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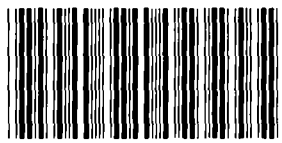
The Evaluation of Potential Limonene Scavengers



Dr. Robert Roth, David Ebert, and Timothy J. Shepodd

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-94AL85000

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The Evaluation of Potential Limonene Scavengers

By

Dr. Robert Roth and Mr. David Ebert
Chemsyn Science Laboratories
13605 W. 96 Terrace
Lenexa, Kansas

and

Timothy J. Shepodd
Sandia National Laboratories
Materials Development and Diagnostics Department
7011 East Avenue
Livermore, California

ABSTRACT

This work is the study of different scavengers of limonene. Limonene is a citrus-based, low toxicity, hydrocarbon solvent for cleaning circuit boards and other parts. Though almost all limonene evaporates after cleaning procedures, trace residual limonene would be a concern if allowed to migrate freely through a sealed system. This work was chartered to investigate materials that would effectively scavenge and permanently immobilize trace limonene.

The requirements of a successful scavenger are the following: it must remove >90% of 30 mg/l limonene from a sealed volume with 3 months, at 20-25° C; it must no release any volatiles over prolonged aging; it must be packaged such that limonene vapors can access the scavenger, but not such that the scavenging medium can migrate; and it must operate in the presence of water, oxygen, pentane, toluene, and carbon dioxide gasses.

A number of adsorbents were evaluated under Sandia contract LA-3971 by Chemsyn Science Laboratories. The work was performed by Mr. David Ebert and Dr. Robert Roth. The original report, as authored by Dr. Robert Roth is attached.

Additionally, a scheme for scavenging limonene by chemical reaction was investigated at Sandia. This attempt was not successful. The details of this investigation are found at the end of this report.

EVALUATION OF POTENTIAL LIMONENE SCAVENGERS

FINAL REPORT

September 10 1993

Sandia Contract No. LA-3971
CSL JOB# 1061

For

Sandia National Laboratories
P. O. Box 969
Livermore, CA 94550

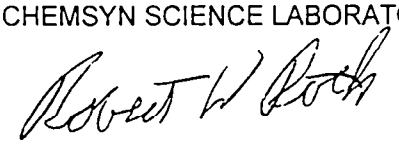
Chemsyn Science Laboratories 13605 W. 96 Terrace, Lenexa, KS 66215 • (913) 541-0525

PREFACE

This report describes work performed under Sandia National Laboratory Contract No. LA-3971 during the performance period of July 31 1992 to July 31, 1993. The work was performed by Mr David Ebert and Dr. Robert Roth...Dr. Roth is the pricipal author of this report.

Approved for:

CHEMSYN SCIENCE LABORATORIES



Robert W. Roth, Ph.D.
Group Leader

September 10, 1993

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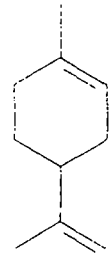
Summary

Several potential adsorbants have been evaluated as potential scavengers for limonene vapor in air. Included were Pelliguard LC-8 (Supelco #5-8293), 10% 123-Tris (Supelco #1-2122), Pelligaurd LC-CN (Supelco # 5-8235), Carbotrap 20/40 mesh (Supelco #2-087), 10% SP-2250 on 100/120 Supelcoport (Supelco) Darco activated carbon (Aldrich Chemical), Aluminum Oxide, neutral Brockman Activity 1 (Aldrich), Molecular Sieve 13X powder (Aldrich) and PTMSP polymer (a gift from Air Products). Preliminary screening showed the Carbotrap, Darco activated carbon, aluminum oxide, molecular sieve and PTMSP to be effective. A custom adsorbant, obtained from solvent casting a 20:80 wt/wt mixture of Darco activated carbon and PTMSP into cutable sheets, was shown to be effective at removing approxamtely 98% of an initial 100 mg of limonene in a closed 3L container at 70° C within 72 hr.

I. INTRODUCTION

Limonene, an inexpensive, naturaly occurring terpene, may be a suitable replacement for ozone-depleting halogenated solvents now used for degreasing electronic circuit boards. However, due to the comparitively low volatility of limonene (bp 175-176) treated boards can have a significant limonene residue. To minimize the uncertainty concerning long term harmful effects of limonene vapor on these systems a means of scavenging limonene is being sought.



Limonene

The goal of the present study is to evaluate several potential limonene adsorbants. The ideal material would meet the following criteria:

- must reduce the amount of limonene present by scavenging the olefin as it is slowly released into a sealed chamber.
- must not release other volatile or reactive species over long aging times.
- must not be a free flowing liquid
- must be packaged in an inert medium that allows the passage of limonene vapor, but not the escape of the material used to scavenge the limonene
- must operate in the presence of oxygen, moisture, and the vapor of other small, non-functional organic molecules such as pentane, toluene and carbon dioxide
- may rely on chemical adsorption or (preferably) a covalent modification to immobilize the limonene
- must operate between -40 °C and 70 °C
- should remove 90% of the free limonene vapor from a closed system in 3 months at room temperature (0.1 g total limonene from a 3 L free volume at 20-25 °C in an atmosphere of 10-100% air; balance nitrogen.

II. Technical Approach

The approach taken in the present study was to screen several commercially available materials known to have generally good adsorbant characteristics for nonpolar organic compounds, followed by more detailed testing of promising candidates. One of the materials chosen was developed only recently and though not yet available commercially, offered the possibility of casting into a single piece which could simplify packaging. Initial screening (conducted at 70°C to shorten equilibration times) was done by placing a relatively large amount of adsorbant in a 0.3 L-test chamber along with 10μL of limone and monitoring the limone level in by GLC. Subsequent testing was done one a custom adsorbant obtained by combining two of the best performing candidates in the initial tests: Darco activated carbon and PTMSP polymer from Air products. This material was produced as a solid cutable sheet which, based on the results of tests described in the next section, meets all of the stated performance requirements for a limonene scavenger.

