

Development of a LiOH Scrubber to Remove CO₂ from Air Samples for ¹⁴C Analysis

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ABSTRACT

A LiOH scrubber system that can be used to remove the CO₂ from up to 1 m³ of ambient air for ¹⁴C analysis of the non-methane organic compounds (NMOCs) was developed and tested. The basic scrubber design consists of a cylinder filled with LiOH with the ends plugged with glass wool. Engineering charts were developed to facilitate the selection of the best geometry for a given sampling task, based on required sampling rates, total sample volume, pump pressure drop capacity, and desired residence time. The residual CO₂ levels and the potential loss of NMOCs in the sample passing through the scrubber were characterized for several LiOH scrubber geometries by using ambient air and synthetic mixtures containing selected volatile organic compounds. For the tested system, the residual CO₂ levels were measured to be typically less than 0.050 ppm, and no significant loss of the C₃-C₁₁ alkene and alkane NMOCs was detected. There is an indication that the concentrations of some of the aldehyde and ketone compounds in another test mixture were reduced upon passing through the LiOH scrubber. Chlorinated volatile organic compounds in the mix were mostly unaffected.

INTRODUCTION

A LiOH scrubber system that can be used in situ to remove most of the CO₂ from up to 1 m³ of ambient air was developed and characterized. Samples collected with most of the CO₂ removed can be used for ¹⁴C analysis of the non-methane organic compounds (NMOCs).¹⁻³ Subsequently, the biogenic and anthropogenic fractions of NMOCs can more easily be determined.

RESEARCH SUMMARY

The developed scrubber design consists of a stainless steel cylinder filled with granular LiOH (1- to 4-mm grain size) with the ends packed with glass wool. Figure 1 shows the laboratory setup that was used to characterize the flow parameters and CO₂ capacity of several test scrubber configurations. The flow and capacity data was used to develop design curve charts to facilitate the selection of the best physical design for the scrubber for a given sampling task. Figures 2, 3, and 4 display the design curves used to select a geometry for a scrubber system that can accommodate sampling rates up to 16 L/min and that has a capacity to remove the CO₂ from at least 1 m³ of ambient air.

The residual CO₂ levels were characterized by passing room air through the test scrubbers at selected flow rates while measuring the CO₂ concentrations with a Model 41 Thermo Electron Corporation Instruments (Franklin, Massachusetts) gas filter correlation CO₂ analyzer, as shown in Figure 1. The detection level of the Model 41 CO₂ analyzer is 0.010 ppm. The variability on the most sensitive scale is ±0.025. For the tested scrubbers, the residual CO₂ levels were reproducibly measured to be less than 0.050 ppm.

The recovery rates of NMOCs in the sample passing through the scrubber were characterized for several LiOH scrubber configurations by using the system shown in Figure 5. These characterization tests were conducted by passing prepared mixtures of 58 C₂–C₁₁ alkene, alkane, aromatic hydrocarbon, and terpene NMOCs, shown in Table 1 (test mixtures prepared for the Photochemical Assessment Monitoring Station [PAMS] network), through the scrubber at the desired sample rate while monitoring the effluent concentrations of each recovered NMOC component with an HP gas chromatograph (GC) system with a flame ionization detector and a mass spectrometer detector. Heated and unheated scrubbers were characterized. The heated scrubbers were maintained at a temperature of 100 ± 5 °C. The unheated scrubbers were operated at an ambient temperature of 21 ± 4 °C. As can be seen in Figures 6 and 7, no significant losses of the C₃–C₁₁ alkene and alkane or aromatic hydrocarbon NMOCs were detected in either the heated or unheated LiOH scrubber systems. (This GC method did not measure ethylene, ethane, acetylene, or α- and β-pinene very well, and thus the recovery rates of these compounds are not included in this comparison.) A mixture of various aldehydes, ketones, and chlorinated volatile organic compounds (VOCs), listed in Table 2, was also used to further characterize the LiOH scrubber. The concentrations of the aldehyde and ketone compounds in the test mixture were reduced upon passing through the LiOH scrubber. The chlorinated VOCs in the mix seemed to be mostly unaffected by the heated or unheated LiOH scrubber. Figure 8A documents the results from passing the mixture through the unheated scrubber, and Figure 8B documents the results from passing the mixture through the heated scrubber.

