

**Destruction of Volatile Organic  
Compound (VOC) Emissions by  
Photocatalytic Oxidation (PCO): Field  
Test Results**

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# **Destruction of Volatile Organic Compound (VOC) Emissions by Photocatalytic Oxidation (PCO): Field Test Results**

Technology Transfer # 96023084A-ENG

**SEMATECH**

*February 29, 1996*

**Abstract:** This report discusses the results of a five-week field trial at a semiconductor manufacturing facility to evaluate photocatalytic oxidation (PCO) as a cost-effective technology for abating volatile organic compound (VOC) emissions from cleaning sinks and phototracks. Data reveal that the PCO process can treat emissions from either a parts cleaning sink or a photolithography track (without hexamethyldisilazane [HMDS]). Over the test period, the PCO system converted an average of 96% of all acetone emissions from a cleaning sink. Overall conversion of the emissions from a planar coating track (primarily ethyl lactate) was lower, averaging 75% to 80%. With the notable exception of HMDS, none of the compounds reduced catalyst activity. The data indicate that PCO systems can achieve high destruction efficiencies under field conditions; however, more work is necessary to optimize the design of PCO systems so that they operate effectively with current industry processes.

**Keywords:** Cleaning Equipment, Lithography Equipment, Photocatalytic Oxidation, Point of Use Abatement, Pollution Control Equipment, Volatile Organic Compounds

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## Table of Contents

1 EXECUTIVE SUMMARY.....	1
2 INTRODUCTION.....	1
3 EXPERIMENT .....	1
3.1 Equipment and Conditions.....	1
3.2 Data.....	3
3.2.1 Parts Cleaning Sink .....	3
3.2.2 Planar Coating Track.....	4
3.2.3 Catalyst Activity Tests.....	6
4 DISCUSSION .....	7
5 CONCLUSIONS AND RECOMMENDATIONS .....	8
5.1 Future Work .....	8
6 WORKS CITED .....	9

### List of Figures

Figure 1 Packed-Bed Photoreactor Used During the Field Experiments.....	2
Figure 2 Schematic of the PCO Field Test System.....	3
Figure 3 Parts Cleaning Sink Data as a Function of Total Time on Stream.....	4
Figure 4 Planar Coating Track Data Set from January 29, 1996, Showing Conversion of What is Mainly Ethyl Lactate .....	6

### List of Tables

Table 1 Results of the Standard Test to Evaluate Catalyst Performance.....	7
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## **1 EXECUTIVE SUMMARY**

The purpose of this joint National Renewable Energy Laboratory (NREL)/SEMATECH project is to evaluate photocatalytic oxidation (PCO) as an abatement technology for air emissions from semiconductor fabs. In 1995, laboratory work and cost analyses suggested that the PCO technology would be a cost-effective means of treating the volatile organic compound (VOC) emissions from point-of-use (POU) applications such as cleaning sinks and phototracks. This report discusses the results of a field trial at a semiconductor manufacturing facility.

Data from the field study reveal that the PCO process can treat emissions from either a parts cleaning sink or a photolithography track. VOCs like acetone react more quickly than the higher molecular-weight compounds (e.g., ethyl lactate) typically used in the phototracks. Despite concentration spikes higher than 5000 ppmv, the PCO system converted an overall average of 96% of all acetone sent to it from a cleaning sink over a five-week test period. Overall ethyl lactate conversion was lower, averaging 75% to 80%. Common phototrack compounds with molecular weights higher than ethyl lactate appear to have too low a volatility to be present in the air at concentrations within the detection limit of 5 ppmv. With the notable exception of hexamethyldisilazane (HMDS), none of the emission streams reduced catalyst activity over the five-week time span of these tests.

The field test data indicate that PCO systems can achieve high destruction efficiencies under field conditions; however, more work is necessary to optimize the design of PCO systems so that they operate effectively with current industry processes. The intermittent operation of both the cleaning sink and the phototrack suggest that efficiency gains are possible by designing a PCO system for handling wide variations in concentration or for rapid startup and shutdown.

