5/1
#

AD

②

AD-E400 124

S

TECHNICAL REPORT ARLCD-CR-77010

ENGINEERING FEASIBILITY STUDY FOR ELIMINATION OF NITROGLYCERIN FROM SOLVENT VAPORS

C. D. MATHES
RADFORD ARMY AMMUNITION PLANT
RADFORD, VA

J. A. CARRAZZA
A. TATYREK
ARRADCOM

MARCH 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

DISPOSITION

18 S[illegible]

19 AD-L411 121

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1 REPORT NUMBER 14
Technical Report [illegible] 77/10

2 GOVT ACCESSION NO.

3 RECIPIENT'S CATALOG NUMBER

4. TITLE ~~(and Subtitle)~~ 6
ENGINEERING FEASIBILITY STUDY FOR ELIMINATION OF NITROGLYCERIN FROM SOLVENT VAPORS.

5 TYPE OF REPORT & PERIOD COVERED 9
Final rept.,

6 PERFORMING ORG. REPORT NUMBER

7. ~~AUTHOR(s)~~
C. D. Mathes,
J. A. Carrazza, ~~Project Leader~~
A. Tatyrek, ~~Project Engineer~~

8 CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Radford Army Ammunition P[illegible]
Hercules Incorporated
Radford, VA 24141

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11 CONTROLLING OFFICE NAME AND ADDRESS
ARRADCOM
ATTN: DRDAR-TSS
Dover, NJ 07801

12. ~~REPORT DATE~~ 11
March 1978

13 NUMBER OF PAGES
40 12 34p.

14 MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)
ARRADCOM, LCWSL
Manufacturing Technology Division (DRDAR-LCM)
Dover, NJ 07801

15 SECURITY CLASS. ~~(of this report)~~
Unclassified

15a DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitroglycerin	Solvent purification	Regeneration
Air pollution	Ethyl alcohol	Permeation
Resin adsorbtion	Acetone	Adsorbtion
Explosive	Solvent recovery	Decontamination
		Styrene divinylbenzene

20. ~~ABSTRACT~~ (Continue on reverse side if necessary and identify by block number)

This report, based on laboratory tests, covers the evaluation of two distinct methods of separating the solvents acetone and ethyl alcohol from nitroglycerin (NG) in an air stream from a multi-base propellant-drying facility. The first method employed a semi-permeable membrane which has been used effectively to remove moisture from a gas stream. The membrane, however, did not effectively remove the NG vapor from the solvent vapors. → over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

410163

CL

20. ABSTRACT (Continued)

The second method evaluated was an adsorption system using a styrene-divinylbenzene copolymer resin for separation of the NG from the solvent vapors. The resin effectively adsorbed the NG and allowed the solvent vapors to pass free of any NG contamination.

The polymeric adsorbents are macroreticular ion-exchange beads without their ionic functionality, but are characterized by a spectrum of surface polarities and variety of surface areas, porosities, and pore-size distributions. These adsorbents have a relatively high thermal stability and NG adsorption capacity.

FOREWORD

ARRADCOM's MMT Project 54114, "Method to Minimize Environmental Contamination," incorporated Task 12 to develop technology for elimination of organic solvent wastes. The efforts under this task were directed toward elimination of hydrocarbon emission in support of an improved Forced Air Dry (FAD) design for the Continuous Automated Multi-Base Line (CAMBL) at Radford Army Ammunition Plant (RAAP).

This report, which documents the results of a feasibility study conducted at RAAP for the removal and/or recovery of NG and solvent vapors, has been reviewed and concurred by the Special Technology Branch, Manufacturing Technology Division, Large Caliber Weapons System Laboratory, ARRADCOM.

TABLE OF CONTENTS

Tables

Figures

SUMMARY

Two methods for the removal of NG vapors from the processing solvents used in the manufacture of multi-base propellants were investigated.

A Nafion semi-permeable membrane, used effectively to remove moisture from a gas stream, was investigated. An air stream containing acetone, ethyl alcohol and NG vapors of concentrations approximating those exiting from the multi-base NG recovery system were passed through the permeation tube. Analysis of samples exiting from the tube showed the presence of NG, as well as dinitroglycerin (DNG).

The second method investigated provided excellent results in separating the NG from the solvent vapors. This method, an adsorbent system, utilized a styrene-divinylbenzene copolymer resin manufactured by the Rohm and Haas Company. The resin, as recommended by Rohm and Haas and confirmed by testing, was found to have a high adsorption capacity for NG with a low capacity for acetone and ethyl alcohol. It was determined that NG saturated resin could be effectively regenerated with acetone.

Additional bench-scale studies should be conducted to more thoroughly evaluate the RH-1601 resin for NG and solvent adsorbent capacities and recovery techniques.

INTRODUCTION

The drying of multi-base propellants results in the removal of the processing solvent, acetone and ethyl alcohol, and small quantities of both water and NG. Drying is accomplished on the Continuous Automated Multi-Base Line (CAMBL) by flowing heated air through the propellant bed in a single pass then exhausting directly to the atmosphere or through a scrubbing system. The exhausting of the exit gases to the atmosphere is limited by EPA Standards to 40 kg/day of hydrocarbons per unit for the new facility and the dryers greatly exceed these limits.

There have been several methods tried in the past in the manufacture of multi-base propellants to recover solvents during drying. Most of these methods have been abandoned because of the excessive hazards that have been experienced. A post dryer water scrubber has been 97 percent effective in removal of the NG contamination in the exhaust air from the dryer.

The objective of Phase I of this project is to provide a satisfactory methodology to remove the hydrocarbons from the CAMBL exhaust gases to meet EPA standards. One approach is to chemically and/or physically separate the NG from the solvent vapors so that the solvents could safely be adsorbed and recovered.

A method is required which will remove the small amount of NG remaining so that the solvents can be safely removed from the exhaust air. Two approaches were to be evaluated: (1) use a permeation tube which will allow the solvents to pass through the walls for recovery and reject the NG vapors or (2) use an adsorbent material which will be selective for NG and adsorb it while allowing the solvents to pass through.

