270	260	272
30-60	40	38	41	40
0-60	184	175	175	178
60-90	24	19	24	22

Highest Blank had 9 ug/m^3.

Grommet weight loss - 1725 mg.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 34

FLUORIDE RESULTS, TEST #6, WITH GROMMETS

Time (minutes)	Sample A	Sample B	Sample C	Average
0-30	395	492	457	448
30-60	106	90	88	95
0-60	327	336	327	330
60-90	39	30	32	34

Highest Blank had 9 ug/m^3.

Grommet weight loss - 2468 mg.

Conditions: Curbside unit on.
Roadside unit off.
Shelter fans off.
Make-up air open.

TABLE 35

MAXIMUM FLUORIDE CONCENTRATIONS

Experiment	Make-up Air	Roadside Unit	Shelter Fans	Maximum Fluoride (ug/m^3)	Weight Loss (mg)
2	Open	Off	Off	62	980
4	Closed	Off	Off	48	430
5	Open	On	On	272	1725
6	Open	On	On	448	2468

polymer fume fever when the concentrations of hydrolyzable fluoride are approximately 50 ug/m^3. This indicates that the hydrolyzable fluoride levels found in the ICC shelter are unacceptably high.

Figures 48 through 51 are plots of the fluoride concentration versus time for Experiments 2, 4, 5, and 6. In every case the highest fluoride levels are observed in the first thirty minutes. This initial peak of fluoride is followed by a sharp decline.

Interpretation Of Results

The results of the Fort Bliss, Texas experiments clearly show that the TFE grommets release unacceptable amounts of decomposition products into the air of the PATRIOT ICC shelter. Based on the Phase I (laboratory) and Phase II (YSE) experiments, this was the expected result. The data did, however, contain a number of surprises.

While planning the experiments, we thought that the fluoride concentrations would be highest when the make-up air flow was lowest as it was in Experiment #4. The make-up air should dilute the decomposition products, so we assumed that blocking the make-up air would be the worst case. In fact, it was the best case. The results from these experiments show that the fluoride concentrations are highest when the heater/air conditioner and the shelter are operated exactly as they are designed to operate. The worst case situation appears to be the normal operating condition. This observation is discussed in the following paragraphs.

A portion of the exhaust air from the PATRIOT Heater/Air Conditioners is recycled internal air from the ICC. When TFE grommets are installed in the units, the recycled air is already contaminated with hydrolyzable fluoride. We expected, therefore, that the concentration of hydrolyzable fluoride would increase as the percentage of recycled air increased. In fact, exactly the opposite occurred. Table 36 presents the return air flow, the exhaust flow, the ratio of the two flows, the