## **2 INTRODUCTION**

This report documents the final element of Phase 1 of the cooperative R&D agreement (CRADA) between NREL and SEMATECH. Under Phase 1 of the CRADA, NREL and SEMATECH were to determine the feasibility of treating VOC emissions from semiconductor plants. Although originally planned to look at a number of simulated waste streams, this work focused on VOC emissions from a parts cleaning sink. During Phase 1, NREL assembled an experimental test system and completed laboratory experiments with compounds of interest to the industry. Optimization work in Phase 1 produced catalyst formulations and operating conditions that increased the performance of the process by a factor of almost 20. This work has been previously discussed [1,2].

As the final task of Phase 1, NREL completed a field test of the PCO process at a semiconductor manufacturing facility (the Hewlett-Packard plant in Fort Collins, CO). Two separate air streams were tested: an organic solvent cleaning hood and a photolithography track (phototrack).

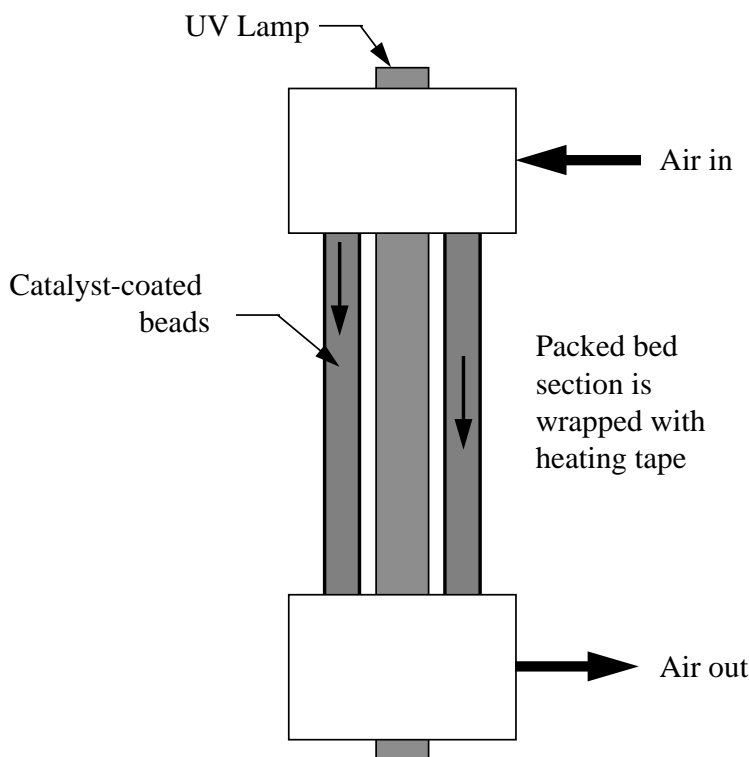
## **3 EXPERIMENT**

### **3.1 Equipment and Conditions**

The laboratory tests used two different photoreactors: an annular reactor with an 8-watt black light and a small packed-bed reactor that used a 15-watt black light. Early plans called for scaling

up the 15-watt system to a 2000-watt mercury arc lamp for the field testing. However, complications with the scale-up effort delayed the completion of the larger system and researchers opted to run the field experiments with the smaller unit. This approach allowed the process to be tested under field conditions and provided valuable information about catalyst activity and lifetime. Use of the smaller system also made it easier to evaluate different compounds and emission streams.