DISCUSSION

Laboratory Permeation Distillation Studies with NG Vapors

Studies on permeation distillation consisted of determining whether NG with acetone and ethyl alcohol vapors penetrate Nafion permeation tubing. Work consisted primarily of determining efficiencies of the removal of acetone and alcohol vapors from moist air by permeation distillation. All work during this investigation with NG vapors was conducted using a Perma Pure Dryer CCD-500-240. This dryer contained all-plastic fittings and a single 6.9-m long, 7.62 mm OD Nafion tube inside a plastic tubular shell.

During the laboratory evaluations, the concentration of acetone, ethyl alcohol, and NG vapor entering the center of the Nafion permeation tube was adjusted to approximate the maximum concentrations found exiting the automated multi-base NG vapor recovery system (0.2 percent by volume for each acetone and ethyl alcohol, and 0.1 to 1.0 ppm NG). This was accomplished by passing air through the following equipment:

1. A carboy of water containing 0.5 percent by volume acetone and 2.5 percent by volume ethyl alcohol.
2. A coil of copper tubing in an oil bath at 75°C to heat the air.
3. A bed of propellant at 75°C to produce NG vapors.

The air was then passed into the center of the permeation tube at a flow rate of 0.32 l/min. A counterflow of ambient air was drawn through the outer shell (along the outer surface of the permeation tube) at 42 l/min and a pressure of 355.6 mm of Hg for two hours prior to sampling.

Samples of air entering and exiting the center of the permeation tube and exiting the shell were collected and analyzed quantitatively for NG per standard Hercules Procedure A-33-2, the diphenylbenzidine method. Collection of NG vapor by this method is accomplished with two adsorption tubes in series. Each tube contained an aqueous solution of 0.3 percent potassium chloride. The method has a sensitivity of detecting 0.01 ppm NG in five liters of gas. The results from Procedure A-33-2 are shown in Table I. Runs I and II were conducted using crushed, dry M30 propellant in the NG vapor generator. For Run III the propellant was 1/3 by volume chopped, partially dried M30, and 2/3 by volume chopped, dry M8 rolled propellant.

TABLE I

PERMEATION DISTILLATION NG EVALUATION

	Gas Flow During Sampling (liters/min)	Volume Collected For Testing (liters)	NG Concentration (ppm by Volume)
Run I			
In	0.32	5	0.42
Out	0.32	5	0.25
Shell Exit	2.00	30	0.02
Run II			
In	0.32	5	0.37
Out	0.32	-	-
Shell Exit	2.00	20	0.01
Run III			
In	0.32	5	1.0
Out	0.32	5	0.76
Shell Exit	2.00	250	0.01

NOTES: (1) Tests conducted using Perma Pure Dryer CCD-500-240 at 30°C.

(2) NG vapors tested per Standard Hercules Procedure A-33-2. Detectability equals 0.01 ppm for 5 liters. Oxides of nitrogen will interfere.

(3) Results may be slightly high due to oxides of nitrogen interference.

These data suggested that NG was penetrating the Nafion tubing. Subsequent analysis of generated NG vapor, however, indicated that oxides of nitrogen (NO_x) were simultaneously being emitted from the generator. Since NO_x will also react with the color-producing reagent in the NG analysis, this placed some suspicion on the results presented above. A positive method was then developed to confirm the existence of NG vapor in any gaseous stream. This method, although qualitative at this point, consisted of adsorbing NG vapors in an aqueous solution, concentrating it by methylene chloride extraction, and making positive identification by a sensitive thin layer chromatographic (TLC) separation and detection technique. After a positive method for detecting NG was developed, the permeation distillation apparatus was reassembled and samples for TLC were collected by two means: (1) bubbling shell exit gas through distilled water and extracting with a small volume of methylene chloride, and (2) washing the shell area with methylene chloride. Nitroglycerin was present in both solutions. Dinitroglycerin was also found to be present in the aqueous solution. These results show the use of the permeation distillation technique to be inadequate for the separation of the NG from the solvent vapors.

Laboratory Evaluation of Adsorption Techniques

Adsorption materials and techniques have been investigated in addition to the permeation tubes. These materials were grouped into two categories:

1. An adsorbent for removal of the NG vapors remaining (0.1 to 0.5 ppm) from the moist gas stream exiting the automated multi-base NG recovery system.

2. An adsorbent for collection and concentration of process solvents (acetone and ethyl alcohol) after the NG vapors are removed.

A literature and vendor search revealed the following adsorbents may be of use:

1. Amberlite RH-1601, a styrene-divinylbenzene copolymer manufactured by Rohm and Haas Company.

2. XFS-4256 and -4258, styrene-divinylbenzene copolymer manufactured by Dow Chemical Company.

3. Tenax-GC, a 2,6-diphenyl-p-phenylene oxide porous polymer developed by AKZO Research Laboratories and marketed by Enka N.V. of the Netherlands.

4. Porapak P, a styrene-divinylbenzene copolymer developed by Dow Chemical Company for Water Associates, Inc. for gas chromatography.

5. Porapak Q, an ethylvinylbenzene-divinylbenzene copolymer developed by Dow Chemical Company for Water Associates.

6. Activated carbon, various types are available.

All of the above materials were found to be compatible with NG except activated carbon. Taliani tests indicated that all types of activated carbon are very probably incompatible with NG.

Of the above materials, the styrene-divinylbenzene copolymers appeared to be best for the initial laboratory investigation. Amberlite RH-1601, XGS-4256, and XFS-4258 can be obtained in production quantities. The availability of Tenax-GC is questionable since it is a new product and is manufactured in the Netherlands. Porapak P and Q are specially prepared for gas chromatography and their costs may prohibit usage.

Both Rohm and Haas and Dow Chemical are leading manufacturers in polymer adsorbents, and each independently recommended styrene divinylbenzene type polymers for the application, i.e., both stated that this type of polymer should have a high adsorption capacity for NG, but may have a lower capacity for acetone and ethyl alcohol. This polymer was selected for more extensive laboratory investigations.