III. Results and Discussion

A. GC Calibration A GC response curve was initially estabished using solutions of limonene in pentane made at known concentrations. A linear response was observed over a range of 0.03 to 2.27 μg of total limonene in a single injection with an average response of 8.36E06 counts/μg (std deviation of ±5%). Tabular and graphical summaries of this data are presented in Table 1 and Figure 2. A new response curve covering the narrower concentration actually encountered in the absoption tests was established for each day that absorption measurements were made. Data from these curves was then used to determine limonene concentrations on the tests for that day.

B. Initital screening. A series of 11 candidate adsorbants was subjected to an initial screening test to select those most likely to meet the overall performance criteria. These tests employed a 300 cc (1/10 scale) vessel (Figure 2) and were conducted at 70°. During initial it was determined significant limonene is absorbed by standard Viton O-rings. All test data reported here were obtained using Teflon encapsulated Viton O-rings. The stopcock on the test chambers was also Teflon. A 2 gram sample of adsorbant was placed in the beaker, 10 μL of D-limonene was appllied to the filter paper, the apparatus was assembeled and placed in an an oven at 70±0.5°C. Limone vapor

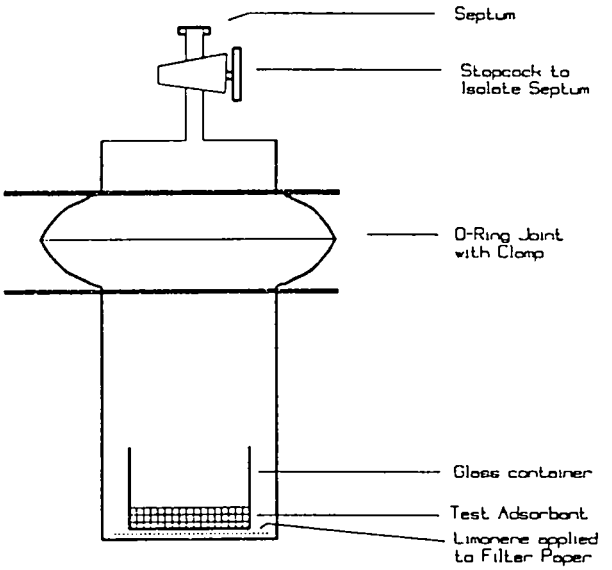


Figure 1 - Test Apparatus for Rapid Screening of Limonene Scavengers

concentration was measured by GLC at approxamately 24 and 48 hour intervals. The sampling procedure consisted of removing the test unit from the oven, opening the stopcock, inserting a gas-tight syringe through the septum, pumping the plunger four times, allowing the plunger to remain cocked for approximately 10 seconds before removing the sample for injection. This operation was performed as quickly as possible so as to avoid cooling the test chamber. Results of these preliminary tests, presented on Tables 2, 3 and 4 show that complete or nearly complete absorption was obtained with Darco activated carbon, neutral alumina, molecular sieves (13X), Supelco Carbotrap 20/30 mesh and PTMSP polymer. Based on these results and other considerations the scope of subsequent testing was narrowed to a custom adsorbant formulation obtained by combining two of the most promising candidates, (1) Darco G-60, a common grade of activated carbon and (2) poly(trimethylsilylpropyne)[1] (PTMSP), a solvent castable polymer supplied by Air Products and Chemicals Inc.[2]

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[1] L. M. Robeson and M. Langsam, Separation Science and Technology, **1992**, 1245-58.

[2] PTMSP was supplied in solid form courtesy of Mr. Lloyd M Robeson of Air Products and Chemicals Inc., Allentown, PA (215) 481-5026.

B. Preparation of PTMSP/Activated Carbon Mixture The polymer (4.0 g) was dissolved in toluene (160 mL) by prolonged heating near reflux. Darco G-60 activated carbon (Aldrich Chemical Co.) (1 gram) was added and the hot mixture was stirred for one half hour and then allowed to cool to 50°C. The opaque mixture was poured into a 5"x5" polyethylene container which was then covered with two layers of Kimwipe secured with an elastic band. The container was placed in a fume hood to permit slow evaporation of the solvent. After 5 days, when most of the toluene had evaporated, the cover was removed to accelerate further evaporation of the solvent which was complete within 48 hours. During the final stages of evaporation the cast polymer tends to curl and pull away from the container. If the evaporation rate is too fast a relatively shapeless mass is obtained. A 10 gram portion of the polymer and 2.5 grams of Darco G-60 were similarly cast using metal pans having a "non-stick" silicone coating.

C. Capacity and Desorption Tests The purpose of these tests was to estimate the maximum adsorption capacity of the getter prior to conducting final tests. The activated carbon-PTMSP material was cut into pieces with weights of 0.6-1.0 g and suspended from a copper wire rack in the test chambers over excess limonene (500 µL). The tests were conducted using three samples each at ambient temperature and 70°C. Samples were weighed daily. The results, summarized in Tables 5 and 6 show an average mass gain of approxamately 90% both at ambient and elevated temperature. At 70°C, however, maximum capacity is reached within only 24 hours. At ambient ternperature maximum adsorption required 7-8 days.

The desorption test was done simply by placing the saturated samples in open 50 mL beakers in a fume hood. Samples were weighed daily until no further mass loss was observed. These results, shown in Table 7, indicated that rapid desorption occurrs within the first 24 hours. Equilibrium was reached within 4 days with an average limonene retention of 27% of the scavenger weight.