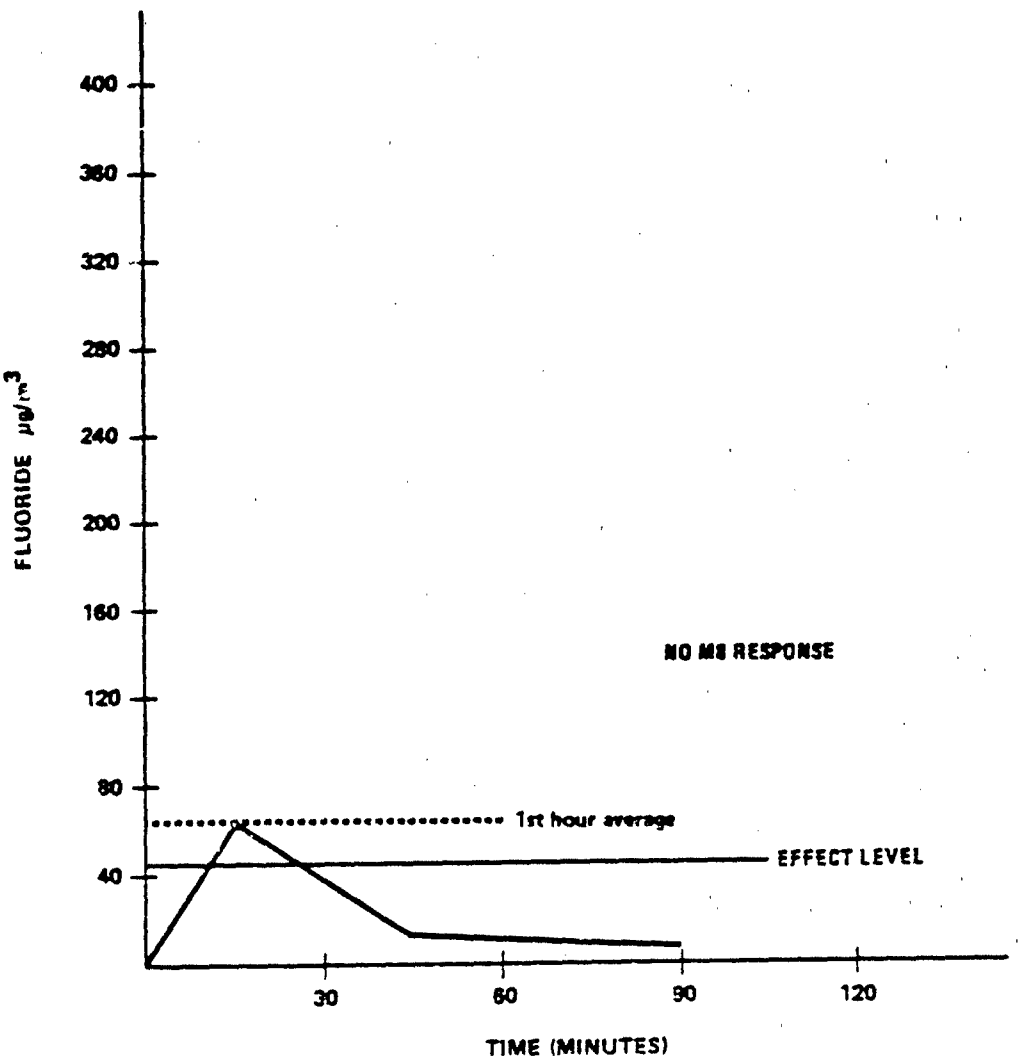

FIGURE 48. FLUORIDE VS. TIME, EXPERIMENT 2

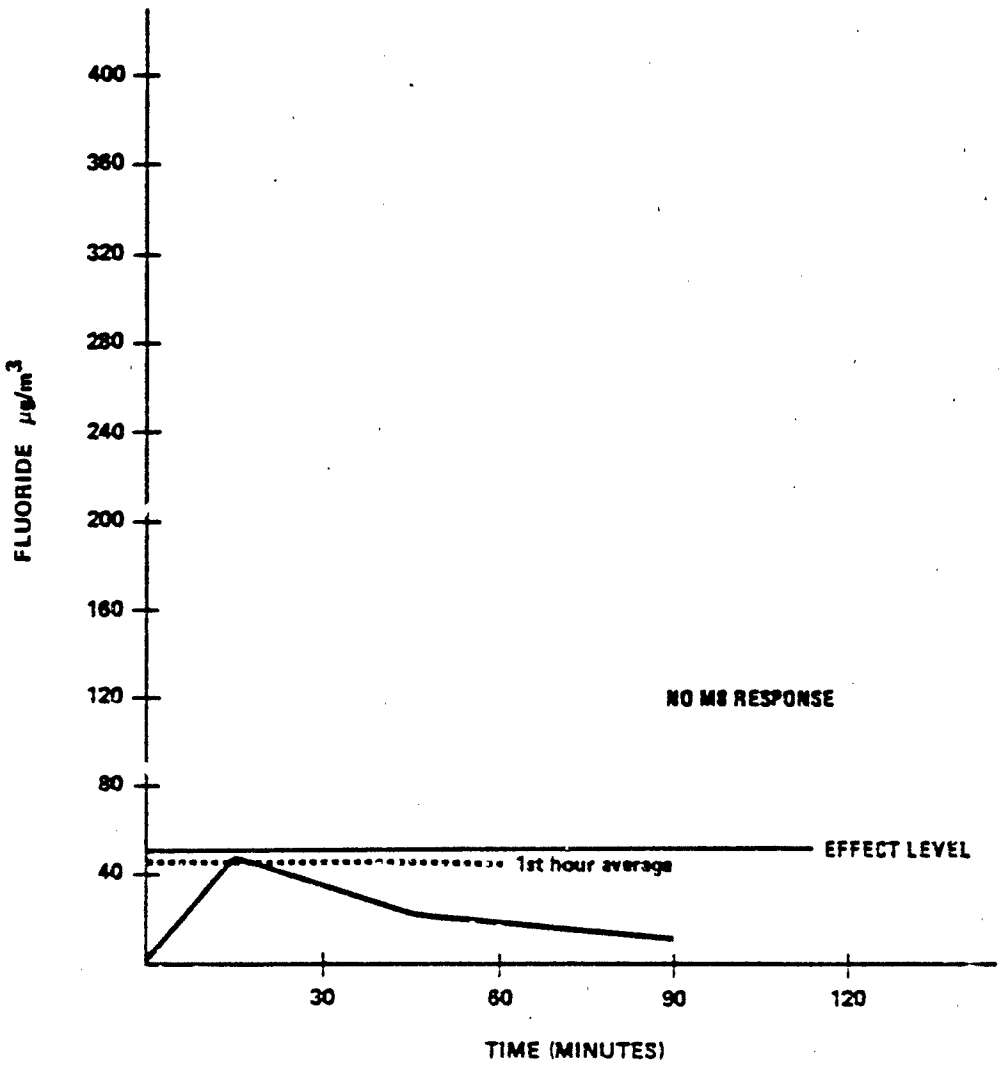

FIGURE 49. FLUORIDE VS. TIME, EXPERIMENT 4

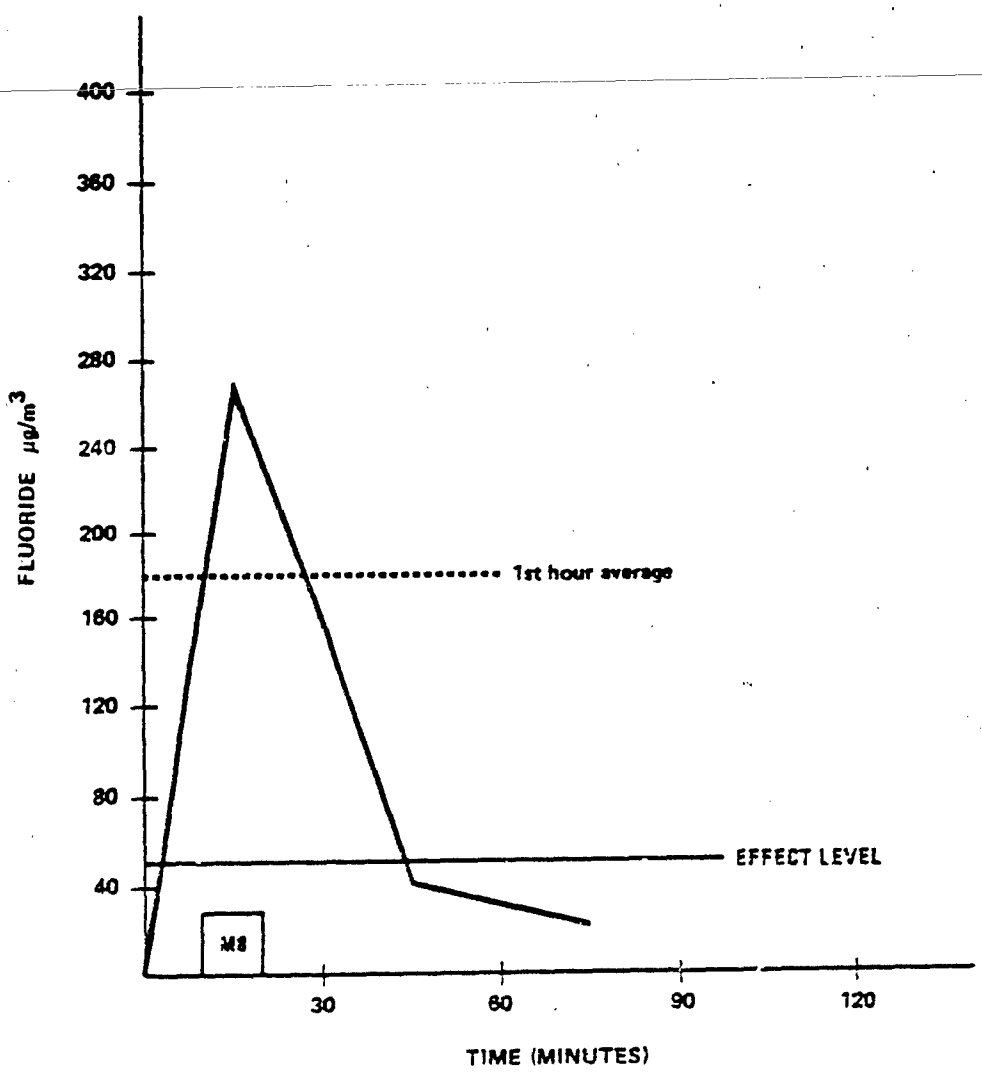

FIGURE 50. FLUORIDE VS. TIME, EXPERIMENT 5

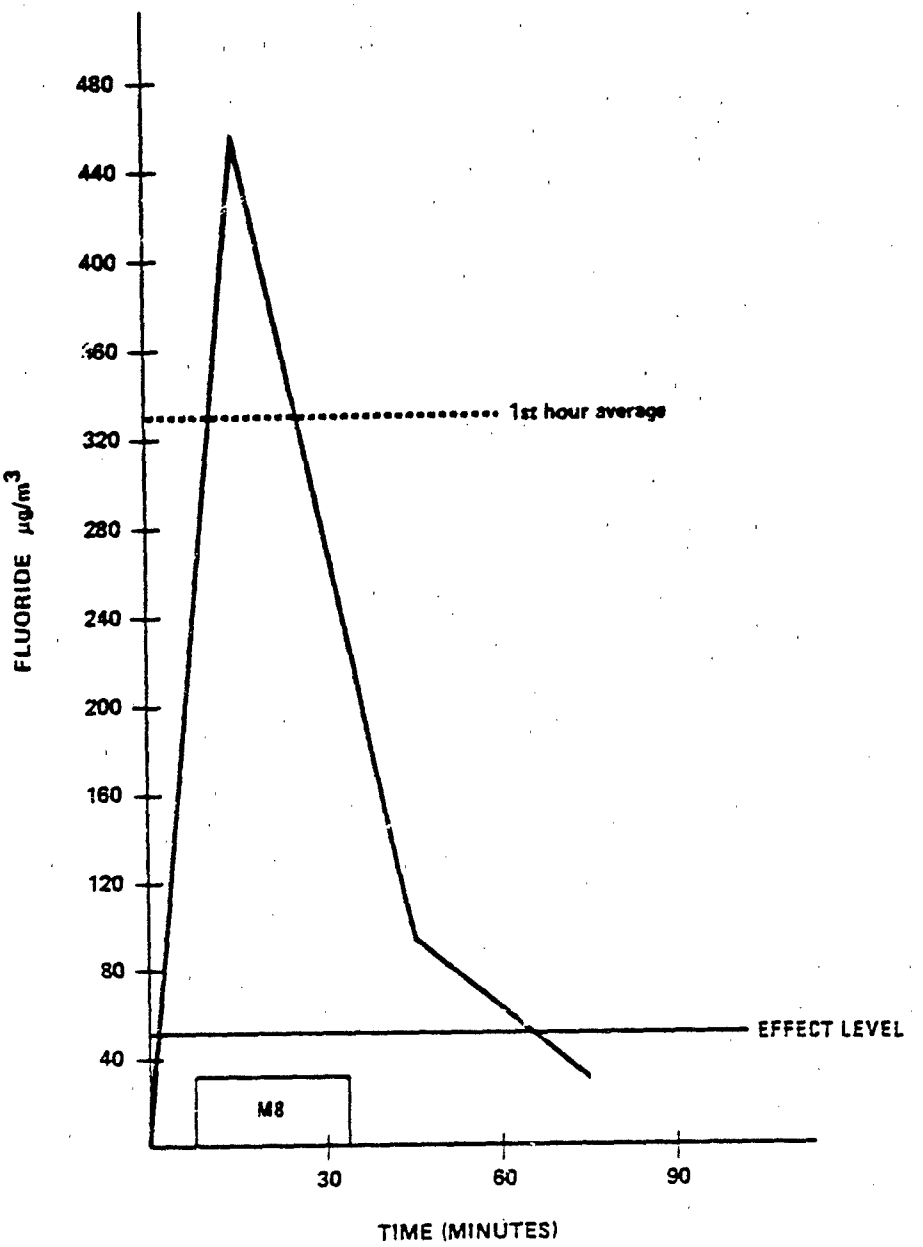

FIGURE 51. FLUORIDE VS. TIME, EXPERIMENT 6

TABLE 36

EFFECT OF RETURN AIR FLOW

	Exhaust	Return	Return Exhaust	Fluoride	Weight Loss (mg)
Experiment 2	570	270	0.47	62	980
Experiment 4	490	320	0.65	48	430
Experiment 5	460	280	0.61	272	1725
Experiment 6	460	250	0.54	448	2468

maximum fluoride concentration found, and the weight loss of the TFE grommets. Experiment 4, with the highest return air flow and the greatest percentage of return air, also has the least weight loss and the lowest fluoride concentrations. In contrast to this, Experiment 6, with the lowest return air flow, had the highest weight loss and the highest fluoride concentration.