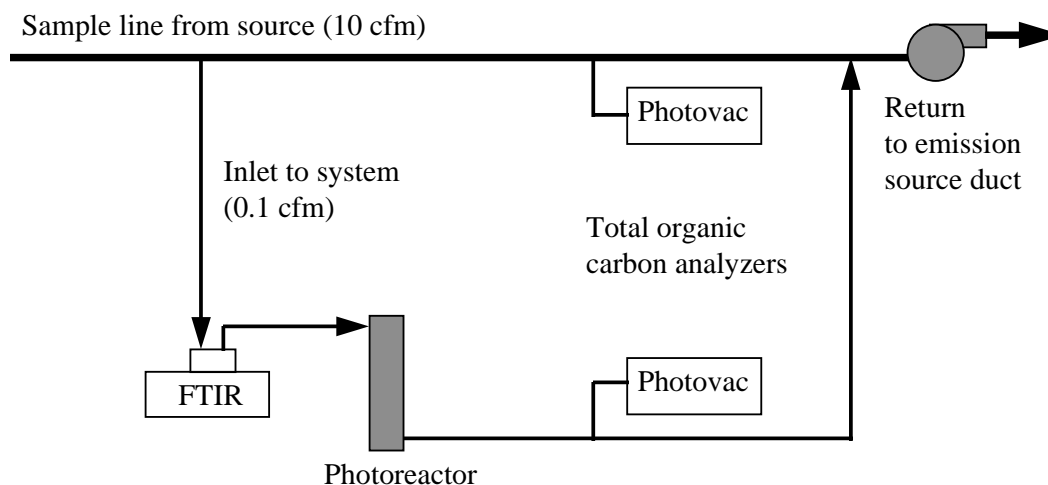
A schematic of the packed bed photoreactor used for the field work is shown in Figure 1. This photoreactor used 3 mm diameter catalyst-coated glass beads placed inside two concentric borosilicate glass cylinders. A 15-watt black light inside the inner cylinder illuminated the bead bed while the process air flow passed through the bed. The inner cylinder had an OD of 3.57 cm, the outer cylinder had an ID of 4.9 cm, and the bead bed depth was 25 cm. The beads themselves hinder light penetration into the bed; therefore, the light intensity at the catalyst surface varied with location within the bed. The intensity measured at the surface of the 2.5 cm diameter lamp was  $80 \text{ w/m}^2$ .



**Figure 1 Packed-Bed Photoreactor Used During the Field Experiments**

The photoreactor was incorporated into a test cart that allowed researchers to vary flow rate, air stream composition, humidity, and temperature. The field test equipment (Figure 2) consisted of a cart mounted photoreactor system with a Fourier transform infrared (FTIR) spectrophotometer and two Photovac total organic carbon analyzers. The system was designed to handle a flow rate of 1 to 5 L/min. FTIR was used to identify specific compounds. Continuous monitoring of the system inlet and outlet lines was provided by the two Photovacs. These units used flame ionization detectors to provide a measure of total VOCs, without differentiating the specific compounds being sampled. Most of the testing was done on a stream that contained acetone, so

the Photovacs were calibrated with a 489 ppmv acetone-in-air standard supplied by Scott Specialty Gases. Although normally set to sample the inlet line (as shown in Figure 2), the FTIR could be set to monitor samples from either the inlet or the outlet of the reactor.