D. Scavenger One Half Capacity Test. The objective of this test was to determine the adsorption performance of the scavenger at 70°C when exposed to relatively large quantities of limonene in a closed system. This was done using 200-300 mg of scavenger in the test vessel shown in Figure 1, charging the vessel initially with a quantity of limonene equal to 45% by wt of the scavenger and measuring limonene in the gas phase by GC as in the initial screening tests. After 92 hours apparent equilibrium was reached and an additional quantity of limonene was added bringing the total amount to 65% by weight of scavenger. The results of these experiments are summmarized in Tables 8 and 9. It should be emphasised that a comparison of scavenger results with the control values is of limited value because the most of the limonene present in the control chambers is in the liquid state and cannot be measured in the gas state. The data do show that at 45% loading the amount of limonene remaining in the gas phase is less than 15% of the saturated level. Even at a limonene:getter ratio of 0.65:1 levels in the gas phase are well be low saturation values.

E. Full Scale Adsorption Tests. This test was designed to demonstrate the ability of the scavenging system to remove "90% of the free limonene vapor from a closed system...containing 0.1g total limonene in a 3 L free volume...". This test would have been conducted at ambient temperature but due to completion deadlines it was accelerated by running at 70°C. This is justified on the basis of the capacity test results above demonstrating no difference total capacity of at 70°C vs ambient temperature. Test units similar to that shown in Figure 1 having an internal volume of approximately 3L were employed. The internal volumes were accurately measured using standard manometric techniques. Limonene (118 µL , 100 mg) and scavenger (1.0 g, suspended from a copper wire hanger) was used to obtain a limonene:scavenger ratio of 1:10. The vessels were assembeled in ambient air. Loading parameters are summarized in Table 10. Sampling was done after 6, 28, 51, and 74 hours. In order to minimize variations in apparent concentrations due to uneven cooling the vessels were allowed to cool to ambient temperature before sampling. Corressponding data are detailed in Tables 11-14 and overall results are summarized in Table 15. Again it should be emphasized that levels of limonene measured in controls represent a saturated condition and are threrfore sensitive to slight variations in ambient temperature and technique. Even so, the average level remaining in the scavenged chambers afer 74 hours , 1.75 mg, is equivalent to 1.75% residual limonene or 98.25% adsorption. Therefore it is concluded that this system meets or exceeds the basic performance requirements outlined in the introduction.

Table 1

G.C. CALIBRATION DATA

JOB#1061

D-Limonene Lot# MF-20 (from Allied Signal) Density (21 deg) 0.84
Limonene Solvent, Pentane, Lot#_ 02520MV,Aldrich 23,670-5

GC Column: glass, 1.7Mx 5mm O.D.,x 3mm I.D. w 3% SP2250 on 80/100 Supelcoport
Inj Temp: 250 deg FID :250 deg
Program: 55 deg Isothermal
FID Atten: 1.00E+01

Raw DATA

Date	Run#	Initial Stock conc uL/mL	Dilution Factor	Final Conc ug/uL	Injection Volume uL	Total Area Counts	ug injected	Area Counts/ug
10/12/92	53	1	1.33	0.63	2.5	1.27E+07	1.58	8.04E+06
10/12/92	55	1	1.33	0.63	3.0	1.47E+07	1.89	7.76E+06
10/12/92	56	1	1.33	0.63	2.8	1.37E+07	1.76	7.75E+06
10/12/92	58	0.5	1.00	0.42	2.5	8.59E+06	1.05	8.18E+06
10/12/92	59	0.5	1.00	0.42	3.2	1.17E+07	1.34	8.70E+06
10/12/92	60	0.5	1.00	0.42	2.8	9.59E+06	1.18	8.15E+06
10/12/92	61	0.5	2.00	0.21	2.8	4.89E+06	0.59	8.32E+06
10/13/92	62	0.5	2.00	0.21	3.2	5.88E+06	0.67	8.74E+06
10/13/92	64	0.1	1.00	0.08	2.9	2.21E+06	0.24	9.05E+06
10/13/92	65	0.1	1.00	0.08	3.1	2.24E+06	0.26	8.62E+06
10/13/92	66	0.1	1.00	0.08	3.0	2.13E+06	0.25	8.44E+06
10/13/92	67	0.1	2.00	0.04	3.2	1.14E+06	0.13	8.47E+06
10/13/92	68	0.1	2.00	0.04	3.1	1.11E+06	0.13	8.51E+06
10/13/92	69	0.1	2.00	0.04	2.8	9.88E+05	0.12	8.40E+06
10/13/92	70	0.1	4.00	0.02	3.4	5.94E+05	0.07	8.33E+06
10/13/92	71	0.1	4.00	0.02	3.4	6.07E+05	0.07	8.50E+06
10/13/92	72	0.1	4.00	0.02	3.4	5.79E+05	0.07	8.11E+06
10/13/92	73	0.1	10.00	0.01	3.5	2.25E+05	0.03	7.67E+06
10/13/92	74	0.1	10.00	0.01	3.2	2.11E+05	0.03	7.86E+06
10/13/92	75	0.1	10.00	0.01	3.7	2.54E+05	0.03	8.19E+06
10/14/92	77	1	1.00	0.84	2.2	1.66E+07	1.85	9.00E+06
10/14/92	78	1	1.00	0.84	2.7	2.02E+07	2.27	8.90E+06
10/14/92	79	1	1.00	0.84	2.7	1.93E+07	2.27	8.52E+06
							Avg	8.36E+06
							Std Dev	3.89E+05
							+/-	4.66%