Although these results are surprising, we think there is a good explanation for them. The return air in the PATRIOT Heater/Air Conditioners enters the units directly in front of the heating rods. As the return air flow increases, the heating rods are cooled and the TFE grommets are exposed to lower temperatures. When the return air flow decreases, the heating rods get hotter, and the TFE grommets are exposed to higher temperatures. On the other hand, the make-up air does not appear to affect the fluoride levels found. The make-up air enters the units very close to the intake of the squirrel cage fans. This air probably does not pass over the heater rods, so it has no effect on the temperatures that the TFE grommets are exposed to. The highest fluoride concentrations were found when both heater/air conditioners were running, and when the shelter cooling fans were on. This increases the total air flow through the shelter, and increases the dilution of the TFE decomposition products. However, it also decreases the return air flow, and therefore increases the amount of TFE decomposition (weight loss) and the concentration of hydrolyzable fluoride. The cooling fans have the same effect as blocking the return air in Phase II. The exit air temperature is raised and the TFE grommets undergo more rapid decomposition.

Figure 52 presents a simplified schematic of the air flow patterns in the ICC shelter. The instrument panels contain fans which pull air over the electronic components. The fans are designed to maintain a negative static pressure inside the instrument panels. Some

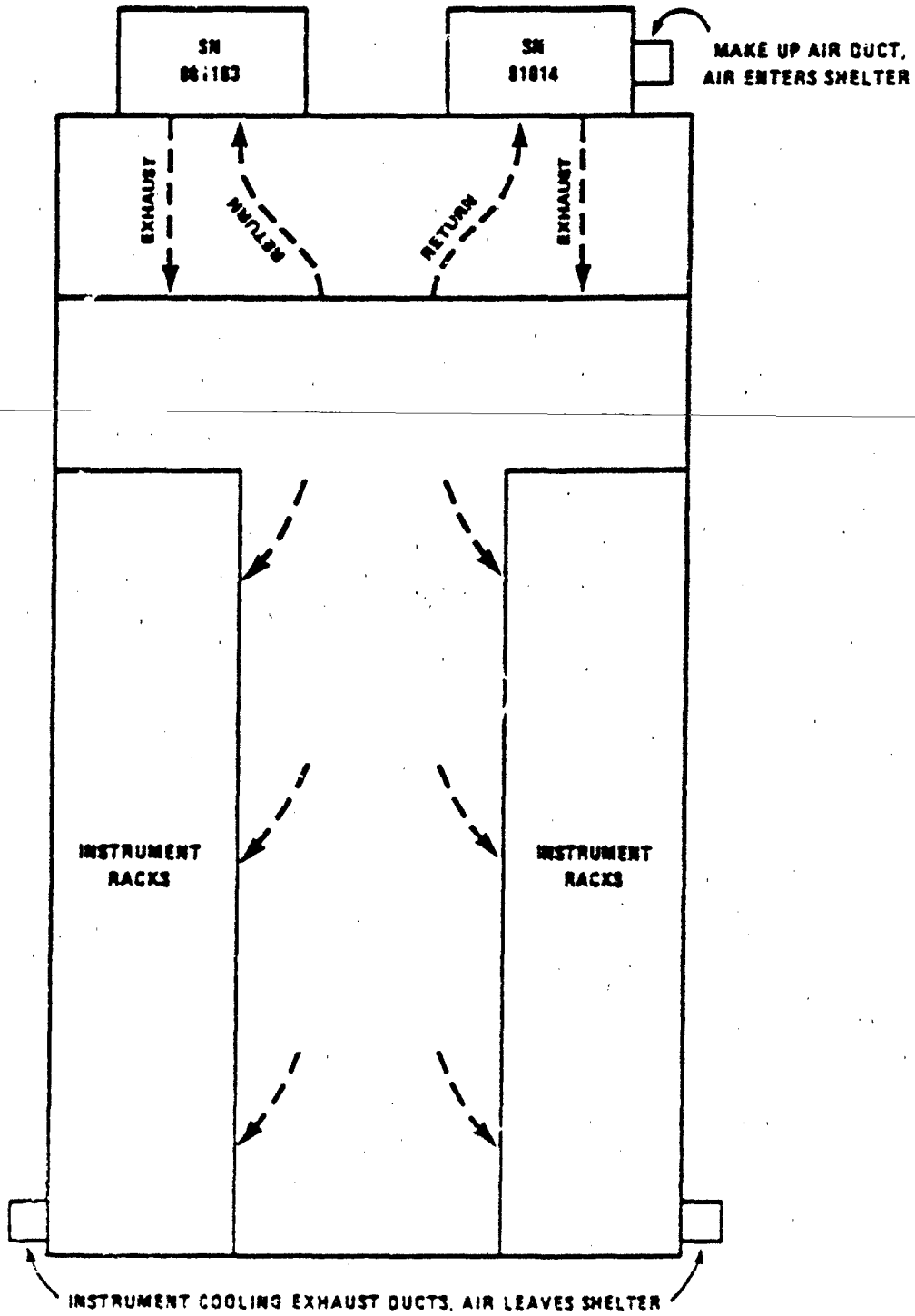

FIGURE 52. AIR FLOW PATTERNS IN ICC SHELTER

of the air which passes through the instrument panels comes from the inside of the shelter. This reduces the static pressure inside the shelter.

Figure 53 shows the effect of the reduced static pressure in the shelter. The return air flow is not fan forced. It is driven by a pressure differential between the interior of the shelter and the inside of the heater/air conditioner. When the instrument cooling fans are turned on, the pressure differential decreases, and therefore the return air flow decreases.

The Phase I and Phase II experiments indicated that 20 percent to 30 percent of the fluoride lost from decomposing TFE appeared as hydrolyzable fluoride. We estimated the percent conversion in the experiments at Fort Bliss using the following procedure. The total weight loss of the grommets was divided by the duration of the experiment to give the average rate of weight loss in mg/min. This was divided by the calculated make-up air flow in m^3/min. This ratio is the average concentration of TFE decomposition products over the duration of the experiment. The average hydrolyzable fluoride concentration in the experiment was divided by the calculated concentration of TFE decomposition products to give a percent conversion of TFE into hydrolyzable fluoride. An example of the calculation is presented in Table 37 along with the percent conversions for the four experiments. The conversions ranged from 4.3 percent to 11.9 percent for the experiments. Given the uncertainties concerning the true air flows, this is reasonable agreement.

Field Exposure Incident

During the testing at Fort Bliss, the access to the ICC shelter was restricted to the Versar sampling personnel and SP5 Carl Wright because of the possible presence of hydrolyzable fluoride during heater

