

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

A MULTISORBENT SAMPLER FOR VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR

### Permalink

<https://escholarship.org/uc/item/1jc3m5hs>

### Authors

Hodgson, A.T.  
Binenboym, J.  
Girman, J.R.

### Publication Date

1986-03-01

c.2



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## APPLIED SCIENCE DIVISION

RECEIVED  
LAWRENCE  
BERKELEY LABORATORY

JUN 30 1986

LIBRARY AND  
DOCUMENTS SECTION

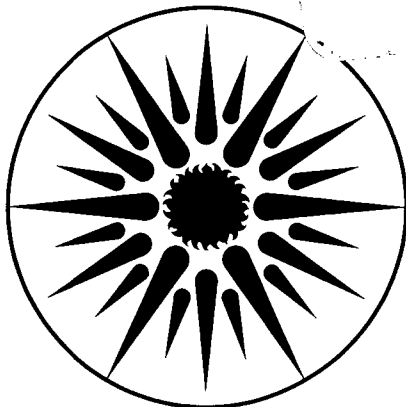
To be presented at the 79th Annual Meeting  
of the Air Pollution Control Association,  
Minneapolis, MN, June 22-27, 1986; and to  
be published in the Proceedings

A MULTISORBENT SAMPLER FOR VOLATILE  
ORGANIC COMPOUNDS IN INDOOR AIR

A.T. Hodgson, J. Binenboym, and J.R. Girman

March 1986

**TWO-WEEK LOAN COPY**  
This is a Library Circulating Copy  
which may be borrowed for two weeks.



**APPLIED SCIENCE  
DIVISION**

LBL-21378

c.2

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Paper 86-37.1 To be presented at  
the 79th Annual Meeting of the Air  
Pollution Control Association,  
Minneapolis, MN June 22-27,  
1986, and to be published in the  
proceedings of this conference.

LBL-21378

A MULTISORBENT SAMPLER FOR VOLATILE ORGANIC COMPOUNDS IN INDOOR AIR

Alfred T. Hodgson, Jehuda Binenboym\* and John R. Girman

Indoor Environment Program  
Applied Science Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

\*Israel Atomic Energy Commission  
Soreq Nuclear Research Center  
Yavne, Israel

March, 1986

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building and Community Systems, Building Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The use of trade and product names does not imply endorsement.

## ABSTRACT

A multisorbent sampler and a compatible gas chromatographic inletting system for the quantitative analysis of ppb concentrations of VOC in ambient and indoor air are described. The sampler contains a gradient of Tenax-TA<sup>®</sup>, Ambersorb XE-340<sup>®</sup> and activated charcoal. Analytes are thermally desorbed from the sampler and are inletted in their entirety onto a capillary column by subsequent adsorption/thermal desorption steps. An on-column cryogenic focusing attachment enhances peak resolution and peak area response. A mass selective detector is used for qualitative and quantitative analyses. Sampler breakthrough volumes for representative low-boiling compounds are  $\geq 10$  L. With a 10 L volume, limits of quantitation are  $< 1$  ppb. Overall precision is normally better than 5% RSD at analyte concentrations ranging between one and several tens of ppb. Accuracy for representative low-boiling compounds is typically  $\pm 5\%$ . The applicability of the method is demonstrated by the quantitative analysis of VOC as a function of ventilation at a large office building.

## INTRODUCTION

The limited data on indoor/outdoor concentration ratios of volatile organic compounds (VOC) in residences, offices and schools show that, for many compounds, these ratios are greater, and in some cases much greater, than one.<sup>1-4</sup> Considerably more data are needed on indoor concentrations of VOC for even rudimentary assessments of population exposures and chronic health risks. Acute health problems, principally mucous membrane irritation, in some buildings have also been postulated to result from elevated concentrations of VOC. The present paucity of data can be largely attributed to the difficulty and expense of analysis for a wide range of VOC. Qualitative and quantitative methods for VOC which are rapid, reliable and relatively inexpensive are needed to survey a variety of buildings, to identify sources of potentially harmful compounds and to evaluate the efficacy of mitigation strategies.

Because most VOC occur at relatively low concentrations, even indoors, an enrichment or concentration step is required prior to chromatographic analysis. Solid adsorption is the most widely used method of sample preconcentration, and many NIOSH procedures use charcoal adsorption followed by solvent desorption. However, to avoid dilution by a solvent, methods have also been developed which use solid sorbents for sample collection in combination with thermal desorption of sample components onto a chromatographic column.

A number of solid sorbent materials have been evaluated for the collection and thermal desorption analysis of VOC. Of these, Tenax® is the most studied and widely used. It has the advantages of inertness, high thermal stability, and low affinity for water vapor. However, retention, or breakthrough volumes, for a variety of highly volatile compounds on Tenax® are low.<sup>5,6</sup> A number of carbonaceous sorbents such as activated charcoals, Ambersorb XE-340® (a pyrocarbon modified charcoal) and similar products have also been evaluated for the collection and thermal desorption analysis of VOC.<sup>7-9</sup> These materials are thermally stable and have very high specific surface areas which make them well suited for the collection of low-boiling compounds; however, they adsorb water, and thermal desorption of high-boiling compounds is not always quantitative.