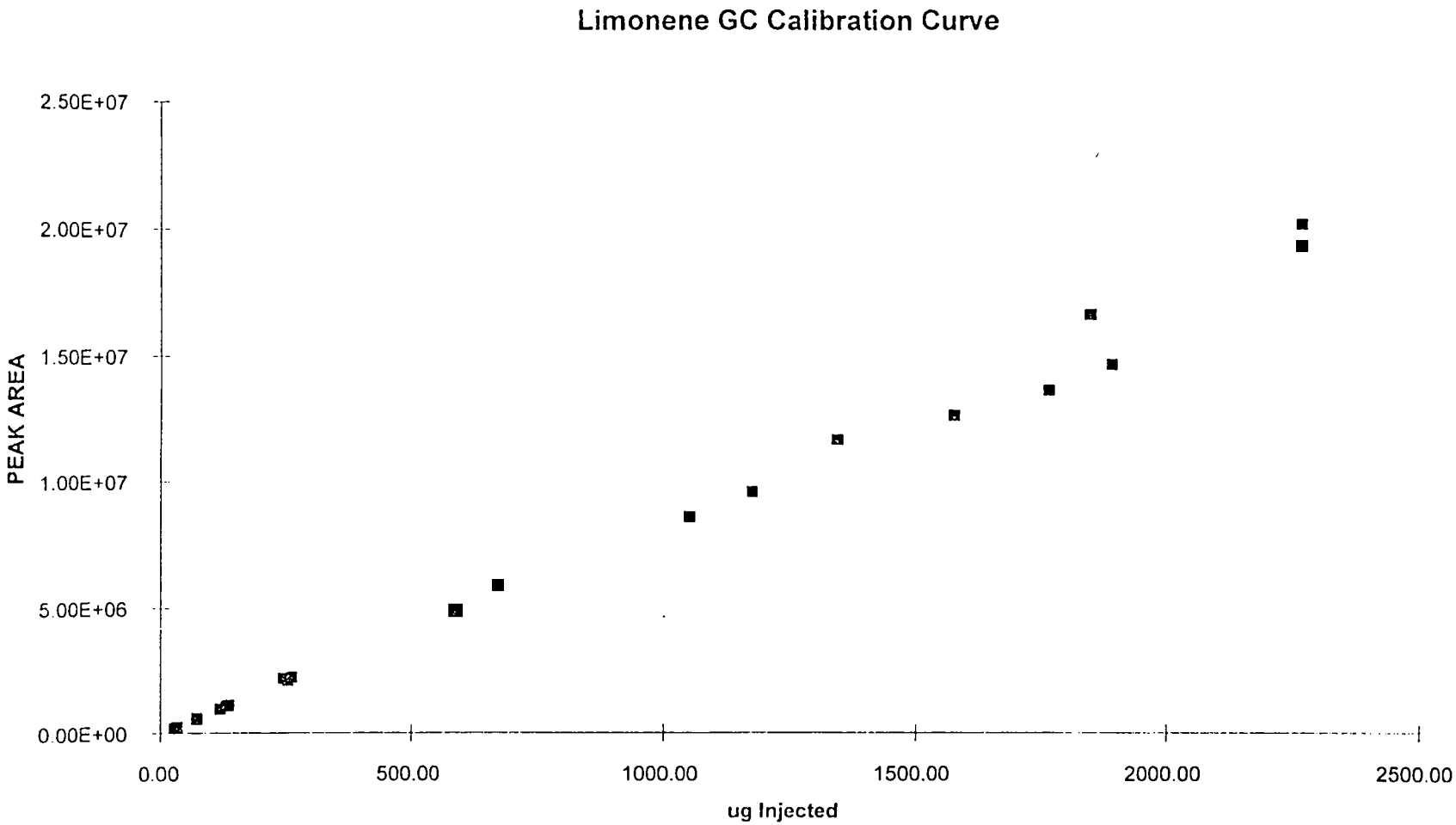

Limonene GC Calibration Curve
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
PEAK AREA
0.00
500.00
1000.00
1500.00
2000.00
2500.00
ug Injected

Figure 2

Table 2

SCAVENGER TEST-PHASE I
INITIAL SCREENING

Limonene lot #MF-20 — Volume of test chambers: 320 to 325 cc

uL Limonene added 10 — Test temperature: 70C

GC column: 1.7 M X 3 mm I.D. glass; 3% SP 2250 on 80/100 Supelcoport

Temperature program: 55C isothermal — Inj. temp: 250C

F.I.D. atten.: 10E1 — Volume Sampled (uL): 100

Test started: 11/23/92: 930 HOURS

		Day 1					Day 2				
		Area Counts			Limonene	%	Area Counts			Limonene	%
Chamber #	Adsorbent	Inj# 1	Inj #2	Avg	mg/L	Control	Ing# 1	Inj# 2	Avg	mg/L	Control
1	Control-No Adsorbent	1.18E+07	1.26E+07	1.22E+07	15.6	100	8.98E+06	4.86E+06	6.92E+06	8	100
2	Pelliguard LC-8; Supelco #5-8293	1.54E+07	1.53E+07	1.53E+07	19.6	126	1.16E+07	1.41E+07	1.28E+07	14	185
3	10% 1,2,3-Tris; Supelco #1-2122	1.01E+07	1.22E+07	1.11E+07	14.2	91	9.79E+06	1.06E+07	1.02E+07	12	147
4	Pelliguard LC-CN; Supelco #5-8235	1.05E+07	1.25E+07	1.15E+07	14.7	94	7.48E+06	1.35E+07	1.05E+07	12	152
5	Carbotrap 20/40 mesh; Supelco #2-087	0.00E+00	2.62E+04	1.31E+04	0.0	0	1.20E+05	8.58E+04	1.03E+05	0	1
6	10% SP-2250 on 100/120 Supelcoport	6.01E+06	5.79E+06	5.90E+06	7.6	48	5.09E+06	6.56E+06	5.82E+06	7	84

G.C. Calibration Data:

Day 1					Day 2				
Stock Conc		uL	Area	Area	Stock Conc		uL	Area	Area
uL/L	mg/L	Injected	Counts	Counts/m	uL/L	mg/L	Injected	Counts	Counts/mg
500	400	3.6	9.79E+06	6.8E+09	500	400	3.4	1.25E+07	9.19E+09
500	400	3.2	9.73E+06	7.6E+09	500	400	3.7	1.31E+07	8.85E+09
10	8	3.4	2.27E+05	8.35E+09	10	8	4.2	3.03E+05	9.02E+09
10	8	2.8	1.90E+05	8.48E+09	10	8	4.2	2.79E+05	8.3E+09
			Average:	7.81E+09				Average:	8.84E+09