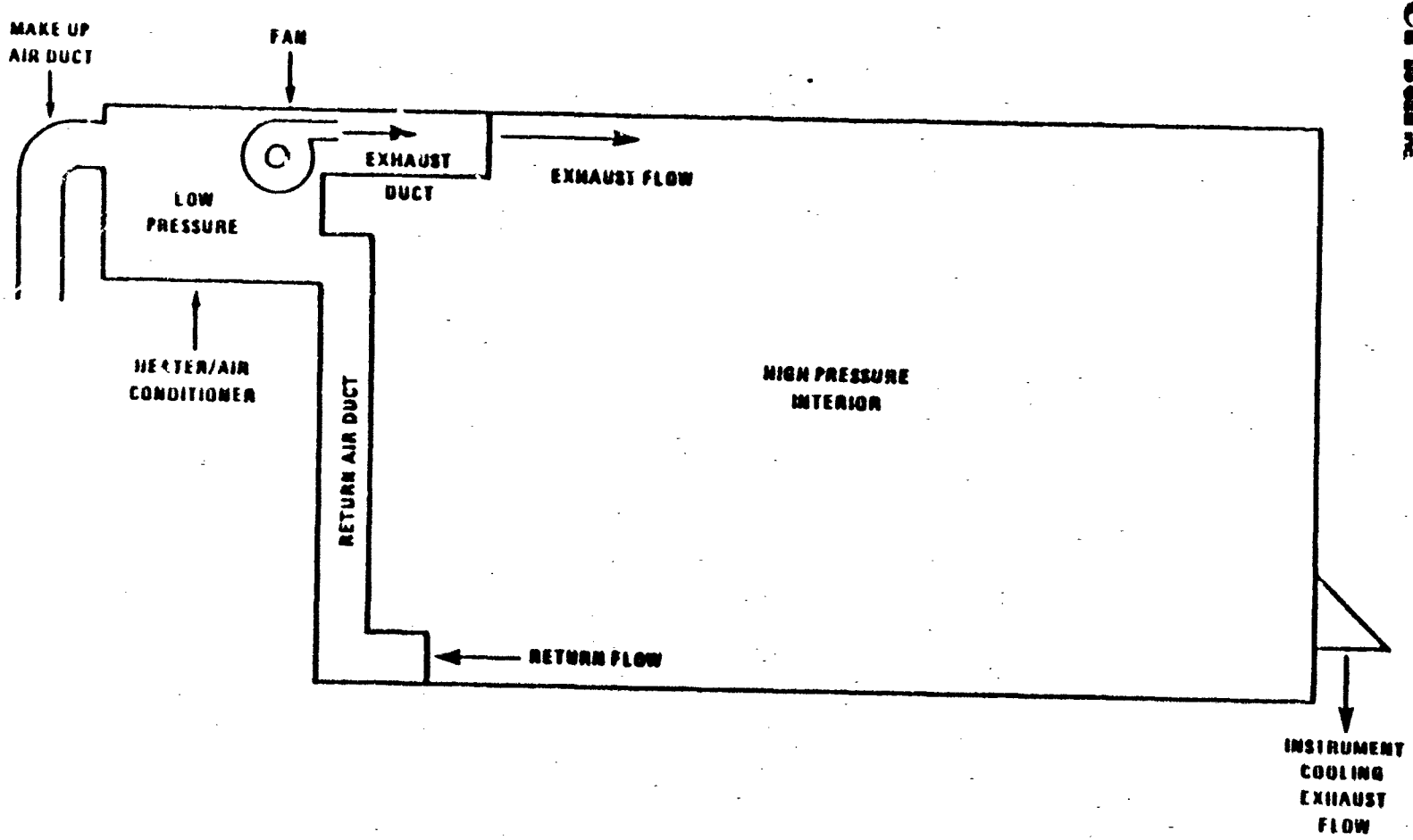

FIGURE 53. INTERIOR PRESSURE AND FLOW

TABLE 37

CONVERSION OF TFE INTO HYDROLYZABLE FLUORIDE

	Average Fluoride Concentration Calculated ug/m^3	Average Fluoride Concentration Observed ug/m^3	Percent Conversion
Experiment 2	676	28.75	4.3
Experiment 4	568	27.6	4.8
Experiment 5	1391	119	8.6
Experiment 6	1778	212	11.9

Example calculation for Experiment 6:

$$\frac{2468 \text{ mg lost} \times \frac{0.76 \text{ mg F}}{\text{mg TFE}}}{90 \text{ min}} = 20.8 \text{ mg/min Fluorine lost}$$

$$413 \text{ cfm} \times \frac{1 \text{ ft}^3}{35.26 \text{ m}^3} = 11.71 \text{ m}^3/\text{min.}$$

$$\frac{20.8 \text{ mg/min}}{11.71 \text{ m}^3/\text{min}} = 1.778 \text{ mg/m}^3$$

$$\frac{212 \text{ mg/m}^3 \text{ found}}{1778 \text{ mg/m}^3 \text{ calculated}} \times 100 = 11.9 \text{ percent}$$

operation. Persons entering the ICC shelter during most testing phases wore protective breathing apparatus. The protective apparatus used was a half face respirator (Mine Safety Appliance type "Confo II Custom Respirator") equipped with cartridges that are approved respiratory protection for acid gases and organic vapors (cartridges produced by Mine Safety Appliance)

On 20 January 1983, during testing conducted in the ICC, Mr. John Richards and SP5 Carl Wright entered the shelter for several short periods (2-9 minutes) without respiratory protection during the time when the TFE grommets were exposed to high heat and the possibility existed for personnel exposure to airborne hydrolyzable fluoride. Figure 54 presents the levels of fluoride and the duration of exposure to fluoride either with (indicated by a letter Y) or without (indicated by a letter N) respiratory protection. For visual clarity the point for zero ug/m^3 of hydrolyzable fluoride is raised above the X axis in Figure 54. The exposure to fluoride apparently occurred during Test #2 (new TFE grommets) when levels of fluoride were below the 50 ug/m^3 level. The hydrolyzable fluoride concentrations were less than 20 ug/m^3 during all exposure periods where respiratory protection was not used. Approximately three hours after the first exposure both Mr. Richards and SP5 Wright began experiencing some mild adverse health effects, which began with a tightness in the chest and coughing. The coughing was shallow. It was uncomfortable to cough deeply. The tightness in the chest persisted for approximately one hour while the coughing lasted for another 2-4 hours. Approximately four hours after the initial exposure, both Mr. Richards and SP5 Wright felt body chills that lasted for 2-4 hours. Mr. Richards had a loss of appetite that evening, although SP5 Wright did not experience the same loss. Both persons went to bed early that evening and felt fine the next morning without any after-effects from the apparent exposure on the previous day.

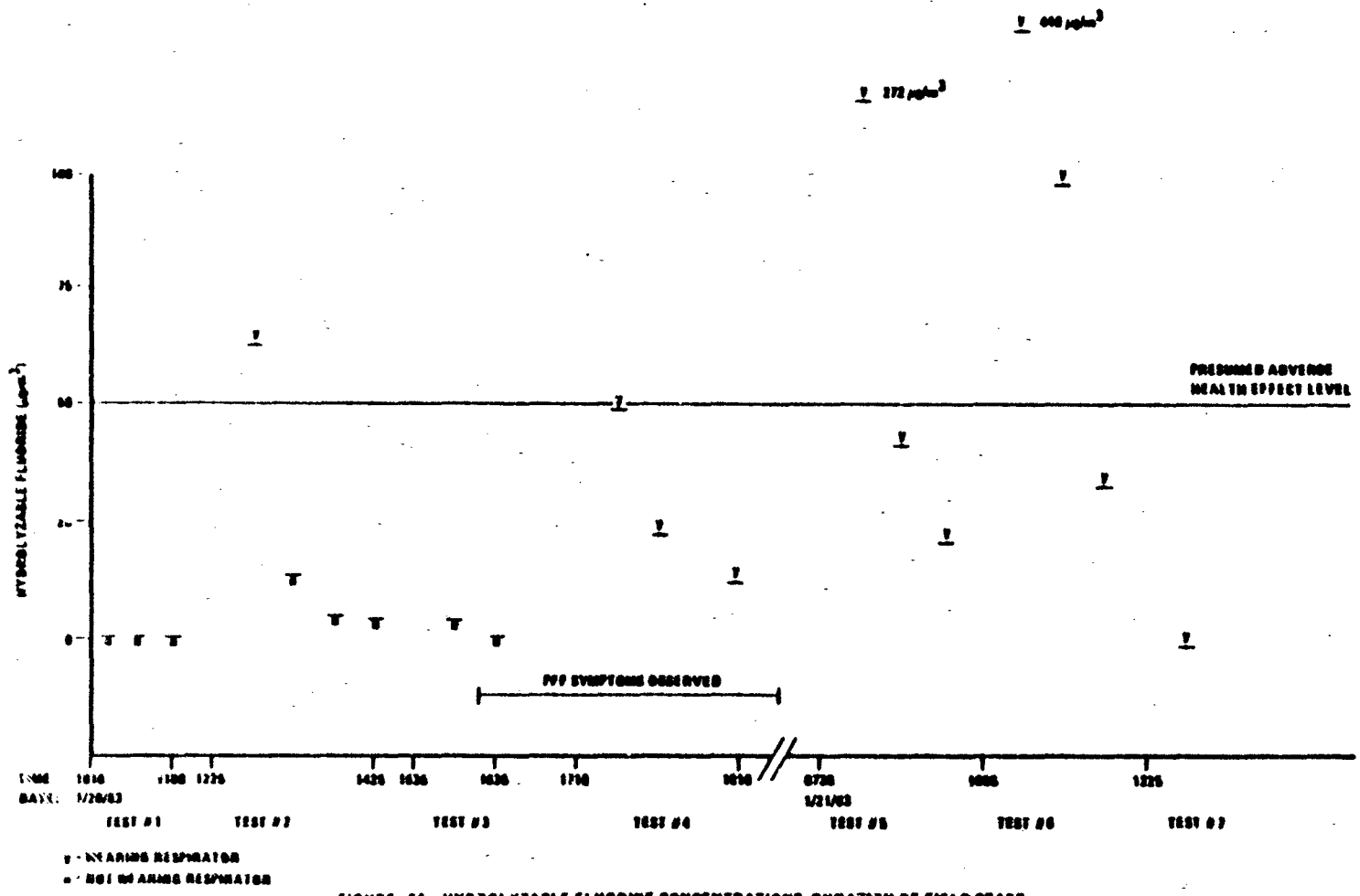

FIGURE 54. HYDROLYZABLE FLUORINE CONCENTRATIONS, DURATION OF FIELD STAFF EXPOSURE AND OCCURRENCE OF POLYMER FUME FEVER (PFF) SYMPTOMS IN THE ICC SHELTER DURING TESTS CONDUCTED 20-21 JANUARY 1983.

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During the day the incident occurred, both Mr. Richards and SP5 Wright were exposed to similar environmental factors, although Mr. Richards may have had a 5-10 minute longer exposure period in the ICC shelter than SP5 Wright. It should be noted that during the day both men had worked outside on a rainy cold (40°F), windy day for two 1.5 hour periods. During that day, both men were exposed to the high temperature conditions inside the shelter and quickly exposed to the coldness outside. Although these conditions may have created the chill feeling they experienced, the other conditions are remarkably similar to related incidents of exposure to TFE breakdown products, referred to as Polymer Fume Fever (PFF). In summary, the exposure period to hydrolyzable fluoride was of short duration, and the levels of fluoride were well below 50 mg/m^3, but both men appeared to experience the typical reactions of exposure to TFE breakdown products.