A LiOH scrubber was used to successfully remove most of the CO₂ from 1-m³ samples collected by employing a Russian doll trap system during a joint EPA–NIST field study in 1995 at Gaithersburg, Maryland.⁴ The sample train was set up as shown in Figure 9. The scrubber design was selected to accommodate a sampling rate of 4 L/min for 4 h by using the design curves shown in Figures 2–4. The residual CO₂ levels measured in the sample lines during collection of the Russian doll samples were also less than 0.050 ppm. The VOC data analysis has not been completed at this time and is not included in this characterization.

A comprehensive manuscript covering this development effort is in preparation for journal submission.

CONCLUSIONS

The following conclusions can be drawn from this research.

- A LiOH scrubber can be designed to remove more than 99.9% of the CO₂ from an ambient sample in situ.
- Scrubbers have been designed by using developed design curves to have the capacity to remove CO₂ from at least 1 m³ of air at sample rates of up to 16 L/min.
- Typical residual CO₂ levels were measured to be less than 0.050 ppm.
- Tested C₃–C₁₁ alkane and alkene NMOCs appear to be unaffected by passage through the LiOH scrubber.
- Tested aldehyde and ketone NMOCs were retained by the LiOH scrubber.
- Tested chlorinated NMOCs appeared to be unaffected upon passage through the scrubber.
- A scrubber geometry that was selected by using the developed design curves was used successfully to remove most of the CO₂ from 1-m³ Russian doll samples at 4 L/min during a joint EPA–NIST field study.

DISCLAIMER

The research described in this document has been funded by the United States Environmental Protection Agency under Contract 68-D5-0049 to ManTech Environmental Technology, Inc. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 1. NMOC compounds in the PAMS mixture.

Ethylene	2,4-Dimethylpentane
Ethane	Methylcyclopentane
Acetylene	Benzene
Propene	Cyclohexane
Propane	2-Methylhexane
Isobutane	2,3-Dimethylpentane
1-Butene	3-Methylhexane
<i>n</i> -Butane	2,2,4-Trimethylpentane
<i>trans</i> -2-Butene	Heptane
<i>cis</i> -2-Butene	Methylcyclohexane
3-Methyl-1-Butene	2,3,4-Trimethylpentane
2-Methylbutane	Toluene
1-Pentene	2-Methylheptane
<i>n</i> -Pentane	3-Methylheptane
Isoprene	Octane
<i>trans</i> -2-Pentene	Ethylbenzene
<i>cis</i> -2-Pentene	<i>m</i> -Xylene
2-Methyl-2-Butene	<i>p</i> -Xylene
2,2-Dimethylbutane	Styrene
4-Methyl-1-Pentene	Nonane
Cyclopentene	<i>o</i> -Xylene
2,3-Dimethylbutane	Isopropylbenzene
Cyclopentane	Propylbenzene
2-Methylpentane	1,3,5-Trimethylbenzene
3-Methyl-1-Pentane	1,2,4-Trimethylbenzene
2-Methyl-1-Pentene	α -Pinene
Hexane	β -Pinene
<i>trans</i> -2-Hexene	<i>n</i> -Decane
<i>cis</i> -2-Hexene	<i>n</i> -Undecane

Table 2. Aldehydes, ketone, and chlorinated NMOCs in mixture.

Methacrolein	Trichloroethene
Dichloromethane	Hexanal
Methyl Vinyl Ketone	Tetrachloroethene
Butanal	Heptanal
1,1,1-Trichloroethane	Benzaldehyde
2-Pentanone	Octanal
Pentanal	Nonanal