Table 3

SCAVENGER TEST-PHASE 1
INITIAL SCREENING

Limonene lot #MF-20 Volume of test chambers: 320 to 325 cc

uL Limonene added 10 Test temperature: 70C

GC column: 1.7 M X 3 mm I.D. glass; 3% SP 2250 on 80/100 Supelcoport

Temperature program: 55C isothermal Inj. temp: 250C

F.I.D. atten.: 10E1 Volume Sampled (uL): 100

Test started: 11/18/92;530 HOURS

		DAY 1					DAY 2				
		Area counts			Limonene	%	Area Counts			Limonene	%
Chamber #	Adsorbent	Inj# 1	Inj #2	Avg	mg/L	Control	Inj#1	Inj# 2	Avg	mg/L	Control
1	Control-No Adsorbent	6.17E+06	3.59E+06	4.88E+06	6.3	100	5.25E+06	4.82E+06	5.04E+06	6	100
2	Darco Activated Carbon G-60	0	0	0.00E+00	0.0	0	0	0	0	0	0
3	Silica Gel, 70-230 Mesh, Aldrich	7.06E+05	5.26E+05	6.16E+05	0.8	13	5.32E+05	5.05E+06	2.79E+06	3	55
4	Aluminum Oxide, neutral Brockman Act 1	5.59E+04	8.78E+04	7.19E+04	0.1	1	1.56E+05	1.57E+05	1.57E+05	0	3
5	Pelliguard LC-18,Supelco	7.73E+06	9.09E+06	8.41E+06	10.8	172	8.31E+06	9.77E+06	9.04E+06	10	180
6	Molecular sieves, 13X, powder, Aldrich	0	0	0.00E+00	0.0	0	0	0	0	0	0

G.C. Calibration Data:

Day 1					Day 2				
Stock Conc uL/L	mg/L	uL Injected	Area Counts	Area Counts/m	Stock Conc uL/L	mg/L	uL Injected	Area Counts	Area Counts/mg
500	400	3.6	9.79E+06	6.8E+09	500	400	3.4	1.25E+07	9.19E+09
500	400	3.2	9.73E+06	7.6E+09	500	400	3.7	1.31E+07	8.85E+09
10	8	3.4	2.27E+05	8.35E+09	10	8	4.2	3.03E+05	9.02E+09
10	8	2.8	1.90E+05	8.48E+09	10	8	4.2	2.79E+05	8.3E+09
			Average:	7.81E+09				Average:	8.84E+09

Table 4

SCAVENGER TEST-PHASE 1
INITIAL SRCEENING

Limonene:lot #MF-20 Volume of test chambers: 320 to 325 cc

uL Limonene added 10 Test temperature: 70C

GC column: 1.7 M X 3 mm I.D. glass; 3% SP 2250 on 80/100 Supelcoport

Temperature program: 55C isothermal Inj. temp: 250C

F.I.D. atten.: 10E1 Volume Sampled (uL): 100

Test started: 1/6/1993;1400 hours

		Day 1					Day 2				
		Area counts			Limonene	%	Area Counts			Limonene	%
Chamber	Adsorbent	Inj# 1	Inj #2	Avg	mg/L	Control	Inj#1	Inj# 2	Avg	mg/L	Control
1	Blank;no adsorbant	1.20E+07	1.40E+07	1.30E+07	14.0	100	1.57E+07	1.27E+07	1.42E+07	16	100
2	PTMSP Polymer;Air Products	0	0	0.00E+00	0.0	0	1.61E+05	3.13E+05	2.37E+05	0	2
3											
4											
5											
6											

G.C. Calibration Data:

Day 1					Day 2				
Stock Conc		uL	Area	Area	Stock Conc		uL	Area	Area
uL/L	mg/L	Injected	Counts	Counts/m	uL/L	mg/L	Injected	Counts	Counts/mg
1000	800	3	2.26E+07	9.41E+09	1000	800	2.5	1.81E+07	9.07E+09
1000	800	4.5	3.38E+07	9.39E+09	1000	800	2.8	2.15E+07	9.59E+09
100	80	3.2	2.21E+06	8.63E+09	100	80	3.7	2 38E+06	8.03E+09
100	80	4.9	3.83E+06	9.76E+09	100	80	4.2	2.90E+06	8.62E+09
			Average:	9.3E+09				Average:	8.83E+09

Table 5

SCAVENGER TOTAL CAPACITY TEST

AMBIENT

Scavenger: 80/20 PTMSP lot#10563-72-2 / Activated Carbon;
Aldrich #24,227-6; lot #04713EY

Limonene lot#MF-20

Volume of test chambers: 320 to 325 cc

uL limonene added: 500

Test Temperature: Ambient

est started: 5/10/93 14:00

Date/time	Elapsed Time(hrs.)	Temp(C)	Unit #	Weight (g.)	Weight Gain(%)	Average Gain(%)
5/10/93 14:00	0	19	1	0.5979	0	0
			2	0.3028	0	
			3	0.395	0	
5/11/93 14:00	24	19	1	0.6782	13%	20%
			2	0.3759	24%	
			3	0.4784	21%	
5/12/93 15:00	49	18	1	0.7511	26%	36%
			2	0.4374	44%	
			3	0.5492	39%	
5/13/93 14:00	72	20	1	0.8175	37%	49%
			2	0.4773	58%	
			3	0.6013	52%	
5/14/93 14:30	96	21	1	0.8772	47%	59%
			2	0.5084	68%	
			3	0.6409	62%	
5/17/93 14:00	168	18	1	0.9829	64%	79%
			2	0.5692	88%	
			3	0.7258	84%	
5/18/93 15:00	193	20	1	1.0039	68%	82%
			2	0.5798	91%	
			3	0.7367	87%	
5/19/93 15:00	217	19	1	1.0269	72%	86%
			2	0.5929	96%	
			3	0.7515	90%	
5/20/93 16:00	242	20	1	1.0472	75%	88%
			2	0.5984	98%	
			3	0.7589	92%	