On 20 January 1983, three other people participated in the sampling and analysis: Dr. C. Carter and Mr. J. Foster of Versar, and Sgt. Lee of the Fort Bliss NBC school. None of them had any PFF symptoms. Dr. Carter and Sgt. Lee never entered the shelter when TFE grommets were installed. Mr. Foster did enter the shelter, but he always wore respiratory protection.

Conclusions

All three phases of this experimental endeavor strongly indicate that the incidents at Fort Bliss in early November were caused by exposure to the decomposition products of TFE grommets. The Phase I laboratory experiments showed that grommets from the PATRIOT Heater/Air Conditioner will decompose when placed on heater rods from the PATRIOT Heater/Air Conditioners. A multitude of decomposition products are produced, many of which are known to be hazardous. The Phase I experiments showed that 20 percent to 30 percent of the weight loss of the grommets was converted to hydrolyzable fluoride. The experiments

also showed that hydrolyzable fluoride measurements could be used as a sensitive indicator of the presence of decomposing TFE.

The Phase II experiments showed three things. First, the PATRIOT Heater/Air conditioners did release substantial quantities of hydrolyzable fluoride when grommets were installed. The levels of hydrolyzable fluoride found were, in some cases, high enough to possibly cause symptoms of polymer fume fever. Second, the amount of decomposition of the TFE grommets was highly dependent on the return air flow. As the return air flow decreased the amount of decomposition increased. Third, the M8 chemical agent alarm did respond to the decomposition products of TFE, but only at levels which are higher than 50 ug/m^3 (Figures 46, 47). Other authors[3] have observed symptoms of polymer fume fever at hydrolyzable fluoride concentrations around 50 ug/m^3.

The Phase III experiments showed conclusively that the PATRIOT Heater/Air Conditioners release unacceptable quantities of TFE decomposition products into the PATRIOT shelters when TFE grommets are installed. The concentration of decomposition products inside the shelter appears to increase as the return air flow decreases. Furthermore, the concentrations are highest when the shelter air handling system is operated exactly as designed.

The Phase III sampling also showed conclusively that the M8 chemical agent alarm was not sensitive enough to serve as an alarm for decomposing TFE. In experiments 2 and 4, the hydrolyzable fluoride reached a maximum of 62 and 48 ug/m^3 (Figures 48, 49). The M8 chemical agent alarm did not respond during either of these experiments. During these experiments, two of the members of our sampling team temporarily removed their respirators. Shortly thereafter, they developed mild symptoms. In Experiments 5 and 6, the hydrolyzable fluoride reached a maximum of 272 and 448 ug/m^3. The M8 chemical agent did respond, but after the hydrolyzable fluoride was well above 50 ug/m^3 (Figures 50, 51). In addition, it stopped responding at concentrations much higher than 50 ug/m^3.

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3. Dwiggins, G.A., M.C. Wiggins, Jr., M.J. Dwyer, "Exposure to Polytetrafluoroethylene Decomposition Products During the Initial Use of Some Pad Heaters", AIHA Journal, pp 319-321 1981.

4. American Conference Governmental Industrial Hygienists, "TLVs Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1982."

APPENDIX I

NEIL JURINSKI TRIP REPORT

NU CHEMCO.

RECEIVED

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APPLIED CHEMISTRY DIVISION

TRIP REPORT

Staff: Neil B. Jurinski and John Richards
Date: 8-9 November 1982
Site: Fort Bliss, El Paso, TX

PURPOSE: To conduct interviews with individuals reporting adverse health effects associated with work activities in shelter units equipped with Keco Industries heating/air conditioning (H/AC) units.

BACKGROUND: Prior events have given indications of the production of a toxic material during use in the heating mode inside the shelters equipped with these H/AC units. It was not known whether the high heat, low heat or both modes of operation were involved.

Extensive sampling and analysis of the suspect units to collect and identify toxic airborne contaminants had given negative results for the presence of significant levels of cyanides, carbon monoxide, carbon dioxide, sulfur dioxide, inorganic fluorides and organic vapors. Low levels of benzene and toluene were observed. One laboratory reported the presence of acrolein in one set of samples. High temperature testing of samples of the materials of construction from the unit gave no positive results to explain the reported health effects.

PRESENT ACTIVITY: A series of unrelated exposures of seven individuals occurred at Fort Bliss, TX over a period of approximately two weeks. Six of the individuals concerned were assembled and interviewed, first individually and then collectively, to assemble the reports of symptoms and to determine any commonality. The following persons were interviewed:

Mr. Daniel J. Young, 44, former smoker, Raytheon
Mr. Philip Kennedy, 32, smoker, Raytheon
Mr. Gary A. Talbot, 35, smoker, Raytheon
SGT Donald B. Olson, 34, non-smoker, DA
SP5 Carl A. Wright, 24, non-smoker, DA
CW2 Henry L. Haberkamp, 35, pipe smoker, DA

One individual, Mr. Mazzochi (Civil Service), was not available due to a previously scheduled, unrelated medical appointment. Reports of their individual statements are appended.

As a result of considering the separate reports plus the comments from the group session, the following generalizations may be made concerning the nature and presence of a toxic agent.

1. There appears to be sufficient evidence to state that one or more toxic chemical substances are produced and released to the air while using the heating mode of operation of the H/AC unit.
2. The material(s) produced can be generated during the low heat mode of operation.
3. The material(s) may be produced rapidly and exhibits its toxic effects rapidly, possibly within 3-5 minutes in some cases.
4. Susceptibility to the materials varies between different individuals.
5. Human recognition of the presence of the material(s) may occur by odor, but not all affected persons noted an odor. Coughing and dryness of throat are the most commonly reported effect first noted.

6. In most cases interviewed there was not a report of irritation or burning sensation. No eye, nose, throat, larynx, chest or skin irritation was reported, except by one individual who reported burning eyes and throat but no other effects. No vision problems were reported.
7. Other common symptoms reported by more than one person were severe headaches, chest pains described as tightness across the upper chest, and inability to sleep normally or sleeplessness.
8. One individual did not report sensing any immediate effects, and had been in the shelter for approximately four hours during heater usage. His symptoms included severe headaches and chest pains lasting for 2 days following his exposure. Subsequently he developed a feeling of nausea, lack of appetite and constipation. In addition he experienced lightheadedness and a sense of disorientation. These symptoms gradually diminished with time, but some still persisted on the day of the interview (6 days following exposure). A biological source of these symptoms can not be eliminated.
9. Similar symptoms were noted by persons working in other shelter enclosures equipped with the same type of H/AC units.
10. Persons having short exposure periods recovered from their perceived symptoms within a short period. Persons with longer duration exposures had persistent, long duration effects.
11. Headaches were developed by persons with longer duration exposures. Since these exposures were not perceived in any way, it may be indicative of a longer term, lower concentration exposure period.
12. Sleeplessness was a common symptom reported by those exposed briefly as well as those with longer term exposures.

An inspection of the H/AC units was performed in several of the units reported involved in producing symptoms. Only the heater section of the H/AC units was inspected. Two different types of defects were observed during the physical inspection of the ICC shelter: heater rod deterioration and teflon grommet damage.

In the roadside unit approximately one third of the heater rods showed visible signs of deterioration. The surface layers were a mottled color and the surface was pitted and irregular over approximately half their length. The remainder of the rods had an [illegible]n colored appearance and showed no visible signs of damage. The damaged rods had a fine-particle layer of brown solid material that could be easily wiped off the surface. A slight odor was associated with this fine-particle substance.

Teflon grommets used to position the heating rods within their metal frame were also noted as damaged. Some grommets were loose and easily rotated, some were partially melted, and at least one was completely missing. Damage to grommets was evident in both the road side and the curb side units.

Subsequent to the physical inspection of the H/AC units of the ICC shelter, an inspection was made of the H/AC units on the nearby CRG shelter, the scene of earlier complaints. The same type of damage to teflon grommets was noted in the CRG shelter as in the ICC shelter. No damage to heating rods was noted in the CRG shelter.

SPECULATIONS: Based upon the previously mentioned reports and observations, several speculations may be proposed to assist in obtaining a solution to this problem during further investigations.

1. One or more toxic material(s) are released during heater operation due to pyrolysis of the teflon polymers of the grommets.
2. At least one acutely toxic substance is released. Observed physiological symptoms correlate well with literature reported symptoms of carbonyl chloride (phosgene) and it is quite possible that carbonyl fluoride is the material in question.
3. Other organic fluoride compounds may be released in addition to carbonyl fluoride, however it is unlikely that significant amounts of hydrogen fluoride or fluorine are contained in the off-gas products of decomposition due to the general lack of reported irritation.
4. Verification of the nature of the toxic contaminants through sampling and analysis should concentrate on the determination of the teflon decomposition products. Since pyrolysis reactions may release different compounds at different conditions of time and temperature, care in defining a sampling protocol is needed to avoid missing the temperature zone of interest during the sampling phase.