Adsorption of NG Vapors

Three tests using Amberlite RH-1601 as the adsorbent were conducted. Due to possible high NG adsorption capacity and long breakthrough time, small packed tubes were used during the investigation. A preliminary test was conducted by passing a 0.32 l/min flow through a small plastic tube containing 0.42 g of Amberlite RH-1601. The air stream was saturated with moisture and contained approximately 0.2 percent by volume each of alcohol and acetone and approximately 1.0 to 1.5 ppm NG. After six hours the tube was dissected to determine the distance NG had penetrated into the bed. Although the detection of NG was difficult since Amberlite RH-1601 itself turned a pale red, the results indicated that NG was only located on the initial portion of the material. Therefore, a second test was conducted to determine NG breakthrough time by monitoring the effluent air for NG. The test was conducted in a glass column containing 0.276 g of Amberlite RH-1601 (50.8 mm long by 4 mm diameter). The column was in a vertical position directly above the NG generator with the air entering the bottom at a flow rate of 0.32 l/min.

Various methods were used in attempts to detect NG vapors of approximately 0.5 ppm concentrations; but because of NO_x emission from the propellant in the NG generator at ambient conditions, none proved successful. Therefore, after seven days the experiment was discontinued. The NG which had been adsorbed by the Amberlite RH-1601 resin was extracted with methylene chloride, and the extract titrated by the $TiCl_3$ method. The average NG loading was found to be 5.45 percent by weight.

Before further work could be accomplished, an adequate method for identification of NG breakthrough was necessary. The following approaches were considered:

1. Chemiluminescent analysis for NO_x after thermal decomposition of NG.
2. Hercules Standard Procedure A-33-2, the diphenylbenzidine method for monitoring NG vapors in ambient air.
3. Adsorption of NG by a second column containing a small amount of Tenax-GC. Tenax-GC had been recommended by Southern Research Institute of the Occupational Safety and Health Administration (OSHA) as an excellent adsorbent for nitrate esters.

Because of the moderate NO_x levels from the NG generator, the chemiluminescent and Hercules procedures definitely could not be used. Use of Tenax-GC was questionable at times due to possible NO_x adsorption. This led to the development of a positive method to confirm the existence of NG vapor in gaseous streams. This method, although qualitative at this point, consisted of adsorbing NG vapors in an aqueous solution (three ml), concentrating it by methylene chloride ($MeCl_2$) extraction (0.5 ml) and making positive identification by a sensitive TLC separation and detection technique. The test will easily detect 0.1 ppm NG after passing the gas through the aqueous solution for only two minutes and spotting 50 microliters (μl) of the $MeCl_2$ portion on a TLC plate. The TLC plate was developed with benzene, and NG was identified with NG detector. For checking the column effluent for NG, the air was passed through the solution for 30 minutes and 100 μl were spotted, thus providing a method capable of detecting at least 0.005 ppm NG.

After the establishment of a suitable method for detecting NG vapor breakthrough, a third test was conducted to determine NG loading capacity on Amberlite RH-1601. The test was conducted with a Bio-Rad glass column 150 mm long and 9 mm ID packed with 1.4493 g of Amberlite RH-1601 (50.8 mm x 9 mm). A glass disc provided with the Bio-Rad column secured the packing at the inlet and a small piece of glass wool was used on the outlet. The packed column was placed in a vertical position directly above the NG vapor generator with vapors entering the bottom of the column. Concentrations of components in the air stream were created to duplicate the effluent reported exiting the automated multi-base pilot line.

An air cylinder was used as the air supply and was regulated at 14.5 kPa. The air was passed through a rotameter to control the flow, then through a carboy containing an aqueous solution of 2.5 and 0.5 percent by volume of ethyl alcohol and acetone, respectively. This created a gas saturated with moisture and containing ethyl alcohol and acetone of approximately 0.22 and 0.24 percent by volume, respectively. The gas stream was then passed through a bed of propellant (approximately .227 kg of chopped M36) at 21°C to generate NG vapor for the adsorption column. The laboratory equipment and arrangement is shown in Figure 1.

Flow rate during the run was 0.65 l/min. The average NG concentration entering the column was 0.465 ppm as calculated by analysis of the adsorbent after termination of the experiment and comparing it to the total volume of air passed through the adsorbent.

After 27.5 days, no NG breakthrough had occurred through the 2.0 inch bed. To estimate the adsorption capacity of NG on Amberlite RH-1601, the column was disconnected and the Amberlite RH-1601 carefully removed in two sections: (1) the first 3.6 cm (0.9058 g) on the inlet side, and (2) the final 1.9 cm (0.5435 g) on the exit side. Each was extracted overnight with $MeCl_2$. The latter 1.9 cm section contained no NG by either TLC analysis or $TiCl_3$ titration. The first section contained 0.1213 g of NG, thus indicating a loading capacity of 13.4 percent or higher since the exact distance of NG adsorption is unknown. The above experiment showed that Amberlite RH-1601 is an excellent resin for adsorption of NG vapor.

After determining that the RH-1601 resin was effective in the adsorption of NG, methods for the regeneration of the resin were studied. Steam treatment was the first technique investigated. A laboratory test was conducted by passing a very high flow of steam for 1/2 hour through 0.41 g of Amberlite RH-1601 coated with 5.4 percent NG. Qualitative tests showed that a large quantity of NG still remained on the resin. During the analysis for NG the presence of DNG was also detected, indicating possible degradation of NG.

Since the RH-1601 resin could not be regenerated with steam, solvent treatment was investigated. Removal of NG from 25 grams of Amberlite RH-1601, coated with approximately 5.4 percent NG, was achieved by the following means:

Acetone was introduced into the column in an upflow direction to flush the air and make complete contact with the particles. When the acetone level reached the top of the resin bed, the flow was stopped and fresh acetone was introduced in a downflow manner, maintaining a 1.27 cm solvent head above the bed. During the regeneration, a total of 375 ml of acetone exited the column. The acetone entering the top was then replaced with water to remove the acetone from the bed. A total of 375 ml