Table 6

SCAVENGER TOTAL CAPACITY TEST

70C

Scavenger: 80/20 PTMSP lot#10563-72-2 / Activated Carbon;
Aldrich #24,227-6; lot #04713EY

Limonene lot#MF-20

Volume of test chambers: 320 to 325 cc

uL limonene added: 500

Test temperature: 70C

Date test started: 5/10/93 14:00

Date/Time	Elapsed Time(hrs.)	Unit #	Weight (g.)	Weight Gain(%)	Average Gain(%)
5/10/93 14:00	0	4	0.3947	0	0
		5	0.5847	0	
		6	0.3469	0	
5/11/93 14:00	24	4	0.7519	90%	83%
		5	0.9452	62%	
		6	0.686	98%	
5/12/93 15:00	49	4	0.6992	77%	73%
		5	0.9058	55%	
		6	0.6526	88%	
5/13/93 14:00	72	4	0.6531	65%	64%
		5	0.8653	48%	
		6	0.6207	79%	
5/14/93 14:30	96.5	4	0.7924	101%	98%
		5	1.02	74%	
		6	0.7539	117%	
5/17/93 14:00	168	4	0.885	124%	120%
		5	1.0655	82%	
		6	0.8846	155%	
5/18/93 15:00	193	4	0.8546	117%	112%
		5	1.0498	80%	
		6	0.8281	139%	
5/19/93 15:00	217	4	0.7715	95%	101%
		5	1.0586	81%	
		6	0.7844	126%	
5/20/93 16:00	242	4	0.7198	82%	93%
		5	1.0338	77%	
		6	0.7643	120%	

Table 7

DESORPTION TEST

AMBIENT

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon
#24,227-6, lot #04713EY

Limonene lot #MF-20

Test conditions: Samples removed from chambers and placed in separate
50 ml. beakers in a fume hood. The beakers were not covered.

Date/Time	Elapsed Time(hrs.)	Temp(C)	Unit #	Weight (g.)	Weight Gain(%)	Average Gain(%)
5/20/93 16:00	0	23	1	1.0472	75%	91%
			2	0.5984	98%	
			3	0.7589	92%	
			4	0.7198	82%	
			5	1.0338	77%	
			6	0.7643	120%	
5/21/93 14:30	22.5	23	1	0.7163	20%	35%
			2	0.3784	25%	
			3	0.4803	22%	
			4	0.5064	28%	
			5	0.7576	30%	
			6	0.6407	85%	
5/22/93 14:30	46.5	22	1	0.7071	18%	32%
			2	0.3741	24%	
			3	0.4777	21%	
			4	0.4928	25%	
			5	0.7329	25%	
			6	0.624	80%	
5/24/93 16:00	96	22	1	0.694	16%	29%
			2	0.3709	22%	
			3	0.4735	20%	
			4	0.4759	21%	
			5	0.7122	22%	
			6	0.6044	74%	
5/25/93 17:00	121	21	1	0.69	15%	28%
			2	0.3696	22%	
			3	0.4716	19%	
			4	0.4708	19%	
			5	0.7053	21%	
			6	0.6	73%	

Table 7 (Continued)

DESORPTION TEST

(CONT.)

Date/Time	Elapsed Time(hrs.)	Temp(C)	Unit #	Weight (g.)	Weight Gain(%)	Average Gain(%)
5/26/93 17:00	145	20	1	0.6885	15%	28%
			2	0.3679	21%	
			3	0.4713	19%	
			4	0.4693	19%	
			5	0.7022	20%	
			6	0.5972	72%	
5/27/93 16:00	168	21	1	0.6868	15%	28%
			2	0.3674	21%	
			3	0.4704	19%	
			4	0.4677	18%	
			5	0.7002	20%	
			6	0.5971	72%	
5/28/93 11:00	187	22	1	0.685	15%	27%
			2	0.3674	21%	
			3	0.4706	19%	
			4	0.4673	18%	
			5	0.6987	19%	
			6	0.5966	72%	
6/2/93 10:00	306	19	1	0.6781	13%	26%
			2	0.3664	21%	
			3	0.4677	18%	
			4	0.4612	17%	
			5	0.6893	18%	
			6	0.5902	70%	
6/3/93 11:00	331	21	1	0.6788	14%	27%
			2	0.3658	21%	
			3	0.4681	19%	
			4	0.4619	17%	
			5	0.6911	18%	
			6	0.5932	71%	

Table 8

SCAVENGER CAPACITY TEST

SCAVENGER WEIGHT & QTY. LIMONENE ADDED

0.3 L. VESSELS

REF:92-417-69

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon #24,227-6, lot#04713EY

Limonene lot#MF-20

Volume of test chambers: 320 to 325 cc

Test temperature: 70C

Density of limonene: 0.842

Date test started: 06/07/93;1500 hrs.

UNIT#	Date	Time	Wt. of Scav.(mg)	Limonene added(mg)	uL limonene
2	6/7/93	1500	none	111	132
3			none	111	132
4			294.6	133	157
5			174.5	79	93
6			270	122	144
2	6/11/93	1600		48	57
3				48	57
4				59	70
5				35	42
6				54	64

Table 9

SUMMARY
ADSORPTION AT ONE HALF CAPACITY
0.3 L. VESSELS
REF:92-417-69

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich
Activated Carbon #24,227-6; lot #04713EY
Limonene lot#MF-20
Volume of test chambers: 320 to 325 cc
Test temperature: 70C
Date test started: 6/7/93 14:00
Volume sampled(uL); 100

G.C. Conditions

GC Column: glass; 1.7 M X 5mm O.D. X 3mm I.D.
Column packing: 3% SP2250 on 80/100 Supelcoport
Inj. temp: 250 C FID temp 250 C
Program: 55 C isothermal