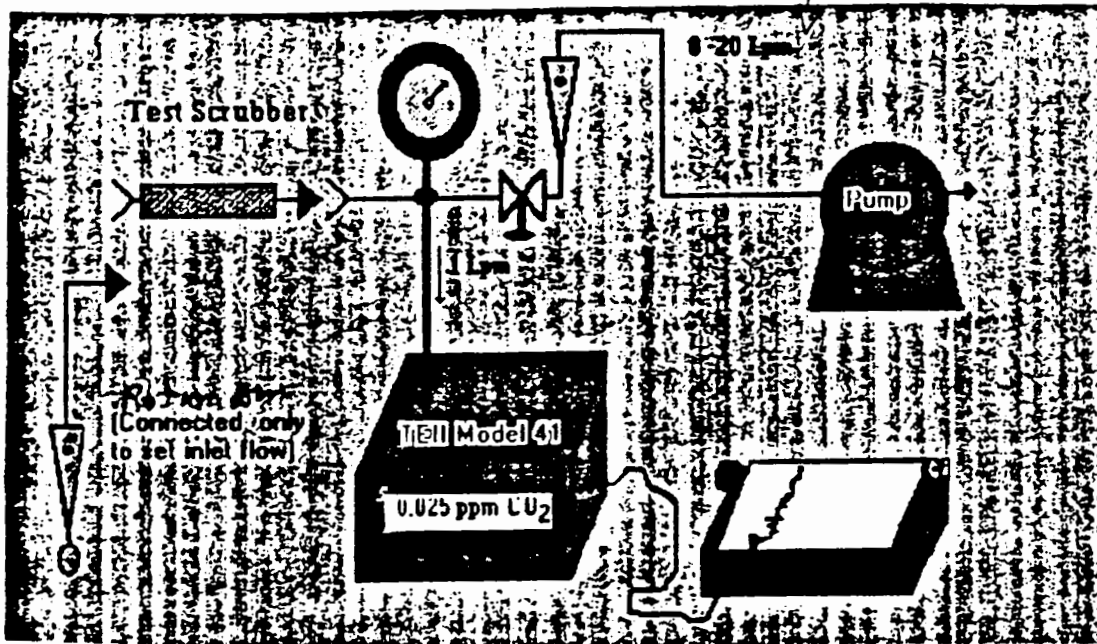


Figure 1. Setup used to characterize scrubbers.

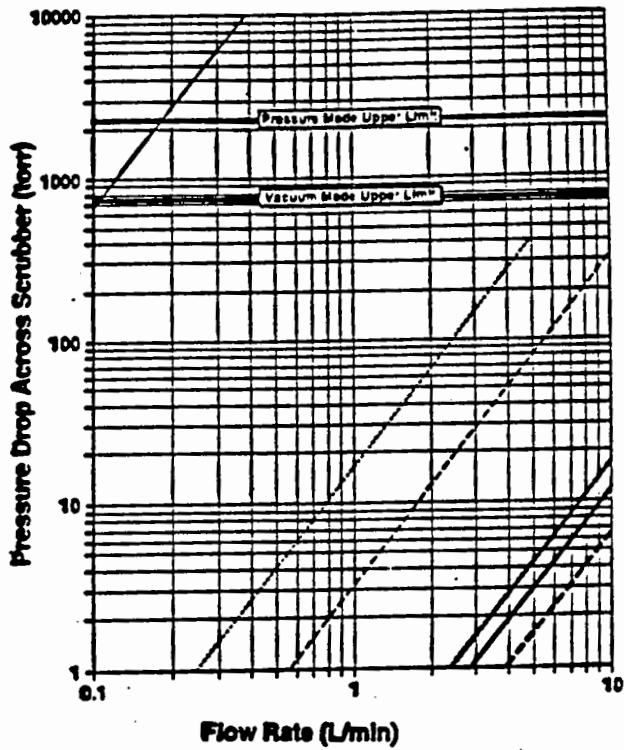


Figure 2. Empirical pressure drop values at various flow rates.