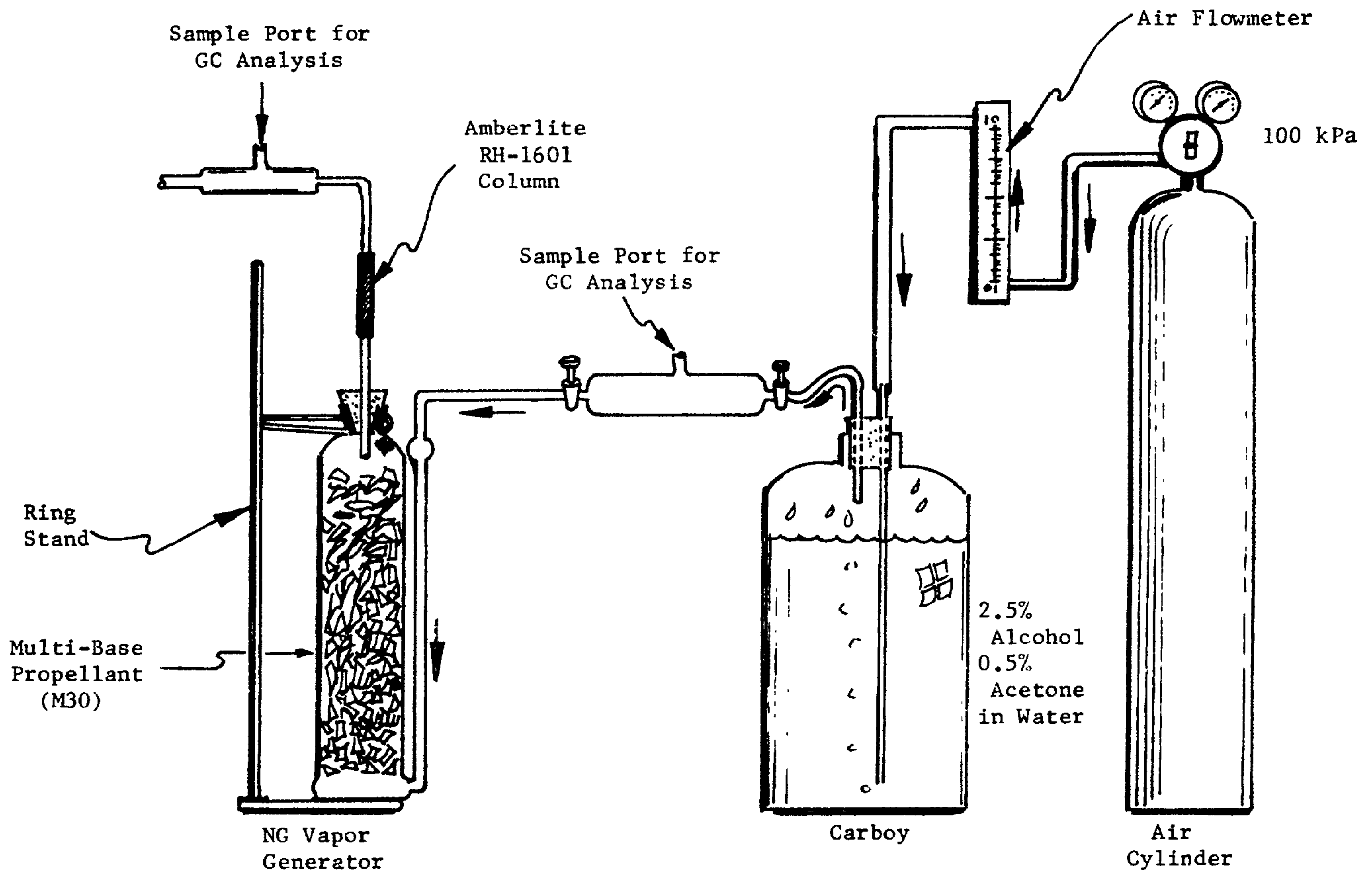

Figure 1 - Laboratory Equipment Arrangement for NG Studies with Amberlite RH-1601

of water was passed through the bed followed by an air purge to remove the moisture. The solvent exiting the bottom of the bed was collected on 25 ml cuts for analysis. The results are shown in Tables II and III.

The results in Table II show that 150 ml of acetone was sufficient for NG removal. A total of 1.3277 g of NG was collected in the first six cuts. Analysis of the Amberlite RH-1601 after completion of the experiment showed only 2.08 mg (0.0083 percent) NG remaining. This accounted for 1.330 g of NG as compared to an initial theoretical value of 1.346 g. The difference may be attributed to a small loss on the beaker surface during the coating process, plus undetected traces in the other cuts and experimental errors. The recovery was better than 99 percent.

The acetone remaining on the Amberlite RH-1601 after NG removal may be flushed off during the next drying cycle into the solvent adsorption section, without resorting to a water wash.

Adsorption of Acetone and Ethyl Alcohol Vapors

Since it was demonstrated that NG vapors can be removed preferentially from the air stream by an adsorption technique, adsorption of the process solvents on a second resin bed was investigated. The Amberlite RH-1601 and Dow's XFS-4256 adsorbents were evaluated and compared to a sample of Filtrasorb 400 activated charcoal from Calgon Corporation. The laboratory bench-scale equipment arrangement is shown in Figure 2.

All laboratory tests were conducted with a moist air stream containing approximately 0.22 and 0.24 percent, by volume, ethyl alcohol and acetone, respectively, which was generated as previously mentioned. The air was then passed down through the adsorption bed while monitoring the effluent for solvent vapor breakthrough. The loading capacities were calculated from breakthrough times, solvent concentration, flow rates, and weight of adsorbent.

The results in Figures 3 and 4 and Tables IV and V were obtained by monitoring the effluent concentration by gas chromatography. These results were obtained for a 61-cm deep bed of Amberlite RH-1601 and provide a typical picture of solvent breakthrough. The experiments were conducted at flow rates of 4.2 and 1.48 l/min. For styrene-divinylbenzene polymers, ethyl alcohol breaks through before acetone.

During the run in Figure 3, the effluent was monitored until the acetone had reached approximately maximum concentration which occurred in three hours. Air without acetone and ethyl alcohol was then passed through the loaded bed at the same flow rate to determine the desorption rate. The results showed that the adsorption rate was greater than the desorption rate.

TABLE II

NG ADSORPTION STUDIES
ANALYSIS OF THE ACETONE CUTS FROM REGENERATION OF AMBERLITE RH-1601 ADSORPTION BED

	NG Analysis		
	TLC Methods		
Acetone Cut No.	Method 1	Method 2	$TiCl_3$ Titration, gram of NG
1A	Present	present	0.1954
2A	Present	Present	0.7773
3A	Present	Present	0.3190
4A	Present	Present	0.0326
5A	Present	Present	0.0031
6A	None detected	Present	0.0003
7A	None detected	None detected	-
8A	None detected	None detected	-
9A	None detected	None detected	-
10A	None detected	-	-
11A	None detected	-	-
12A	None detected	-	-
13A	None detected	-	-
14A	None detected	-	-
15A	None detected	-	-

Notes: (1) Method 1 of TLC - 50 µl spotted on TLC plates for testing.