**Figure 2 Schematic of the PCO Field Test System**

## 3.2 Data

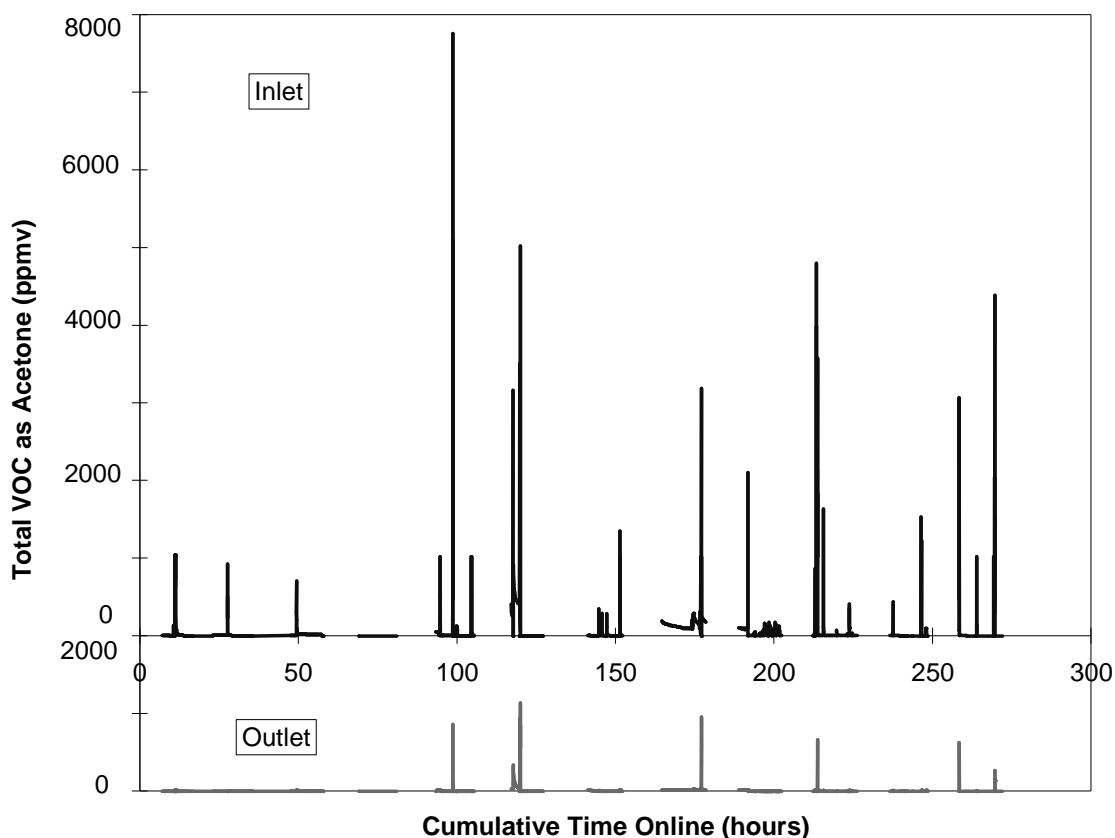
### 3.2.1 Parts Cleaning Sink

The majority of the field test was spent testing the system's ability to destroy the emissions from a parts cleaning sink. The FTIR analysis showed that this stream contained acetone almost exclusively. Therefore, the total organic carbon analyzers were calibrated with acetone, and data from those instruments are displayed as acetone equivalents. Over the three weeks, the photoreactor system logged a total of 270+ hours on this emission stream. During that time, the system was operating at 150°C with a flow rate of 2.0 standard L/min. The cumulative data for that time span are shown in Figure 3.

Gaps in the data in Figure 3 occur during periods when the photoreactor was operating but the analytical instruments were off line. These periods occurred because the Photovacs can operate for only 8 to 10 hours unattended before their internal hydrogen supply is exhausted. Thus the instruments typically ran out of hydrogen and shut down every night around midnight.

Several trends are apparent from the data in Figure 3. The most obvious is the intermittent operation of the cleaning sink. Short, high-concentration spikes are interspersed with long periods of inactivity. The spikes typically lasted for a few minutes or less and were associated with the loading and unloading of acetone cleaning baths. Acetone concentrations frequently exceeded the 400 ppmv average that was expected, at times reaching levels over 5000 ppmv. Conditions in the emission stream changed so rapidly that it was difficult to calculate instantaneous conversion data. In general, the PCO system eliminated the lower spikes of acetone (i.e., less than 1000 ppmv) to below detection limits. During the high concentration spikes, conversion averaged around 80%. Overall conversion, determined by integrating the entire data set, was 96%. That is, the PCO system destroyed 96% of the acetone sent to it over the three-

week test period. Analysis of the air exiting the photoreactor detected carbon dioxide and water as the reaction products. No other intermediate compounds or byproducts were detected.



Note: Over this period, the PCO system converted an average of 96% of the acetone in the inlet stream.

**Figure 3 Parts Cleaning Sink Data as a Function of Total Time on Stream**

Figure 3 clearly shows that although short spikes of high concentration were often completely handled, longer periods resulted in acetone breakthrough. This behavior indicates that the system has some buffering capacity. One likely explanation is that the high concentrations of acetone adsorb to the catalyst surface and slowly break down to  $\text{CO}_2$  and water. Short spikes can be completely adsorbed and subsequently destroyed, even though continuous operation at such a feed level would result in breakthrough. This capacity is a valuable trait for a system treating the emissions from intermittent operations because it allows the treatment system to be a smaller size than would be needed if it were required to instantly destroy the entire spike.