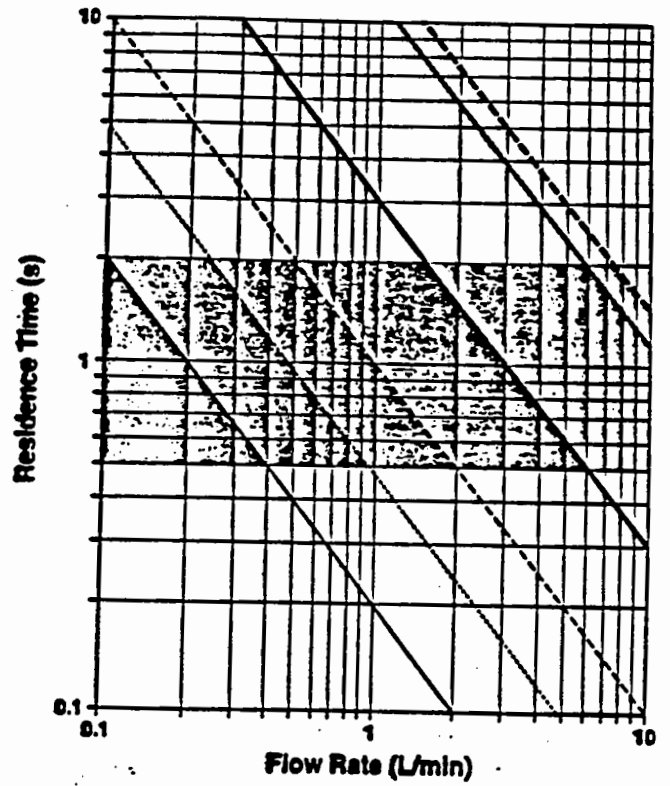
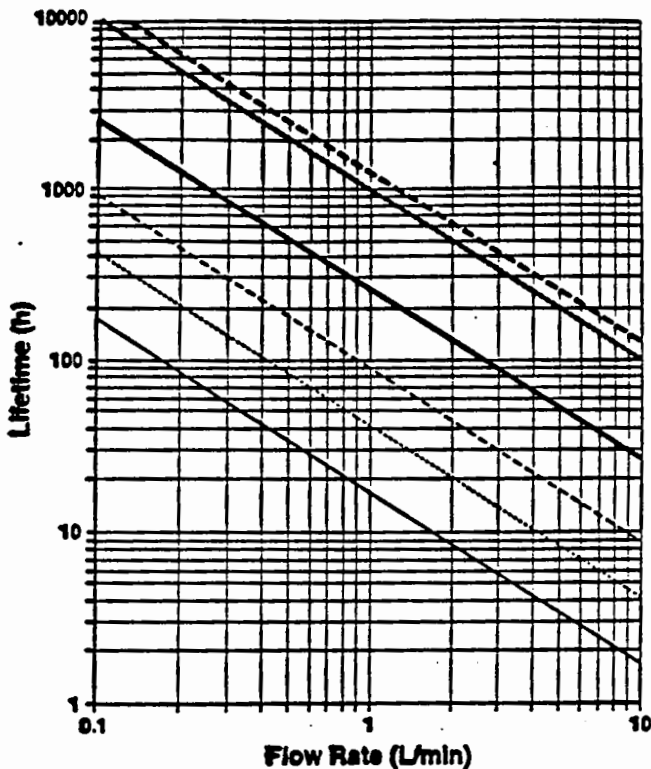


Figure 3. Estimates of residence time at various flow rates.



—	4 x 200 mm, Ld.	—	24 x 200 mm, Ld.
- - -	7 x 200 mm, Ld.	- - -	48 x 200 mm, Ld.
- · - · -	10 x 200 mm, Ld.	- · - · -	80 x 100 mm, Ld.

Legend for Figures 2, 3 and 4

Figure 4. Estimates of lifetime of scrubber at various flow rates.