(2) Method 2 of TLC - 100 µl spotted on TLC plates after concentrating the samples from 25 ml to 2 ml by evaporation

(3) Each cut originally consisted of 25 ml.

TABLE III

NG ADSORPTION STUDIES
ANALYSIS OF WATER CUTS FROM
REGENERATION OF AMBERLITE RH-1601 ADSORPTION BED

	Gas Chromatographic Analysis	
Water Wash Cut No.	H_2O, % by Weight	Acetone % by Weight
16W	13.01	86.99
17W	57.95	42.05
18W	74.83	25.17
19W	85.41	14.59
20W	92.66	7.34
21W	96.70	3.30
22W	98.07	1.93
23W	98.68	1.32
24W	99.02	0.98
25W	99.27	0.73
26W	99.43	0.57
27W	99.55	0.45
28W	99.62	0.38
29W	99.70	0.30
30W	99.73	0.27

Note: (1) Each water wash cut contained 25 ml.

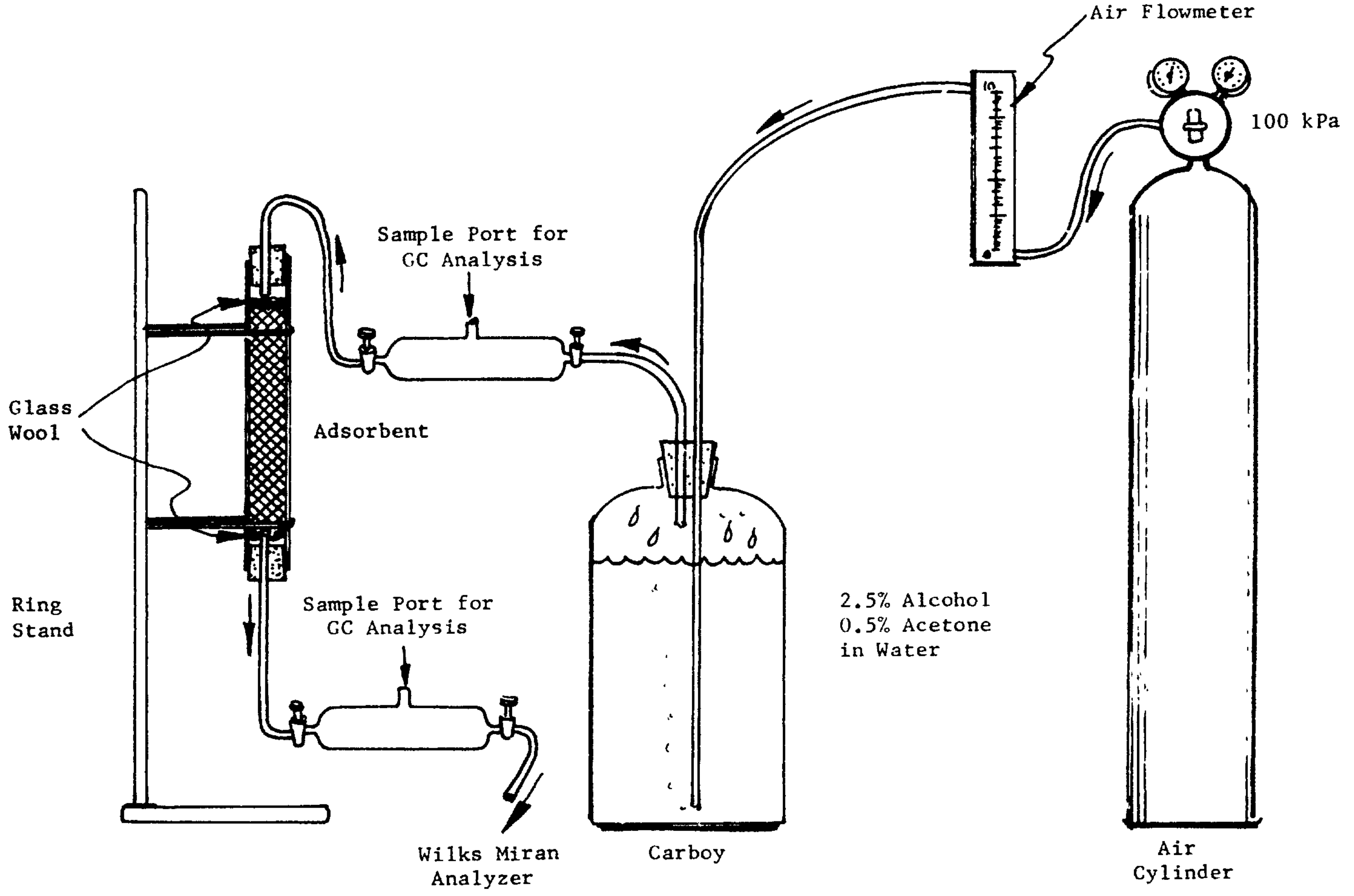

Figure 2 - Bench-Scale Equipment Arrangement for Acetone and Ethyl Alcohol Adsorption Studies