	Elapsed Time(hrs.)						
	20	45	72	92	166	189	214
UNIT #	Gas(mg.)						
2(blank)	12.18	9.57	2.4	1.61	5.49	4.08	4.47
3(blank)	9.85	10.85	1.9	1.74	5.29	2.8	4.43
4	5.44	6.11	1.26	1.02	4.34	1.51	3.28
5	6.67	6.62	0.78	0.81	3.77	1.76	2.84
6	5.51	5.82	0.76	0.74	3.68	2.58	3.55
	45 wt.% limonene				65 wt.% limonene		

Table 10

ADSORPTION AT 10% LOADING

WEIGHT AND DIMENSIONS OF SCAVENGER

3 L. VESSELS

UNIT #	Volume (cc's)	Wt. Scav. (g.)	Dimensions of Scavenger
1A	2843	none	n.a
2A	2861	none	n.a.
3A	2772	1.052	60 X 39 X 0.5 mm.
4A	2779	1.035	58 X 38 X 0.6 mm.

Table 11

ADSORPTION AT 10% LOADING

3 L. VESSELS

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon #24,227-6, lot#04713EY
Limonene : Lot # MF-20
Amount limonene added to each vessel: 100 mg (118 uL).
Test temperature: 70C
Volume sampled(uL); 100

Date:06/21/93

Units removed from oven , placed in a hood and
allowed to reach r. t. Unit placed back in 70C oven
after sampling.

Date test started: 06/21/93; 1020 hrs.

Time removed from oven	UNIT #	RUN DATA Run #	Time	Area cts.	Wt. Gas (mg.)	Average (mg.)
1501	1A	196	1524	1.15E+07	39.20	45.85
		197	1540	1.54E+07	52.50	
1520	2A	198	1554	7.93E+06	27.03	30.35
1545	3A	199	1609	4.65E+06	15.85	14.34
		200	1623	3.76E+06	12.82	
1607	4A	201	1637	8.36E+05	2.85	1.98
		202	1651	3.25E+05	1.11	

Calibration data

Limonene solvent: pentane, Aldrich 23,670-5; Lot #02520MV
GC Column: glass; 1.7 M X 5mm O.D. X 3mm I.D.
Column packing: 3% SP2250 on 80/100 Supelcoport
Inj. temp: 250 C FID temp 250 C
Program: 55 C isothermal

Area cts./ug.(from Cal.curve): 8.36E+06

Table 12

ADSORPTION AT 10% LOADING

3 L. VESSELS

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon #24,227-6, lot#04713EY

Date:06/22/93

Limonene : Lot # MF-20

Amount limonene added to each vessel: 100 mg (118 uL).

Test temperature: 70C

Volume sampled(uL); 100

Units removed from oven , placed in a hood and allowed to reach r. t. Unit placed back in 70C oven after sampling.

Date test started: 06/21/93; 1020 hrs.

Time removed from oven	UNIT #	RUN DATA Run #	Time	Area cts.	Wt. Gas (mg.)	Average (mg.)
1309	1A	203	1331	1.65E+07	54.82	85.83
		204	1344	3.53E+07	117.28	
		205	1358	2.57E+07	85.38	
1338	2A	206	1411	2.49E+07	82.72	93.36
		207	1428	3.26E+07	108.31	
		208	1441	2.68E+07	89.04	
1410	3A	209	1458	2.71E+06	9.00	8.21
		210	1519	2.23E+06	7.41	
1456	4A	212	1546	4.77E+05	1.58	1.35
		214	1617	3.37E+05	1.12	

Calibration data

Limonene solvent: pentane, Aldrich 23,670-5; Lot #02520MV

GC Column: glass; 1.7 M X 5mm O.D. X 3mm I.D.

Column packing: 3% SP2250 on 80/100 Supelcoport

Inj. temp: 250 C FID temp 250 C

Program: 55 C isothermal

Stock Conc. uL/mL	Dilution Factor	Final Conc. ug/uL	Injection volume uL	Total area counts	ug injected	Area counts/ug
0.01	1	0.0084	3.4	2.45E+05	0.02856	8.58E+06
0.01	1	0.0084	2.2	1.73E+05	0.01848	9.36E+06

Average= 8.58E+06

Table 13

ADSORPTION AT 10% LOADING

3 L. VESSELS

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon #24,227-6, lot#04713EY

Date: 06/23/93

Limonene : Lot # MF-20

Amount limonene added to each vessel: 100 mg (118 uL).

Test temperature: 70C

Volume sampled(uL); 100

Units removed from oven , placed in a hood and allowed to reach r. t. Unit placed back in 70C oven after sampling.

Date test started: 06/21/93; 1020 hrs.

Calibration data

Limonene solvent: pentane, Aldrich 23,670-5; Lot #02520MV

GC Column: glass; 1.7 M X 5mm O.D. X 3mm I.D.

Column packing: 3% SP2250 on 80/100 Supelcoport

Inj. temp: 250 C FID temp 250 C

Program: 55 C isothermal

Time removed from oven	UNIT #	RUN DATA			Wt. Gas (mg.)	Average (mg.)
		Run #	Time	Area cts.		
1040	1A	224	1104	2.48E+07	84.55	75.51
		225	1118	1.95E+07	66.48	
1111	2A	226	1137	1.89E+07	64.43	100.74
		227	1152	4.02E+07	137.05	
1154	3A	228	1222	2.63E+06	8.97	9.09
		229	1314	2.70E+06	9.20	
1315	4A	233	1447	8.36E+04	0.29	0.26
		234	1513	6.64E+04	0.23	

Area Cts./ug(G.C. Cal. curve): 8.36E+06

Table 14

ADSORPTION AT 10% LOADING

3 L. VESSELS

Scavenger: 80/20 PTMSP lot#10563-72-2 / Aldrich Act. Carbon #24,227-6, lot#04713EY
Limonene : Lot # MF-20
Amount limonene added to each vessel: 100 mg (118 uL).
Test temperature: 70C
Volume sampled(uL); 100

Date:06/24/93

Units removed from oven , placed in a hood and
allowed to reach r. t. Unit placed back in 70C oven
after sampling.