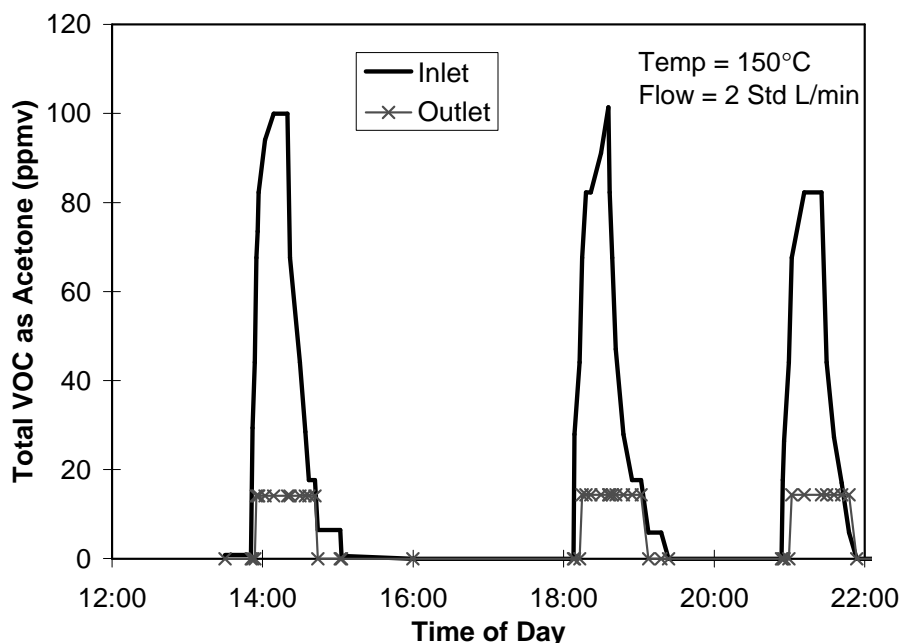
The final test using the cleaning sink was intended to look at the treatment of Citrasafe, a commercial citrus-based cleaner. In this experiment a basin of Citrasafe was left uncovered in the fume hood. The Citrasafe was not heated. Under these conditions, no VOCs were detected in the air stream, indicating the low vapor pressure of the cleaner.

### 3.2.2 Planar Coating Track

The PCO system was next moved to the vent line of a planar coating track for the final two weeks of testing. The compounds currently used in this process include ethyl lactate, acetone,

isopropanol, novolak resin, ethyl-3-ethoxypropionate, hydroxybenzophenone, 1-methoxy-2-propanol acetate, and naphthoquinone diazide; however, FTIR analysis of the emission stream detected only ethyl lactate. It is possible that other VOCs were present at levels below the detection limit (approximately 5 ppmv). The operation of the track differed from that of the cleaning sink in that the emission spikes typically lasted for an hour or more. A typical day's activity is shown in Figure 4. Again, because the total organic carbon analyzers were calibrated with acetone, the VOC concentration is reported in acetone equivalents. The FTIR was used only to identify the stream compounds (not to determine concentrations); it is not shown.

Integration of the data in Figure 4 revealed that 78% of the incoming ethyl lactate was fully converted to carbon dioxide (CO<sub>2</sub>) and water. No ethyl lactate was detected in the outlet stream. The remaining 22% of the incoming carbon was reacted to intermediate organic compound(s) that could not be positively identified. Longer residence times increased conversion levels, but an organic residual remained. No carbon monoxide was seen. There are several reasons why the ethyl lactate (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>) conversion is lower than the acetone (C<sub>3</sub>H<sub>6</sub>O) conversion. The lower conversion efficiency may simply reflect the greater difficulty in fully oxidizing the higher-molecular-weight compound to CO<sub>2</sub> and water. Conversely, there may be significant differences in the adsorption affinity or reaction rates among the various intermediates on the reaction pathway to CO<sub>2</sub> and water. The absence of any ethyl lactate in the reactor effluent indicates that it adsorbs well (as it should based on its molecular structure). The presence of an organic residual in the effluent stream gives credence to the possible formation of a slow reacting or poorly adsorbing intermediate species.