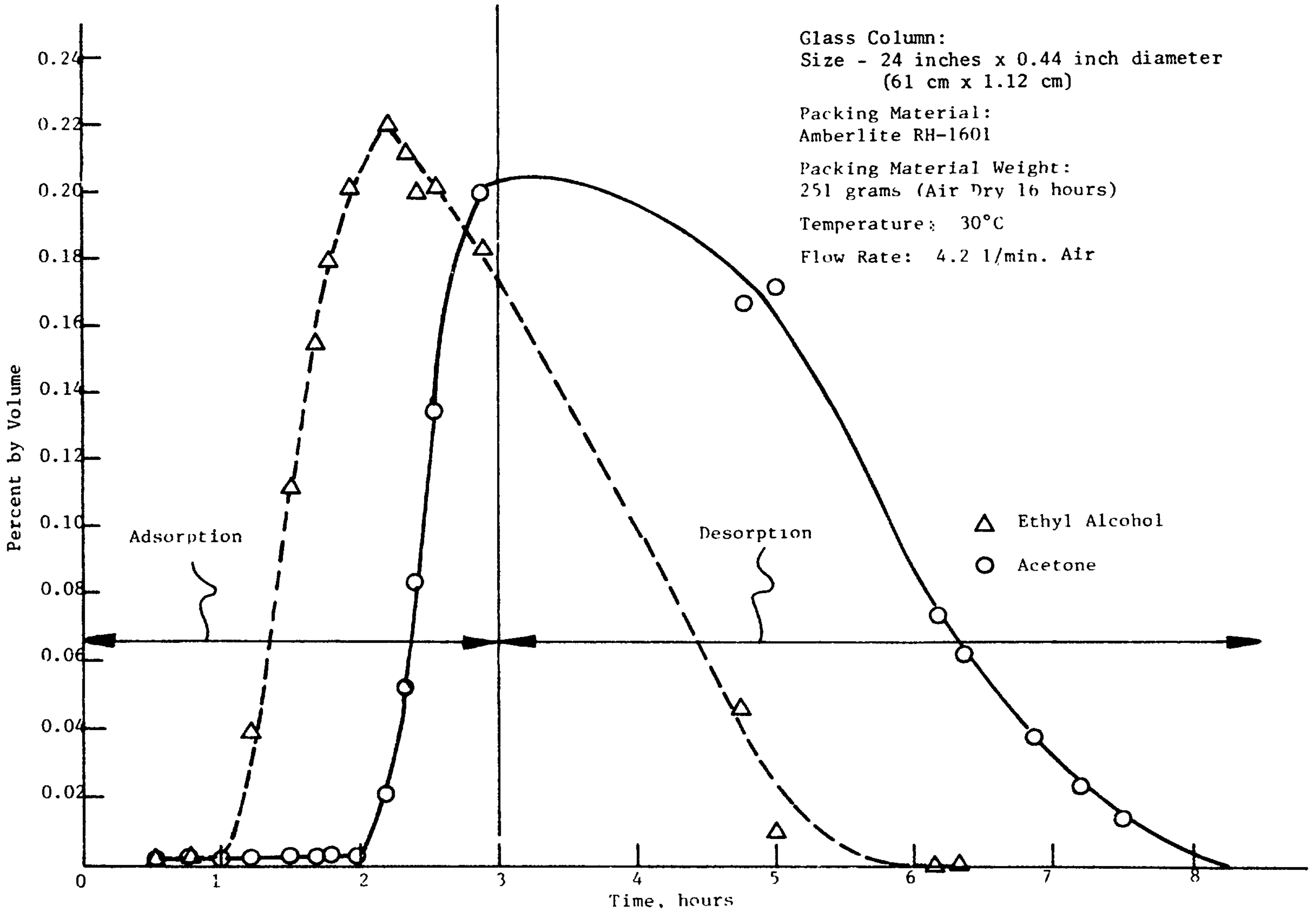

Figure 3 - Solvent Adsorption and Breakthrough for Amberlite RH - 1601

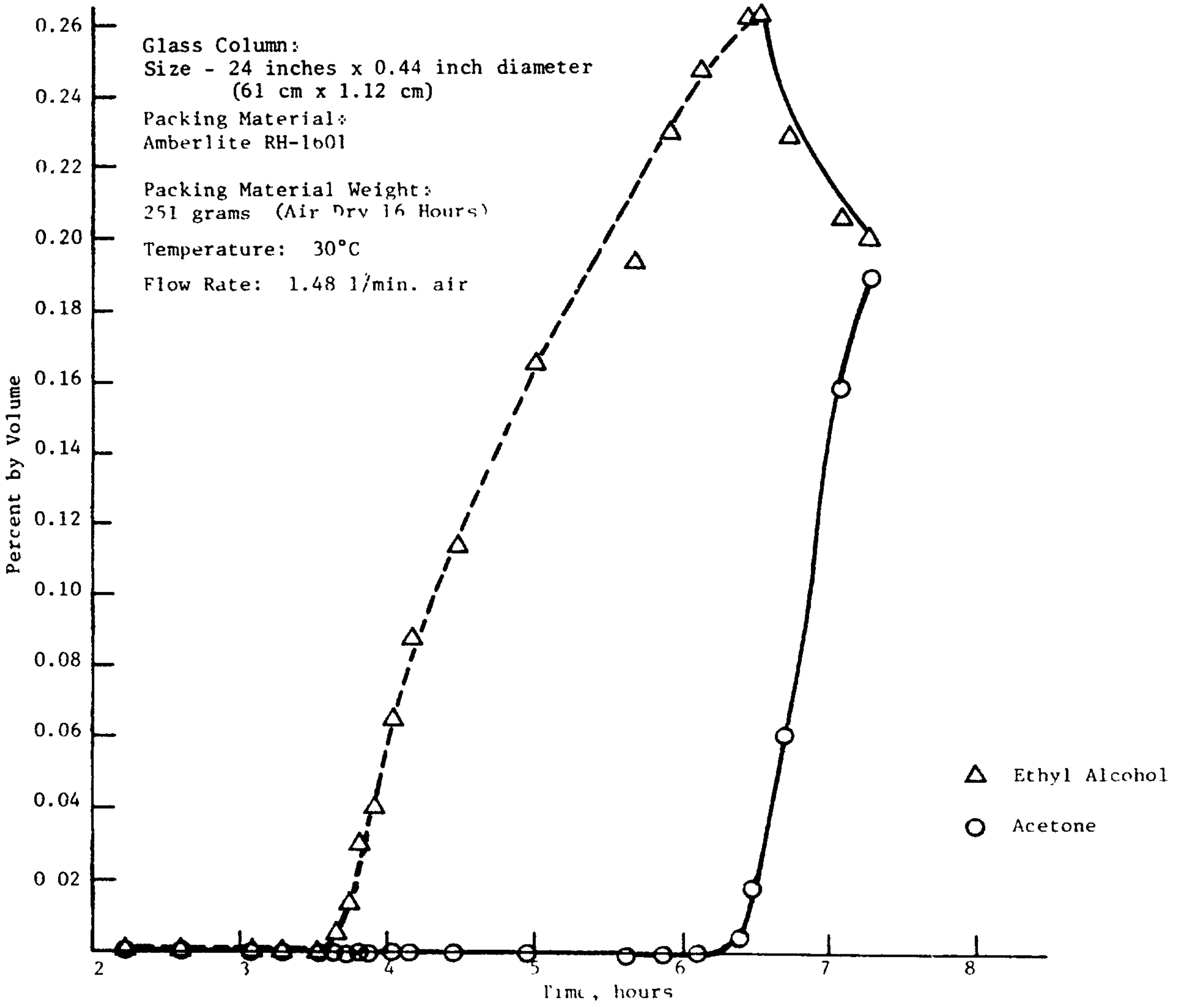

Figure 4 - Solvent Adsorption and Breakthrough for Amberlite RH - 1601

TABLE IV

SOLVENT ADSORPTION STUDIES
EVALUATION OF AMBERLITE RH-1601
FOR ACETONE AND ETHYL ALCOHOL LOADING CAPACITY,
4.2 l/min FLOW RATE DATA

Run Time, Hours	Gas Chromatographic Analysis	
	Acetone, ppm	Ethyl Alcohol,ppm
0.50	trace	None detected
0.75	trace	None detected
1.00	3	12
1.20	trace	380
1.50	trace	1110
1.67	3	1550
1.75	3	1790
1.92	1	2030
2.17	197	2200
2.28	521	2110
2.35	819	1990
2.50	1340	2000
2.83	1990	1830
3.00	Desorption Started	
4.75	1670	455
5.00	1710	100
6.17	730	None detected
6.33	620	None detected
6.83	380	None detected
7.17	230	None detected
7.50	140	None detected

Notes: (1) Test column was glass consiting of a bed 2 ft (61 cm) deep x 1-7/16 in. (3.65 cm) OD of 251 grams of Amberlite RH-1601 at 30°C.

(2) Influent gas concentration: Alcohol = 0.222 % by vol.
Acetone = 0.235 % by vol.

(3) Bed was air dried overnight prior to conducting the experiment.

TABLE V

SOLVENT ADSORPTION STUDIES
EVALUATION OF AMBERLITE RH-1601
FOR ACETONE AND ETHYL ALCOHOL LOADING CAPACITY
1.48 l/min FLOW RATE DATA

Run Time, Hours	Gas Chromatographic Analysis Acetone, ppm	 Ethyl Alcohol, ppm
0.83	1	None detected
2.25	trace	None detected
2.63	2	None detected
3.08	trace	None detected
3.28	trace	None detected
3.55	trace	trace
3.60	1	31
3.65	None detected	60
3.72	None detected	140
3.83	4	299
3.92	1	407
4.05	None detected	656
4.17	None detected	879
4.45	1	1140
4.97	3	1660
5.63	trace	1950
5.88	None detected	2310
6.10	None detected	2490
6.40	53	2650
6.50	185	2650
6.70	596	2300
7.03	1590	2070
7.25	1910	2020

Notes: (1) Test column was glass consiting of a bed 2 ft (61 cm) deep x 1-7/16 in. (3.65 cm) OD of 251 grams of Amberlite RH-1601 at 31°C

(2) Influent gas concentration: Alcohol = 0.223 % by vol.
Acetone = 0.237 % by vol.

(3) Bed was air dried overnight prior to conducting the experiment.

The loading capacities for the two runs on the two-foot (61-cm) deep bed of Amberlite RH-1601 are shown in Table VI. Loading capacities were calculated at initial breakthrough and at 0.02 percent, by volume, breakthrough (10 percent of the maximum concentration). The loading capacities increase slightly with decrease in flow rate. The total loading capacities at initial ethyl alcohol breakthrough were 1.07 percent and 1.33 