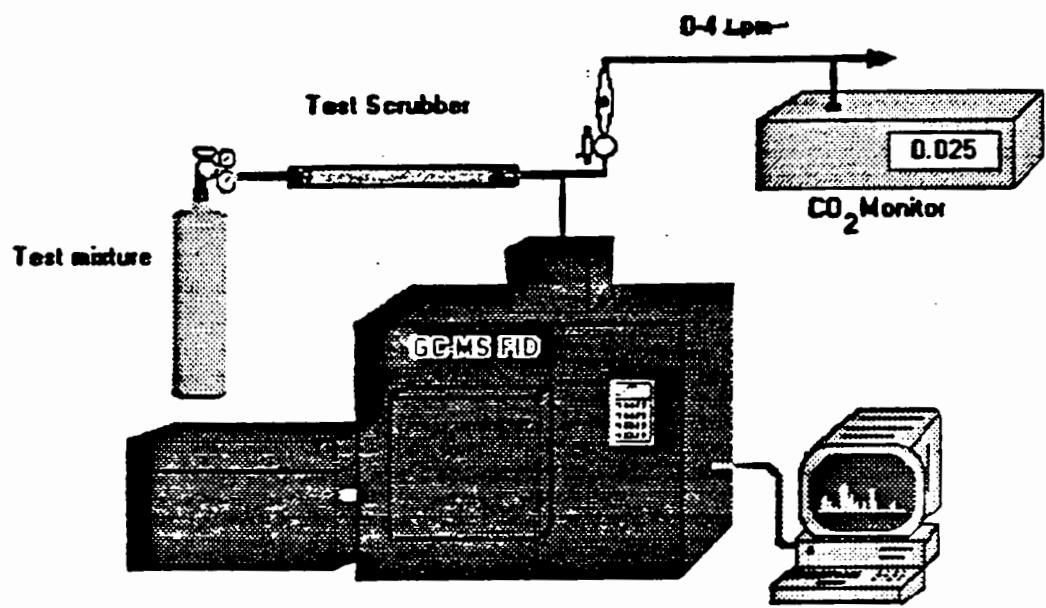
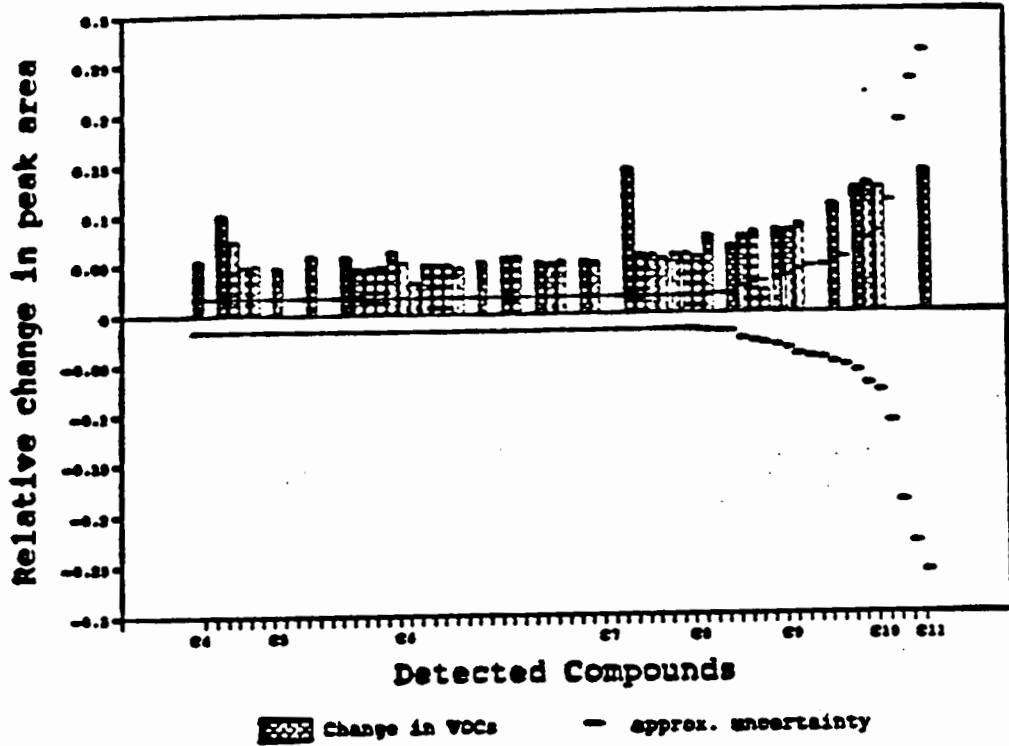


Figure 5. Setup used to characterize NMOC loss in scrubber.