RECOMMENDATION: In the future, any person known to receive an exposure to these substances should be referred to a physician for observation for carbonyl halide exposure and checked for the possible development of pulmonary edema.

Neil B. Jaworski 11/12/82

INDIVIDUAL EXPOSURE REPORT

Subject: Mr. Daniel J. Young, Raytheon Corp., age 44, former smoker.

Date of Incident: approximately 26 October 1982 (2 weeks ago).

Summary of the Scene: On the day of incident, 4 other persons were in the shelter but showed no effects. People were engaged in software work and did no activities to generate any contaminants. Subject was dressed with a tie and short sleeve shirt. Outside weather was dry and sunny, temperature about 40°F, outside air pollution level was about normal, time was about 9 AM. Both heaters were on low heat.

Effects Noted: Upon entering the shelter he closed the door, turned around and immediately began coughing. The cough was a high cough, as if something was stuck in the throat. He was standing directly in the air stream from the H/AC units in front of the rear door. His throat was very dry, and he had trouble sustaining his breath. After staying about 4-5 minutes, he couldn't stop coughing and left the shelter. Once outside he stopped coughing in about 1-2 minutes. Since that time he has noted a problem sleeping, but can not be sure that this is related to the incidence. He recalls having a sharp headache across the rear crown of his head, and reports that he seldom gets headaches. He did not seek medical attention since the coughing stopped so rapidly.

Other Observations: Other persons in the shelter did not appear to experience any symptoms of which he was aware. An odor or fragrance was noted that he described as "sweet", but he could not further identify it. At the present time he felt that he was fighting an allergy or possibly something "...related to pollen".

INDIVIDUAL EXPOSURE REPORT

Subject: Mr. Philip Kennedy, Raytheon Corp., age 32, smoker.

Date of Incident: 4 November 1982

Summary of the Scene: On the day of incident, 1 other person (G. Talbot) was in the shelter. Both were engaged in software work and did no activities to generate any contaminants. Subject was dressed with casual clothing with no restrictions around neck. Outside weather was dry and sunny, temperature about 45°F, outside air pollution level was moderate, time was about 7 PM. Both heaters were on low heat with maximum setting.

Effects Noted: Within 4-5 minutes of turning on the heater (low heat, maximum setting) he noted a dryness in the throat and his mucous membranes. He also had an irritation of the eyes and throat, but did not experience coughing. He had some blinking and watering of the eyes. His chest felt tight, similar to the feeling you get when you are in a dry sauna. It took about 3-4 hours for the dryness to leave his throat. He reported some difficulty in sleeping at night for that one night. During the subsequent group discussion, he recalled having had a strong headache the week prior to this event, right after having worked inside the ECS unit under similar conditions.

Other Observations: His work partner (G. Talbot) experienced more reaction than he himself did, as indicated by his coughing. He noted an odor like an "electrical element" smell similar to "burned oxide like heated copper", plus some other odor. The odor could not be further described, but was not pleasant. He noted that his "...eyes are not sensitive to CS or tear gas." No medical attention was sought. He did not necessarily relate the sleeplessness to the effects of exposure, but thought it might be due to some anxiety. He is aware that he has some allergies and so wasn't worried by his symptoms. After the first event, the heaters were turned up to maximum heat to "burn in the heater" for about one hour while the two went to dinner. Upon return, the shelter was vented and they continued work. He had no effects at the time of re-entry.

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INDIVIDUAL EXPOSURE REPORT

Subject: Mr. Gary A. Talbot, Raytheon Corp., age 35, smoker.

Date of Incident: 4 November 1982

Summary of the Scene: On the day of incident, 1 other person (P. Kennedy) was in the shelter. Both were engaged in software work and did no activities to generate any contaminants. Subject was dressed with casual clothing with no restrictions around neck. Outside weather was dry and sunny, temperature about 45°F, outside air pollution level was moderate, time was about 7 PM. Both heaters were on low heat with maximum setting.

Effects Noted: The primary effects noticed were severe coughing and a chest pain similar in feeling to pleuracy. He also experienced a dryness of throat and difficulty in sleeping. The coughing lasted for about 3-5 minutes after leaving the shelter. Chest pain was noted only when he took a deep breath. On the second time in the shelter (after the high heat period) he reentered and started coughing after 1-1.5 minutes. After venting the shelter he coughed for about 5-10 minutes, then continued to work with the unit on in the air conditioning mode for the rest of the shift. Difficulty sleeping lasted for about 4 nights. The chest pains lasted for about 2 days and then were gone. He experienced some tearing in his right eye. He attributed this to the fact that his right eye has very active tear ducts as a result of former eye surgery on his right eye, and to the extensive coughing which he did. This eye was a little painful, but similar to the effect he notices from cigarette smoke.

Other Observations: His work partner (P. Kennedy) was bothered by irritated eyes, but apparently no other problems. His first idea of any problem was from the coughing. He was not aware of any odor or that the heater had been turned on. He noted a peculiar odor when he stood up from the sitting position in which he was working. This odor resembled the smell from new electrical equipment. He did not receive any medical attention, but had considered seeing a doctor if the chest pain did not subside within another day or two. He has no known allergies.

INDIVIDUAL EXPOSURE REPORT

Subject: SGT Donald B. Olson, US Army, age 34, non-smoker.

Date of Incident: 3 November 1982

Summary of the Scene: On the day of incident he was performing training sessions inside the shelter. He trained 4 groups of 4 students/group, 40 minutes/group during the period from 0830-1330. Approximately 0630 he first entered the shelter and turned both heaters on low heat. By 1030 the air had warmed sufficiently that he turned off the heaters and placed the units in the air conditioning mode for the remainder of the day. The day was a normal day with no severe weather extremes. No high levels of air pollution were remembered. Morning temperature was about 37-40°F. None of the persons in the shelter on that day exhibited any apparent symptoms at the time except for one person, PVT Wilson. Wilson complained after about 10 minutes inside the shelter while the heaters were on, that he felt nauseous and had to leave. He went on sick call for the rest of the day. Wilson had previously shown flu symptoms and thus this event was considered to be related to the prior flu problem. Olson had previously worked inside the trailer on both Monday and Tuesday with no apparent symptoms on those days.

Effects Noted: Olson first noted a headache about 1500 after finishing the training sessions. He described it as a sinus-like headache, across the front of his eyebrows and the temples. That evening it got worse and he laid in bed after dinner from about 2030 to 2230, during which time the pain got worse and was located all throughout his head. He then got up and took an aspirin (an unusual event for him) and shortly felt asleep. The next morning (Thursday) the headache was gone and he went back in the shelter for approximately 1 hour. The heater was not on that day. In the afternoon his headache returned as a dull ache. On this day he started to experience a nauseous feeling, and in the afternoon he noted a catch in his throat, similar to that experienced by draining sinuses. By Friday the nauseous feeling was very pronounced and he doesn't recall whether he had any headache associated with it. On Saturday although he had no headache, the feeling of nausea persisted, but at a somewhat lessened level. By Sunday this feeling had fairly well left. Olson experienced no bowel movements from Wednesday through till Saturday afternoon. During the time of constipation he also experienced stomach cramps. At this time he had a diminished appetite, but otherwise could eat or drink normally. He noted that 30-40 minutes after eating, he experienced sharp pains in the stomach. On Sunday he felt fairly normal. During the period (from Thursday until the Monday interview) Olson felt somewhat highly disoriented. He described it as being unable to concentrate adequately on a task. This feeling has slowly diminished with time, and by 8 November was almost at a normal level, but he felt still somewhat at an impaired level of performance.

Other Observations: No unusual odors were noted, aside from "the normal smell". During the Wednesday training sessions the thermal (hard copy) printer was heavily used and its smell was quite strong. No operations were performed which would have generated any fumes except use of a thermal printer. No apparent signs of a problem were ever noted while in the shelter.

On Friday, a civilian instructor (Mr. Mazocchi) using the shelter reported that he had a headache. He spent considerable time in the van on Friday, but the heaters were apparently not in use on that day except perhaps early in the morning. Olson has no known allergies. He reported that he had received a flu shot in the week of 25 October and subsequently experienced a 102°F fever. Aside from that he had no apparent illnesses.

NU CHEMCO.

INDIVIDUAL EXPOSURE REPORT

Subject: SP5 Carl A. Wright, US Army, age 24, non-smoker.

Date of Incident: 5 November 1982

Summary of the Scene: On entering the shelter at 1430 to test the heaters there were 3 Raytheon people already inside working. Wright and Mr. Haberkamp entered and Wright turned on the two heater units, one to high heat and one to low heat modes. No operations were conducted that would generate contaminants. Raytheon persons were not soldering or smoking, only performing maintenance checks. The outside weather was overcast, about 65°F with no wind and no noticable smog levels.

Effects Noted: Wright was standing in front of the unit trying to smell an odor. He noted some feeling of lightheadedness, which he attributes to his hyperventilating to detect an odor. This feeling arose in 3-4 minutes. He also experienced a dry mouth and running nose in about 5 minutes. The symptoms lasted for approximately 1-1.5 hours, and no lasting effects persist. After 5 minutes in the shelter he turned off the heaters and left the shelter. No other symptoms were noted.