percent at flow rates of 4.2 and 1.48 l/min, respectively. During the two runs it was determined that the initial ethyl alcohol breakthrough could be detected with a Miran IR gas analyzer equipped with a 20-meter sample cell. Therefore, all other experiments were conducted with the Miran analyzer monitoring the effluent for ethyl alcohol at a wavelength of 9.5 microns.

Laboratory data collected by Rohm and Haas for another application are shown in Table VII. Results were collected under two conditions: (1) no flow, and (2) 0.50 l/min flow. The results show that the loading capacity is a function of the solvent concentration and that maximum loading capacity is almost double that at initial breakthrough. The literature data received from Rohm and Haas for their adsorption tests with low acetone concentrations agree with the studies conducted at RAAP.

When comparing the loading capacities of acetone and ethyl alcohol on Dow's XFS-4256 with Rohm and Haas Amberlite RH-1601, testing had to be conducted with a 1.5-foot (45.72-cm) bed depth due to insufficient quantity of XFS-4256. The results are shown in Tables VIII and IX. The loading capacities of acetone and ethyl alcohol on XFS-4256 were much lower than those found for Amberlite RH-1601. Part of this may be attributed to particle size and surface area of the material. The XFS-4256 is of 8-10 mesh size where the Amberlite RH-1601 is of smaller size material.

During the runs given in Tables VIII and IX, it was found that moisture remaining on the bed after regeneration aided the loading capacity. The loading capacity increased from 2 to 2.5 times that found with air-dried beds. The moisture on the bed came from the steam regeneration.

The Amberlite RH-1601 had a total loading capacity of 4.05 percent at a flow of 3.0 l/min. Filtrasorb 400 activated carbon tested under the same conditions had a total loading capacity of 11.1 percent at initial breakthrough (or 6.07 percent for acetone and 5.04 percent for ethyl alcohol). Although the loading capacity on the Amberlite RH-1601 polymer is not as high as that on activated carbon, the Amberlite RH-1601 is compatible with NG and less steam would be required for regeneration of the RH-1601 than for the activated carbon.

Table X shows the composition of the effluent when steam is used to regenerate the Amberlite RH-1601 bed. The concentration of solvents in the first two cuts appears to be sufficient for reclamation by distillation.