Note: The PCO system was running at 2 standard L/min and 150°C.

**Figure 4** Planar Coating Track Data Set from January 29, 1996, Showing Conversion of What is Mainly Ethyl Lactate

### 3.2.3 Catalyst Activity Tests

One of the goals of the field work was to evaluate the life of the catalyst under actual process conditions. To track catalyst activity, NREL periodically performed a standard test to determine if the catalyst performance were changing. Table 1 depicts the results of those tests. The initial tests were run at 400 ppmv acetone and 2.0 L/min to verify that 95+% conversion could be obtained under the conditions anticipated at the site. Subsequent tests were intentionally run at a lower conversion to provide greater sensitivity to possible changes in catalyst activity. At first glance, the conversions at 460 ppmv and 2.4 L/min, corresponding to a throughput of 38% more acetone, seem inconsistent with the high conversions at the lower feed rate (this result is discussed further in the next section).

Within the level of experimental uncertainty, there was no change in the catalyst performance between the fresh sample and the sample tested on January 12, 1996. On January 18, the catalyst was exposed to a small amount of HMDS in the emission stream. Earlier laboratory experiments demonstrated that even small amounts of HMDS can reduce catalyst activity [2]. Clearly, as indicated by the conversion change from ~77% to 67%, the exposure to HMDS in the field also affects the catalyst performance. However, within the time periods before and after the HMDS exposure, catalyst performance did not appear to vary. These data confirm earlier laboratory results that indicate no loss in activity when treating common solvents like acetone or isopropanol. Although these results are encouraging, longer term testing will be necessary to fully assess the operational life of the catalyst.

**Table 1 Results of the Standard Test to Evaluate Catalyst Performance**

Date	Acetone Feed Conc. (ppmv)	Flow Rate (L/min)	Catalyst Time on Parts-Cleaning Stream (hrs)	Conversion
11/30/96	400	2.0	0	98%
1/8/96	400	2.0	50	98%
1/12/96	400	2.0	145	95%
fresh*	460	2.4	0	75%
1/8/96	460	2.4	50	77%
1/12/96	460	2.4	145	78%
1/18/96	460	2.4	220	HMDS exposure
1/23/96	460	2.4	275	67%
1/26/96	460	2.4	348	67%

\* Test performed on 1/29/96 with fresh catalyst from the same batch

Note: The tests consisted of feeding a known concentration of acetone in air to the Reactor.

Reactor conditions: 150°C, 11.6 psia, feed air 15% RH (measured at 20°C)

The data in Table 1 track the catalyst activity during the time spent on the parts cleaning stream. After testing the parts cleaning line, the emissions from the planar coating track were tested for 90 additional hours. A check on February 1, 1996, showed no discernible decrease in catalyst activity at the end of those tests.

#### 4 DISCUSSION

The primary objective of the field tests was to determine if the PCO process could achieve and maintain 95+% conversion of VOCs under field conditions. The data from Figure 3 indicate that both goals were obtained for the emissions from a typical parts cleaning sink. Despite an exposure to HMDS that reduced the catalyst effectiveness, the process recorded an average conversion of 96% for three weeks of testing on the bench emissions. One of the more exciting results was that the system received high concentration (>5000 ppmv) spikes of acetone yet still maintained its high average conversion efficiency. This behavior is believed to result from the adsorptive capacity of the catalyst. In PCO systems, adsorption rates normally exceed reaction rates. Thus, if a large spike of VOC enters the reactor, it can be rapidly adsorbed (thus removing it from the air stream) and slowly oxidized from the surface. However, if the high concentration feed is continuous, the bed's adsorptive capacity will be overwhelmed and the VOC removal rate will correspond to the surface reaction rate.