Other Observations: The odor noted was described as similar to a stove heating element. No other odors were noted. Mr. Haberkamp was observed to experience chest tightness. One Raytheon person complained his eyes burned, but during this time the unit was used in the vent mode. One Raytheon man mentioned lightheadedness also. Wright has no known allergies. He did not seek any medical attention.

INDIVIDUAL EXPOSURE REPORT

Subject: CW2 Henry L. Haberkamp, US Army, age 35, pipe-smoker.

Date of Incident: 5 November 1982

Summary of the Scene: On entering the shelter at 1430 to test the heaters there were 3 Raytheon people already inside working. Mr. Haberkamp entered with SP5 Wright. No operations were conducted that would generate contaminants. Raytheon persons were not soldering or smoking, only performing maintenance checks. The outside weather was clear, scattered clouds, about 70°F with no wind.

Effects Noted: After Wright turned on the heaters (left unit on high, right unit on low) Haberkamp went to rear of ICC and closed door. He turned around and stayed about 2 feet in from door, in the air stream from the heater. He immediately noted a smell and immediately felt a tightness of the chest described as a constriction of the upper chest, similar to what one would feel with a cold. This chest pain lasted for about 1 hour. That night he had trouble sleeping, but attributed it to other personal items on his mind. He also experienced a dryness of the throat. No other symptoms were noted.

Other Observations: The odor was described as like a new heating element plus another smell. It was stronger than just a heater heating up. He reported no other persons appeared to be affected, but one Raytheon person reported noticing an odor. He did not seek any medical attention. No symptoms persisted beyond 1 hour or returned. He did not note any other signs of malfunction of the units.

APPENDIX O

Report of Investigation - Selection of Overtemperature Switch Setting

REPORT OF INVESTIGATION

SUBJECT: Selection of Overtemperature Switch Setting for Relocated Switches in the PATRIOT 18,000 BTUH, Split-Package Air Conditioner.

CONTRACT: DAAK70-81-D-0109, Task Order 0055

DATES OF INVESTIGATION: November 24, 1982 - February 11, 1983

INVESTIGATION LOCATION: VSE Corporation, 2550 Huntington Avenue, Alexandria, Virginia

REPORT WRITER: Robert B. Sherfy, Project Engineer

INVESTIGATION OBJECTIVES:

a. Determine proper settings for overtemperature switches relocated to the back wall of the evaporator.

b. Retrofit one air conditioner with the selected switches and check for proper operation.

BACKGROUND: Engineer change proposal (ECP) 82CE0387 modifies the PATRIOT air conditioner heater elements from unfinned to finned to increase heater element life. Part of this ECP will also relocate the heater overtemperature switches from a position just above the right fresh air intake to a location on the evaporator compartment back wall, directly behind the heater elements. This relocation was needed because cold outside air entering the right hand fresh air intake would envelop the overtemperature switches, preventing them from detecting an overtemperature condition in the vicinity of the heaters. The relocation of these switches to the evaporator back wall will make them less affected by the fresh air intake and more responsive to excessive temperatures within the unit. The close proximity of the relocated switches to the finned heater elements requires that the switch opening settings be changed from 150°F to 210°F. These changes will be incorporated in the third year quantity of air conditioners to be fabricated under production contract DAAK70-80-C-0114.

However, by the time this change proposal can be implemented, approximately 244 split-package air conditioners will have been manufactured with unfinned heater elements and overtemperature switches located near the fresh air intake. The U.S. Army Mobility Equipment Research and Development Command (MERADCOM) has requested VSE Corporation, under Task Order No. 0055 of Contract DAAK70-81-D-0109, to investigate a "quick fix" involving the relocation of the overtemperature switches while retaining the unfinned heater elements. This report documents that investigation.

DISCUSSION: A PATRIOT air conditioner, S/N 81013, was operated in the high heat-warmer mode in shop ambient air with up to approximately 80 percent of the return air opening area restricted. Results of the tests are presented in Attachment 1. With 70°F ambient return air a high temperature of 166°F was experienced on the back wall of the evaporator section in the approximate future position of the relocated overtemperature switches. Allowing an additional 10°F rise in return air temperature, a safety factor of 20°F to prevent nuisance tripping

and account for discrepancies in test set-up and unit fabrication, and a $\pm 6^{\circ}F$ tolerance in switch manufacture, the resulting switch setting would be $202^{\circ}F$. The writer's opinion is that this is close enough to the $210^{\circ}F$ setting of the final switches to be used with ECP 82CE0387, to justify using this $210^{\circ}F$ setting. The advantage would be a one time change in overtemperature switch setting and switch location.

New overtemperature switches were ordered with $210^{\circ}F \pm 6^{\circ}F$ settings. These were installed at the new back wall location in air conditioner S/N 81013. Tests were again performed with a restricted return air opening. With a $70^{\circ}F$ shop ambient air temperature, no switches tripped, up to an 85 percent restricted return air opening. However, with a 90 percent restriction, the switches tripped regularly. The maximum temperature recorded at the right drain tube was $203^{\circ}F$, well below the 450°-$500^{\circ}F$ maximum tolerance of silicone tubing. See test results in Attachment 2.

CONCLUSIONS: The $210^{\circ}F$ overtemperature switch setting is satisfactory. It is high enough to prevent nuisance tripping under any but the worst adverse conditions, and low enough to prevent major damage and dangerous outgassing of susceptible materials in the evaporator compartment.

RECOMMENDATIONS: Implement the "quick fix" change using $210^{\circ}F$ overtemperature switch settings.

APPENDIX P

Transition of PATRIOT Air Conditioner, 18K BTU

DEPARTMENT OF THE ARMY
US ARMY BELVOIR RESEARCH & DEVELOPMENT CENTER
FORT BELVOIR, VIRGINIA 22060

STRBE-EPAT

DEC 09 1983

SUBJECT: Transition of PATRIOT Air Conditioner, 18K BTU

Commander
US Army Troop Support &
Aviation Materiel Readiness Command
ATTN: DRSTS-TIB (Mrs. Beckman)
4300 Goodfellow Blvd
St Louis, MO 63120

1. Reference is made to DRSTS-TIB letter dated 4 Nov 1983, SAB.

2. The additional information requested in the referenced letter is as follows:

a. The Belvoir R&D Center has removed the teflon grommets from all PATRIOT air conditioners.

b. The schedule for the replacement and relocation of the over temperature switch in PATRIOT air conditioners with 80.... and 81.... serial number is as follows:

Award contract for modifying 172 air conditioners	15 Mar 84
First delivery of modified air conditioners	15 Jun 84
Complete	30 Sep 84

Note: (1) 62 air conditioners were modified under separate purchase order in Aug 83.

(2) Completing the schedule by 30 Sep 84 is dependent upon the replacement and return to Ft Belvoir of air conditioners that are currently fielded with the PATRIOT Missile System.

(3) PATRIOT air conditioners with 82 serial numbers have the new and relocated over temperature switch.

c. The action to incorporate all known ECP's into the Technical Data Package will be completed by 1 Jan 84.

Encl 1

STRBE-EPAT
SUBJECT: Transition of PATRIOT Air Conditioner, 18K BTU

3. If additional information is required, request that you contact this office.

FOR THE COMMANDER:

ROBERT M. McKECHNIE
Development Project Officer
PATRIOT Support Project Office

CF:
DRSTS-WX (Pillarick)
DRCPM-MD-T-C (Huie)
DRCPM-MD-M-G
STRBE-EPAT (Brantly, Sams)
-EM (Good)
-TQ (Graham)
-DA (Gutman)

[illegible]

[illegible]EPAT

FEB 24 [illegible]

SUBJECT: PATRIOT Air Conditioners

Project Manager
PATRIOT Missile System, DARCOM
ATTN: DRCPM-MD-M-G
Redstone Arsenal, Alabama 35898

1. Belvoir R&D Center is in the process of modifying the 1st and 2nd Production year air conditioners with 80--- and 81--- serial numbers. Enclosure 1 is a list of modifications that will be made to the air conditioners. Sixty-two air conditioners have been modified to date. A contract is in negotiation and should be awarded in early March 1984 for the modification of the remaining 170 air conditioners.

2. In order to complete the modification program, it will be necessary to return all the 80--- and 81--- serial numbered air conditioners to Belvoir. The applicable air conditioners (105) located at NCAD have been shipped to Belvoir and will be modified as soon as the contract is awarded. Action is necessary to have the air conditioners located at Raytheon, Fort Bliss/ASMR, LEAD, and MICOM shipped to Belvoir. Enclosure 2 lists the air conditioners at those locations. Plans are to replace these Air conditioners with the 82--- serial numbered units currently in NCAD. Personnel from this office will assist in the changes, etc.