An obvious solution for a generalized sampler for VOC is to use several complementary materials, such as Tenax® and a carbonaceous sorbent, in series in order of increasing affinity for low-boiling compounds.<sup>5,9</sup> The major objection to using carbonaceous backup sorbents has been the trapping of excessive amounts of water. However, some water is tolerable as long as it does not significantly decrease breakthrough volumes for analytes<sup>5</sup>, react with the sorbents or analytes, or otherwise interfere with the analysis, e.g., ice blockage of cryogenic traps. To minimize the difficulty and expense of analysis, it is most desirable to combine the sorbents within a single sampler.<sup>10</sup> For thermal desorption, the sampler must be reversed in the gas stream so that high-boiling compounds which are trapped by sorbents with low affinity do not contact sorbents with higher affinity as they elute. One such sampler which contains a series of Tenax-TA®, Ambersorb XE-340®, and activated charcoal is commercially available.

In this paper, we describe an analytical method for the quantitation of part-per-billion concentrations of VOC in ambient and indoor air, which employs this sampler. We assembled the instrumental components, including fabrication of an on-column cryogenic focusing attachment, and developed procedures for the method. Using this method in laboratory experiments, we determined breakthrough volumes for low-boiling compounds under simulated use conditions. In a large office building, the method was used to evaluate the effect of ventilation rate on air quality.

## EXPERIMENTAL

All sorbent tube samplers are constructed of borosilicate glass tubing, 203 mm in length with 6 mm O.D. and 1 mm wall thickness. A glass frit holds the sorbents in place at the inlet of a sampler. Small plugs of silanized glass wool separate sorbent layers and hold the sorbents in place at the exit of a sampler.

Multisorbent samplers (Part No. ST032, Envirochem, Inc., Kemblesville, PA) are packed in series with glass beads at the inlet followed by Tenax-TA<sup>®</sup>, Ambersorb XE-340<sup>®</sup> and activated charcoal in order of increasing affinity for low-boiling compounds. The average lengths and weights of the sorbent layers are: glass beads - 14.2 mm, 294 mg; Tenax-TA<sup>®</sup> - 30.1 mm, 85.5 mg; Ambersorb XE-340<sup>®</sup> - 29.4 mm, 167 mg; and activated charcoal - 8.8 mm, 48.0 mg. The relative standard deviation (RSD) in the lengths of individual sorbent layers is approximately 10%. Weights of individual sorbent layers are more variable. The charcoal layer was removed from some multisorbent samplers prior to laboratory experiments.

Tenax<sup>®</sup> samplers (Part No. ST023, Envirochem, Inc.) are packed with glass beads at the inlet followed by Tenax-TA<sup>®</sup>. The average lengths of the layers of glass beads and Tenax-TA<sup>®</sup> are 12.4 mm and 61.0 mm, respectively.

Prior to use, samplers are conditioned by heating them to 300°C for 10 min with a helium purge flowing at 100 cm<sup>3</sup> min<sup>-1</sup> in the reverse direction of gas flow during sample collection. Samplers are sealed at each end with nylon tube caps and 6-mm Teflon<sup>®</sup> ferrules. Capped samplers are stored at -10° C in elongated Kimax culture tubes with screw caps with Teflon<sup>®</sup> liners.

After exposure, a sample is thermally desorbed from a sampler and introduced into a capillary gas chromatograph (GC) with a UNACON<sup>®</sup> Model 810A (Envirochem, Inc.) sample concentrating and inletting system. The programmed sequence of events and temperatures for the UNACON<sup>®</sup> are shown in Table I. First, the exposed sampler is inserted into the tube desorption chamber of this instrument so that helium flows through the sampler in the reverse direction of sample gas flow. After air has been purged from the sampler, it is heated over a period of several minutes to ~275° C. Next, the instrument passes the sample through dual sequential traps of decreasing internal diameter to

concentrate the sample. These traps are packed with a series of sorbents similar to the sorbents in the samplers but do not contain activated charcoal. The first trap has a 4-mm I.D. enabling it to retain compounds from the relatively large volume of gas used in the desorption of the sampler. The second trap has a 1-mm I.D. to permit efficient desorption of the sample at typical carrier gas flow rates for capillary columns. A heated transfer line connects the instrument with the GC.

The UNACON® is equipped with a flame-ionization detector (FID). At several points in the concentrating sequence, a small portion of the sample (4-8%) is automatically diverted to the FID for monitoring of trap desorption and for an indication of total organic carbon concentration.

Sample components are resolved with a GC (5970A series, Hewlett Packard Co., Palo Alto, CA) equipped with liquid nitrogen (LN) subambient cooling and a crossed-linked 5% phenylmethylsilicone, fused-silica capillary column (Model 19091J Opt. 202, Hewlett Packard Co.).