Date test started: 06/21/93; 1020 hrs.

Time removed from oven	UNIT #	RUN DATA Run #	Time	Area cts.	Wt. Gas (mg.)	Average (mg.)
924	1A	243	1059	5.07E+06	19.32	20.73
		244	1113	5.81E+06	22.14	
1004	2A	245	1129	8.37E+06	31.90	32.64
		246	1143	8.76E+06	33.38	
1128	3A	248	1234	9.62E+05	3.67	3.25
		250	1335	7.46E+05	2.84	
1158	4A	251	1351	6.37E+04	0.24	0.25
		252	1405	6.77E+04	0.26	

Calibration data

Limonene solvent: pentane, Aldrich 23,670-5; Lot #02520MV
GC Column: glass; 1.7 M X 5mm O.D. X 3mm I.D.
Column packing: 3% SP2250 on 80/100 Supelcoport
Inj. temp: 250 C *FID temp 250 C*
Program: 55 C isothermal

Stock Conc. uL/mL	Dilution Factor	Final Conc. ug/uL	Injection volume uL	Total area counts	ug injected	Area counts/ug
0.01	1	0.0084	3.9	2.45E+05	0.03276	7.48E+06
0.01	1	0.0084	4.3	2.86E+05	0.03612	7.92E+06

Average= 7.48E+06

Table 15

SUMMARY
ADSORPTION AT 10% LOADING
3 L. VESSELS

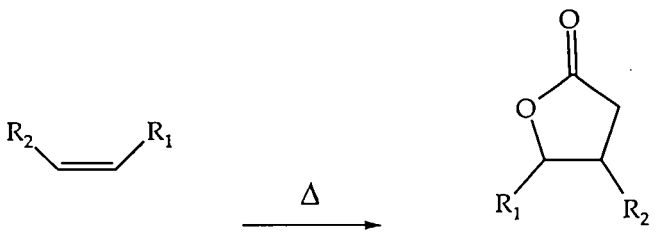
Date test started: 6/21/93 10:20

	Elapsed Time(hrs.)			
	6	28	51	74
UNIT #	Gas(mg.)			
1A(blank)	45.85	85.83	75.51	20.73
2A(blank)	30.35	93.36	100.74	32.64
3A	14.34	8.21	9.09	3.25
4A	1.98	1.35	0.26	0.25

RESULTS

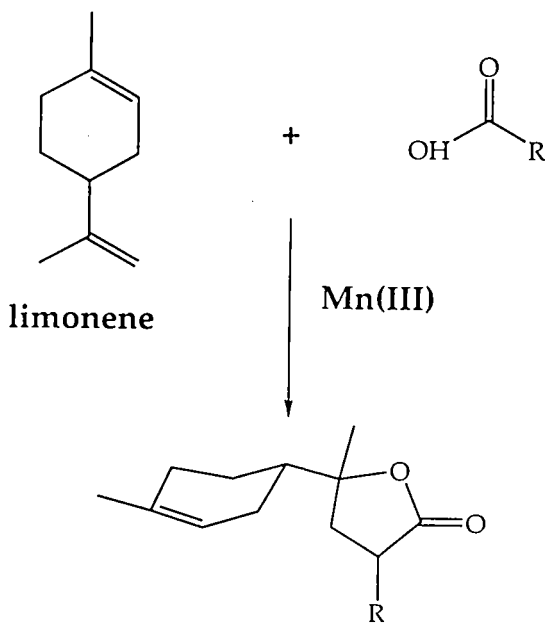
Though the adsorbents evaluated by Chemsyn Science Laboratory are effective, the adsorption is reversible. Thermal gradients or other environmental changes could cause the migration of previously scavenged limonene. We investigated a scavenger system that would permanently immobilize the limonene by covalent attachment to a larger molecule.

Manganese (III) acetate and acetic acid react with olefins to make γ-lactones.[1] The reaction and its stoichiometry is illustrated generically below.



2/3 $Mn_3O(OAc)_3(HOAc)$ $2Mn(OAc)_2 + HOAc$

This reaction occurs with a variety of both carboxylic acids and olefins.[2] Less volatile acids would combine with limonene forming higher molecular weight species, less likely to migrate within a sealed system. This reaction, as it would occur between limonene and a higher molecular weight manganese (III) carboxylate complex, is shown below. Many products are possible, but the net effect of any lactone formation is to lower the vapor pressure of the limonene moiety.



Limonene could react at either or both of the double bonds.
No selectivity of stereochemistry or regiochemistry is implied.

The lactone syntheses described above are typically conducted in excess acid at 120-180° C achieving reasonable yields in several hours. These conditions are such that the reaction would be very slow at room temperature. We conducted a simple experiment to see if these reactions might proceed at a rate sufficient to irreversibly scavenge limonene vapor from a sealed space.

Manganese (III) acetate and octanoic acid were mixed forming a paste. This was placed in a vial. In a separate vial was placed several grams of limonene. The two open vials were placed in a sealed desiccator at room temperature (22±5° C) for two years under a laboratory air atmosphere.

The experiment was not successful. Extraction of the manganese/acid mixture yielded no limonene or limonene-derived products. Aside from a slight yellowing, no changes were observed in the gas chromatograph or nuclear magnetic resonance spectra of the limonene. We conclude that, at least at room temperature, there is no reaction between the manganese complex and the ambient limonene vapor. Though this reaction would probably proceed at higher temperature, where the reaction is faster and the concentration of limonene vapor higher, we did not investigate these conditions.

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[2]Heiba, E. I.; Dessau, R. M.; Rodewald, P. G. *j. Am. Chem. Soc.* **1974,** 96, 7977-7981.

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