A



B

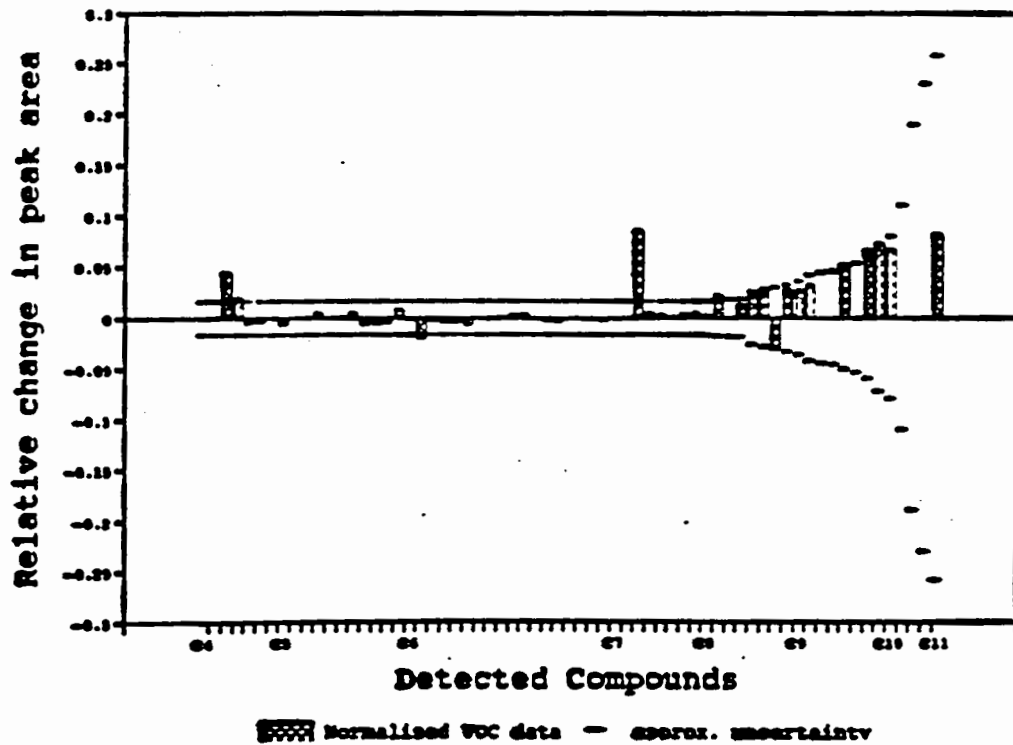


Figure 6. VOC loss in a scrubber made of LiOH-filled Whitey cylinder at 4-L/min flow rate. A. Average relative change in peak response as the PAMS mix passed through the scrubber. B. Normalized results from Figure 6A, adjusted to account for systematic changes in response.