The phenomenon described above also explains the results depicted in Table 1. In those tests, the PCO provided 95% conversion of a 400 ppmv acetone stream at steady-state. Yet, for a feed of 38% more acetone per time (based on flow rate times concentration), the steady-state conversion was only ~77%. Under both these feed conditions, the reaction model indicates that the catalyst is virtually saturated with acetone and the system should follow zero-order kinetics. That is, the rate of acetone conversion will remain constant regardless of increases in concentration. This situation makes conversion very sensitive to changes in the mass of acetone fed and is typical of catalytic systems. On the other hand, the adsorption/reaction nature of catalytic systems can be

used to advantage by designing systems to dampen concentration spikes by rapid adsorption. The bed capacity is used to adsorb the incoming mass of VOC, which is subsequently destroyed on the catalyst surface. PCO systems used on streams that have intermittent emissions can incorporate this spike-handling ability to advantage. For example, the small unit was sized to handle a continuous 400 ppmv concentration stream yet was effective on short duration spikes of ten times that level.

Conversion for the planar coating track (Figure 4) was not as high as obtained for the parts cleaning sink. This stream contained almost exclusively ethyl lactate at concentrations around 100 ppmv (total VOC as acetone). Conversion averaged 75% to 80% under the same reactor conditions (150°C, 2.0 L/min) that achieved the 96% conversion for the acetone stream. These data indicate that more rigorous conditions (e.g., longer residence time or higher temperatures) would be required for 90+% destruction of ethyl lactate with the current catalyst.

The scale of the present field experiments was too small to provide much information about the cost of a full-scale unit. They yielded important information about catalyst activity and life, but there are still many uncertainties associated with scale-up to a full-size system. The earlier cost estimates [2] and the current field data both suggest that further advances in the catalyst performance would have the greatest impact on the process cost of ownership. Additional work on the catalyst and the operating conditions (e.g., temperature) should be undertaken to reduce the estimated cost of ownership before the larger scale field work is attempted.

## **5 CONCLUSIONS AND RECOMMENDATIONS**

Data from the field study reveal that the PCO process can treat emissions from either a parts cleaning sink or a photolithography track. VOCs like acetone react more quickly than the higher molecular weight compounds (e.g., ethyl lactate) typically used in the phototracks. Despite concentration spikes exceeding 5000 ppmv, the PCO system converted an overall average of 96% of all acetone sent to it over a five-week period. Overall ethyl lactate conversion was lower, averaging 75% to 80%. Higher molecular weight compounds such as Citrasafe and hydroxybenzophenone appear to have too low a volatility to be present in the gas phase at concentrations above the detection limit of 5 ppmv. With the notable exception of HMDS, none of the emission streams reduced catalyst activity over the five-week time span of these tests.

Questions about system scale-up and mode of operation must still be answered before proceeding with the design of a full-scale unit. Also, although high conversions have been demonstrated, additional gains in catalyst efficiency would provide the biggest impetus to making this technology an effective VOC treatment option for the semiconductor industry.

### **5.1 Future Work**

Starting in 1996, this project will build on the results of Phase 1 to further improve the technology cost of ownership. The goal of Phase 2 is the design of a commercial PCO system. NREL will continue the catalyst development effort that resulted in Phase 1 rate gains of almost a factor of 20. The catalyst screening work done in Phase 1 will be augmented by a more methodical study of those promising catalysts identified in the earlier work.

Concurrent with the catalyst work, NREL will contract with a PCO technology supplier to survey member companies regarding the most desirable applications and operating conditions of a PCO

system. This information will provide insight for designing a PCO system to account for the physical requirements (power, size, etc.) of the equipment and the variation in process emissions. Once the optimal system size and mode of operation (e.g., instant-on or continuous) is defined, NREL will investigate options for both the light source and heating requirements of the photoreactor. Finally, following an update of the cost of ownership estimates, NREL and the PCO supplier will address the scale-up issues moving from a laboratory unit to a pilot and full-scale prototype system.

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