3. Assistance is requested from your office in obtaining approval from Raytheon, Fort Bliss/ASMR, LEAD, and MICOM for the changeout of the air conditioners. This is required at an early date so that the air conditioner can be provided to the Belvoir contractor for modification. It should be noted that the effort is required to be completed by 30 Sep 84.

Encl 2

[illegible]

[illegible]

[illegible] for [illegible] [illegible], [illegible] 14-1871.

FOR THE COMMANDER:

[illegible]

Robert M. McKechnie

ROBERT M. McKECHNIE
[illegible] Support
Project Office

CF: DNCPM-MD-T-C (Huie)
-S-DS (Blackwell)
-T-R ([illegible])
DPSTR-LIB ([illegible])
-WX ([illegible])
STRBE-EPAT ([illegible], Brantly, Sams)
-TQ ([illegible])
-EM ([illegible])

MODIFICATION OF PATRIOT AIR CONDITIONERS

(80--- & 81--- Serial Numbers)

1. Remove heater limit switches.
2. Relocate and install new heater limit switches.
3. Alter heater (Cal Rod) mounting brackets.
4. Rewire Time Delay Relay (K5).
5. Replace condensate drain tubes.
6. Inspect, assemble, and operationally test the unit.
7. Recrate to Level B/A packaging.

APPENDIX Q

MERADCOM Letter - PATRIOT Air Conditioners

DEPARTMENT OF THE ARMY
US ARMY BELVOIR RESEARCH & DEVELOPMENT CENTER
FORT BELVOIR, VIRGINIA 22060

STRBR-EPAT

DEC 09 1983

SUBJECT: PATRIOT Air Conditioner

Project Manager
PATRIOT Missile System, DARCOM
ATTN: DRCPM-MD-T-C (Huie)
Redstone Arsenal, AL 35898

1. Reference letter, DRDME-EPAT dated 3 Oct 1983, SAB.

2. The referenced letter forwarded the results of Belvoir R&D Center (formerly MERADCOM) evaluation of the odor problem with the 82 series PATRIOT air conditioners. It recommended that the 82 series air conditioner be mounted on a PATRIOT shelter and allow personnel from this office to sit in the shelter during the operation of the air conditioner.

3. Belvoir R&D Center personnel (Mr. Dave Larson and Mr. Frank Good) visited Raytheon, Andover, on 10 November 1983 and demonstrated the operation of two PATRIOT air conditioners (SN 82406 and SN 82396) on an ICC shelter. They sat in the ICC shelter for approximately four hours and operated the two air conditioners in both the high heat and low heat modes without feeling any ill effects. They concluded that the PATRIOT air conditioners with 82 serial numbers pose no special hazard, are safe and usable in the heat modes. A copy of their trip report dated 17 November 1983 is attached.

3. Based on the results of Belvoir R&D Center's extensive test and evaluation of the PATRIOT air conditioner including the demonstration of the 82 series on the ICC shelter at Raytheon on 10 Nov 83, it is recommended that the 82 series be released for use in the PATRIOT system.

FOR THE COMMANDER:

Robert M. McKechnie

Encl

ROBERT M. McKECHNIE
Development Project Officer
PATRIOT Support Project Office

CF:
DRCPM-MD-M-G (O'Donnel)
-S-D (Gustine)
DRSTS-TIB (Beckman)
STRBE-EPAT (Brantly, Waddick, Sams)
-EM (Good)
-TQ (Graham)

DEPARTMENT OF THE ARMY
US ARMY BELVOIR RESEARCH & DEVELOPMENT CENTER
FORT BELVOIR, VIRGINIA 22060

STRBE-EME 16 November, 1983

SUBJECT: Trip Report, 9-10 November 1983, to Andover Mass, Raytheon Corp, regaring PATRIOT GFE Air Conditioners.

THRU: Chief, Environmental Control Systems Branch

Chief, Electromechanical Division

DPO, PATRIOT Support Project Office

TO: Chief, Engineer Service Support Laboratory

1. Short Synopsis of Travel. This was a follow up visit on an earlier trip in July in relation to an alleged odor problem with the air conditioners.

2. Person contacted.

Mr. Larry Somes, Raytheon Bedford

3. Discussion.

a. At the end of June this year, Raytheon reported an objectionable odor coming from the first of the "82" serial numbered GFE air conditioners that they had begun using on the PATRIOT shelters. Because of an earlier experience with an unidentified "toxic substance" being given off by the early model air conditioners everyone involved was "gun shy" about the odor report. We immediately banned use of the "82" units and launched an investigation into what had caused the "odor". After three months of thorough investigation we are completely convinced that the problem arose from a new paint odor coming from the new style finned heaters used beginning with the 82 model units. The odor comes from amounts of outgassing from the paint which are almost too small to measure. Tests indicated that no toxic substances were present in the outgassing. The odor is present each time the heaters are started after being off for a while, is most intense when the heaters first start and diminishes as the heaters are used for a time. Different sample air conditioners used during our tests exhibited varying amounts of odor-apparently because of normal production variations in the amount of paint used or the variations in using the paint.

b. Mr. David Larson and I visited Raytheon on 10 November for the express purpose of carrying out a recommendation in a letter from the Patriot Project Support Office to the PM, dated 3 October, that "Belvoir R&D Center personnel---sit in the shelter during use of the air conditioner to prove it safe". Our purpose was to restore by our example the Raytheon people's confidence in the GFE air conditioners.

c. What we did was to stay for four, hours in an ICC shelter located in the High Bay Area of Raytheons Andover plant and run the two air conditioners in various heat modes. Although a somewhat unnatural use of the equipment, we felt it would make our point. The room temperature outside the shelter was probably on the order of 68 to 72°F. The High Heat mode of the air conditioner is intended for initial warm up when starting a cold system and Low Heat mode for normal thermostat-controlled heating. High Heat might also be used when outdoor temperatures are extremely low. The two air conditioners on the ICC involved were SN 82406 which had 14.1 hours on the run-time meter at the end of our stay and SN 82396 which had 69.1 hours. The thermostat controls for the air conditioners are supposed to have a range from 60°F ("Colder") to 90°F ("Warmer").

d. We entered the ICC at 0800 hours on 10 November and started both air conditioners in High Heat mode with the temperature controls turned to full Warmer. Both started and ran normally. Raytheon provided us with a thermocouple and an Omega meter so that we could spot check temperatures during our stay. Both air conditioners' fresh air inlets were open with filters in place. Several times durng our stay in the shelter Raytheon employees entered to bring things in and out of the shelter and several times Mr. Somes came in and visited with us for a few minutes.

e. From 0800 to 1045 we ran the two units constantly in the High Heat/Warmer mode. Outlet temperatures coming from the air conditioner discharge ranged from 120°F to 150°F. After interior temperatures had stabilized (about an hour) the thermocouple clamped to a metal interior bracket registered 110°F which was probably a reasonable estimate of the mean interior temperature, which when measured in the return air stream varied from 100 to 115F. When first started, the units gave off the same odor that had been detected back in June and July but at a lower level, it appeared. We have noted during tests at Ft. Belvoir that different units smell at different intensities. After the first hour we no longer detected the hot-new-heater odor and began to detect other odors such as the interior shelter wall odor or our own body odors (we were perspiring).

f. During that first period the thermostat had the Low Heat elements turned off so long as the room temperature was over 90°F. The High Heat elements run constantly, controlled only by a limit device which would not have swithed them off at the temperatures we were experiencing. At 1045 we switched both units to Low Heat/Warmer to exercise the Low Heat elements . When we made the changeover there was a fresh period of odor, about as strong as the original start up.

STRBE-EME 17 November, 1983
SUBJECT: Trip Report, 9-10 November 1983, to Andover, Mass., Raytheon Corp., regarding PATRIOT GFE Air Conditioners

Within just a few minutes we no longer smelled it, however. In Low Heat/Warmer the room temperature dropped to about 100°F. We experimented for a few minutes with the two thermostat controls and found that the curbside unit controlled at 100 to 103°F in the full Warmer position and roadside unit at 95 to 99°F. With both on full, the curbside unit dominated, being able to maintain the shelter at temperature by itself. In this experimenting we found that the roadside unit produced no noticeable change in odor when switched on whereas the curbside unit produced a brief noticable burst of odor when turned on. Interestingly the non-smelling roadside unit showed the higher run time (69.1 hours vs 14.1).

g. At 1200 hours we shut both units down and ended our demonstration-of-confidence. Neither of us felt ill effects. The 4 hours stay in the cramped quarters of the ICC at 100 to 115°F was less-than-pleasant but we feel sure that there is no risk of harm from the heater odor.

4. Conclusion. The GFE PATRIOT air conditioners with 82 serial numbers pose no special hazard because of the use of the new painted heater elements. There is an odor that apparentlly varies from one unit to another and that recurs as a "new paint smell" each time the heaters are restarted for some undetermined length of operating time. In short, the air conditioners are safe and useable in the heat modes.

FRANKLYN P. GOOD
Project Engineer

I have read Mr. Good's report, concur with his statements and conclusions and wish to make this a joint trip report.

DAVID A.LARSON
Patriot Project Support Office