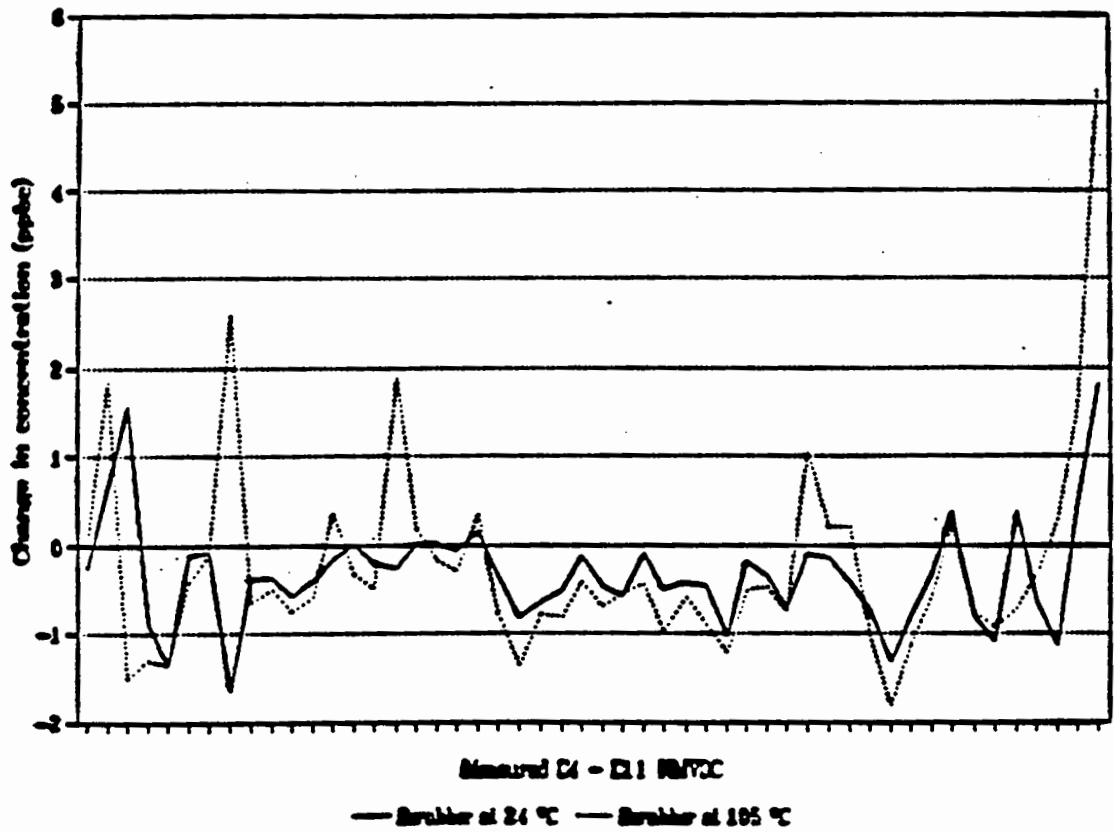
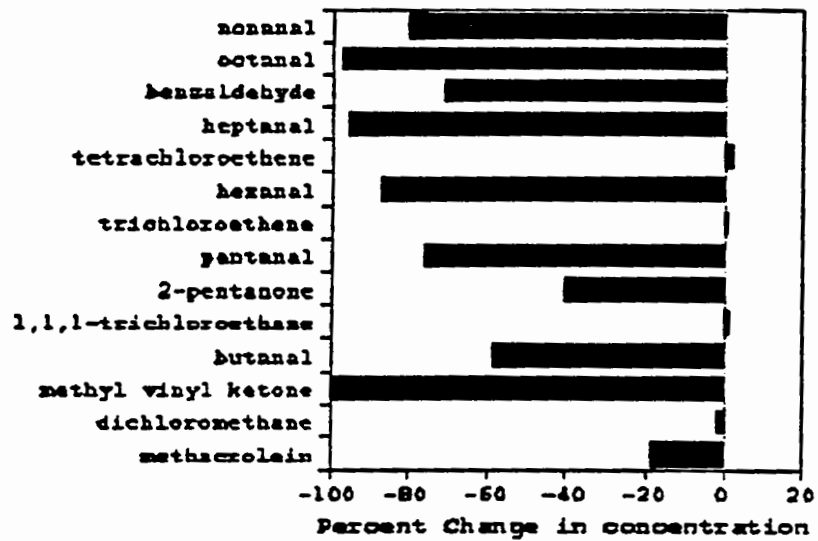


Figure 7. Change in measured NMOC concentrations for a heated and an unheated scrubber operated at 4 L/min (Whitey cylinder).

A



B

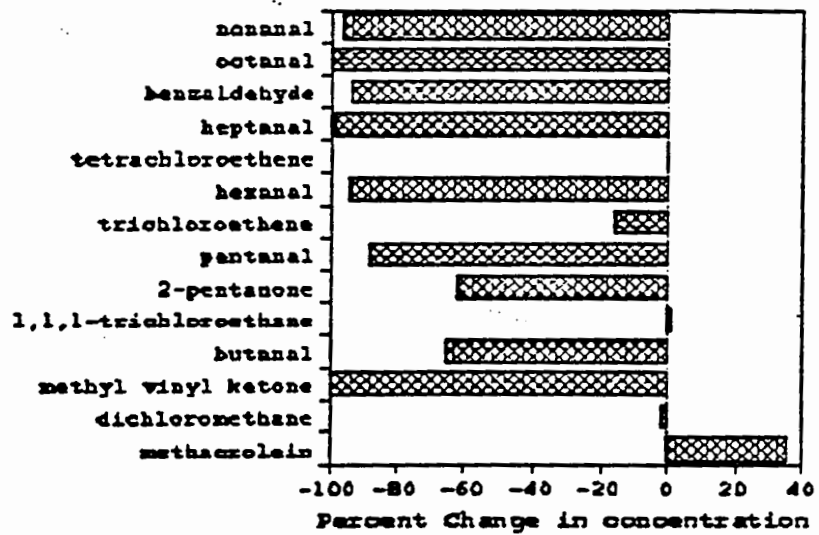


Figure 8. Change in VOCs upon passing through scrubber. A. Unheated scrubber. B. Heated scrubber.