TABLE VI

SOLVENT ADSORPTION STUDIES
LOADING CAPACITIES VERSUS FLOW RATES
FOR ACETONE AND ETHYL ALCOHOL ON AMBERLITE RH-1601

	Loading Capacities, % by Weight			
	At Initial Alcohol Elution	At 0.02 % by Vol. Alcohol Elution	At Initial Acetone Elution	At 0.02 % by Vol. Acetone Elution
A. 4.2 1/min Flow Rate				
Alcohol	0.46	0.53	----	----
Acetone	0.61	0.71	1.21	1.31
Total	1.07	1.24	----	
B. 1.48 1/min Flow Rate				
Alcohol	0.57	0.61	----	----
Acetone	0.76	0.82	1.35	1.45
Total	1.33	1.43	----	----

Notes: (1) **Column:** Glass packed with 251 grams of Amberlite RH-1601 2 ft x 1-7/16 in. (61 cm x 3.65 cm) at 30°C. Bed air dried overnight prior to testing.

(2) **Influent Gas Concentration:** Alcohol = 0.22 % by Volume
Acetone = 0.24 % by Volume

TABLE VII

ACETONE LOADING CAPACITY ON AMBERLITE RH-1601 ROHM & HAAS RESULTS

A. Test A - No Flow

Gas Concentration, % by Volume Acetone	Maximum Loading Capacities	
	g. Acetone/g. Amberlite	% By Weight
14.9	0.312	31.2
12.56	0.219	21.9
1.23	0.048	4.8
0.22	0.023	2.3

B. Column Work, 0.50 l/min

100 cc of Amberlite RH-1601
Gas Concentration = 13.6 % by Volume Acetone
Breakthrough Loading = 11.3 % by Weight Acetone
Maximum Loading = 20.7 % by Weight Acetone

TABLE VIII

SOLVENT ADSORPTION STUDIES
FLOW RATES VERSUS LOADING CAPACITIES
AT INITIAL BREAKTHROUGH
FOR DOW'S XFS-4356

Flow Rate liters/min	Percent By Weight					
	Air Dry Bed			Water Wet Bed		
	Alcohol	Acetone	Total	Alcohol	Acetone	Total
4.2 l/min	0.14	0.17	0.31	0.32	0.38	0.70
1.5 l/min	0.27	0.33	0.60	0.51	0.61	1.12

Notes: (1) Column: Glass packed with 178 g of Dow's XFS-4256 1.5 ft. deep x 1.438 in. diameter (3.81 cm x 3.65252 cm). Temperature = 22°C

(2) Influent Gas Concentration: Alcohol = 0.23 % by Volume
Acetone = 0.22 % by Volume

TABLE IX

SOLVENT ADSORPTION STUDIES
FLOW RATES VERSUS LOADING CAPACITIES
AT INITIAL BREAKTHROUGH
FOR AMBERLITE RH-1601

Flow Rate liters/min	Percent By Weight					
	Air Dry Bed			Water Wet Bed		
	Alcohol	Acetone	Total	Alcohol	Acetone	Total
4.2 l/min	0.63	0.76	1.39	1.26	1.51	2.77
3.0 l/min	–	–	–	1.84	2.21	4.05
1.5 l/min	-	-	-	2.24	2.70	4.94

Notes: (1) Column: Glass packed with Rohm & Haas Amberlite RH-1601 1.5 ft deep x 1.438 in. diameter (3.81 cm x 3.65 cm), 186.5 grams at 22°C

(2) Influent Gas Concentration: Alcohol = 0.23 % by Volume
Acetone = 0.22 % by Volume

TABLE X

DESORPTION OF ACETONE AND ETHYL ALCOHOL FROM AMBERLITE RH-1601 WITH STEAM

Cut No.	Volume Per Cut	Composition of Cut, % by Weight		
		Acetone	Alcohol	Water
1	125 ml	3.82	5.04	91.14
2	125 ml	0.22	0.25	99.53
3	125 ml	0.028	0.006	99.97
4	125 ml	0.002	trace	99.998
5	110 ml	trace	None detected	—

Column: A 1.5 ft x 1.438 in. (3.81 cm x 3.65 cm) OD bed of 186.5 grams of Amberlite RH-1601

CONCLUSIONS AND RECOMMENDATIONS

Performing Organization's Summary

Conclusions

1. The laboratory studies have shown that NG and solvent vapors cannot effectively be separated by a permeation column.

2. The polymeric adsorbent, Amberlite RH-1601, in laboratory studies for 27 continuous days, proved to be an excellent adsorbent for NG vapors of low concentrations (0.1 to 1.0 ppm).

3. A bed of the polymeric adsorbent saturated with NG can effectively be regenerated with acetone without any deleterious effect on the adsorbent.

4. Steam is a very effective method for desorbing acetone and ethyl alcohol from the polymeric adsorbent. The quantity of steam required to regenerate the polymeric adsorbent was approximately one-half the amount required to regenerate activated carbon.

5. The adsorbing capacity of the polymeric adsorbent for acetone and ethyl alcohol was approximately 2.5 percent, but can be increased to 6 percent by having the bed water wet before the start of the adsorption cycle.

Recommendations

1. Additional studies should be conducted using the bench-scale CAMBL dryer, approximately 15 pounds (7.0 kilograms) capacity, to more thoroughly evaluate the RH-1601 resin for NG adsorption capacity and regeneration techniques.

2. The bench-scale studies should include solvent adsorption and recovery using the polymeric resins to further evaluate a wider range of temperatures and air flows.

ARRADCOM's Summary

Of the two nitroglycerin (NG) removal methods described in this report, permeation and adsorption, only adsorption using the styrene-divinylbenzene copolymer resin (RH-1601) will be considered for the large-scale removal of NG from the waste processing solvents used in the manufacture of multi-base propellants. This method is preferred because RH-1601 resin yields excellent results in separating NG from solvent vapors and can be effectively regenerated with acetone without any deleterious effect on the resin adsorbed. Any residual-adsorbed acetone could be effectively desorbed from the resin using steam.

The benefits to the Government resulting from this study can be realized on a large-scale plant system where several distinctive advantages can be gained:

1. It would provide for a practical cost savings through the economic recovery of solvent mixed with acetone/ethyl alcohol.

2. The explosive and health hazards caused by NG in the solvent vapors would be eliminated.

3. The pollution caused by exhausting the solvent vapors directly into the atmosphere would be eliminated.

4. A practical and economical method has been developed for the regeneration of adsorbing RH-1601 resin.

Further studies should be directed to testing this system on a pilot plant scale.