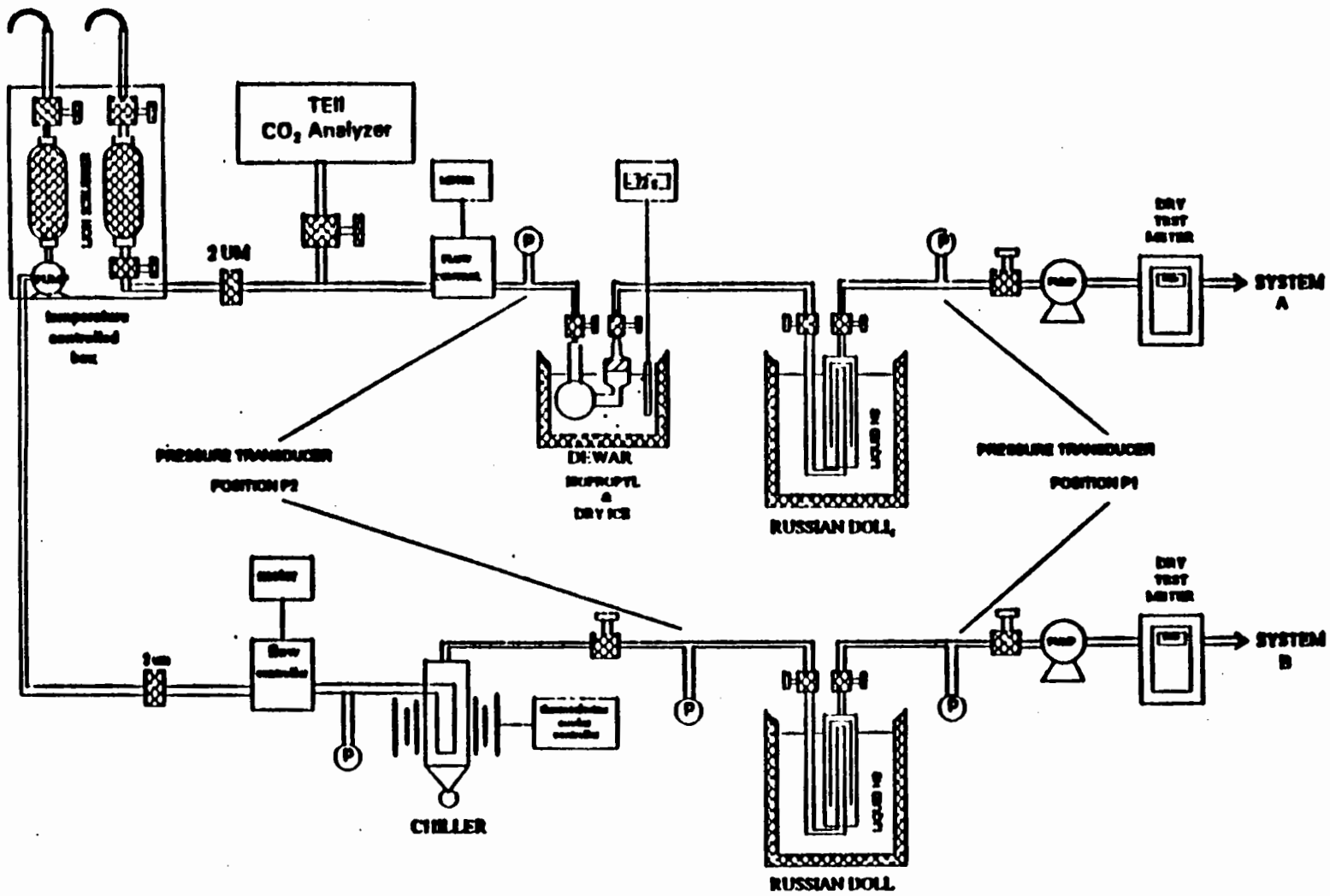


Figure 9. Schematic of System A and System B deployed in Gaithersburg, Maryland, September 1995.

Key word index: Volatile organic compounds, ^{14}C analysis, CO_2 removal, LiOH scrubbers.

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