Chromatographic peak shape, peak resolution and peak area response for low-boiling compounds are enhanced with an on-column cryogenic focusing attachment we developed for the GC. This device sprays LN directly on a 5-mm section of the capillary column, 30 mm from the within-oven juncture of the column and the UNACON® transfer line. The LN at 60 kPa is obtained from the same line supplying the GC cryogenic valve assembly. Flow is controlled with a solenoid on-off valve (Part No. 8262A203, ASCO®, Automatic Switch Co., Florham Park, NJ) positioned in the unoccupied detector compartment of the GC. The transfer line from the valve to the spray nozzle is 3.2-mm O.D. stainless-steel tubing insulated with ceramic wool. The nozzle is a 3.2- to 1.6-mm tube-fitting reducer bored through to 1.6 mm. The nozzle is positioned in the center of the GC oven at the point of minimum air velocity. The section of the column to be cooled is positioned 7 mm from the nozzle with wire eyelets. The cryogenic focusing attachment is operated so that the sample is concentrated at the head of the column as it is desorbed from the second trap in the UNACON®. When LN flow to the device is turned off, the cooled section of column rapidly rises to the temperature of the oven.

The GC is connected via a direct capillary interface to a 5970B series Mass Selective Detector (MSD) equipped with a 59970A series workstation (Hewlett Packard Co.) Each day prior to analyzing samples, the MSD is tuned and calibrated using perfluorotributylamine.

For qualitative analyses, the MSD is typically scanned from  $m/z$  33 to  $m/z$  250 with a continuous scan cycle time of ~0.5 sec. Identifications of compounds are made by: 1) comparing unknown spectra and retention times to spectra and retention times of known compounds analyzed using identical conditions; or 2) by comparing unknown spectra to spectra contained in the NBS mass spectral library<sup>11</sup> or in an eight-peak index<sup>12</sup> with confirmation by analyses of known compounds whenever possible.



For quantitative analyses, the MSD is operated to monitor multiple, individually-selected mass ions. For each compound of interest, a mass ion with high relative intensity is chosen as the quantitative ion, and a characteristic ion of equal or lower intensity is chosen as a qualifying ion for confirmation of compound identity. A typical analytical run for a sample containing multiple compounds is broken down into sequential groups of 6-10 mass ions, each with dwell times chosen to give a scan cycle time for each ion group of ~0.25 sec.

A standard gas mixture for qualitative or quantitative analysis is prepared by injecting an aliquot of a liquid mixture of the analytes of interest into a helium-filled 2-L flask with septum cap which is then heated and maintained at 65° C.<sup>13</sup> Samples are withdrawn from the flask with a gas-tight syringe and are injected into a helium gas stream flowing at 100 cm<sup>3</sup> min<sup>-1</sup> through a conditioned sampler in the direction of sample gas flow. Flow is maintained for 5 min after which the sampler is analyzed using the normal procedure. Standard gas mixtures are prepared daily.

Air sampling flow rate in both laboratory and field experiments is typically ~100 cm<sup>3</sup> min<sup>-1</sup> (20° C, 760 mm Hg). The vacuum source for replicated field samples is provided by a diaphragm pump (Air Cadet®, Cole-Parmer Instrument Co., Chicago, IL). Sample flow rates are regulated with electronic mass-flow controllers placed between samplers and the pump. Typically, samples are simultaneously collected in triplicate in laboratory experiments, and samples are simultaneously collected in duplicate in field experiments. Separate replicated samples are collected for qualitative and quantitative analyses. Sample volumes are varied according to expected analyte concentrations. Typical sample volumes for urban outdoor air are 5 or 10 L. Sample volumes for indoor air may be lower.

Laboratory experiments for the direct determination of sample breakthrough volumes under simulated use conditions are conducted in a 20-m<sup>3</sup> environmental chamber. All interior surfaces of the chamber are clad in stainless steel. The natural ventilation rate of the chamber with the air inlet and outlet closed is 0.03 ± 0.01 h<sup>-1</sup>. Prior to an experiment, the chamber is mechanically ventilated at 12 h<sup>-1</sup>. The ventilation is then turned off, and the inlet and outlet are closed. Samples (5 L) for the determination of the chamber background are collected. The chamber is spiked with the analytes of interest to known concentrations by injecting microliter volumes of liquid mixtures of the analytes into a heated port connected to an air stream flowing to a mixing fan. If required, the humidity in the chamber is increased by the addition of water vapor. Air and dewpoint temperatures in the chamber are monitored throughout an experiment. Breakthrough volumes are determined from the analysis of backup samplers which are placed in series with the samplers being investigated and are exchanged at predetermined volume intervals.

Field samples were collected at the site of a five-month old office building. The six-story building has a ventilated volume of  $\sim 36700 \text{ m}^3$ . Ventilation rates were calculated for the entire building from air velocity measurements made with a hot-wire anemometer at the building's air inlet vents on the roof. On a single day, air samples for VOC were collected outdoors on the roof (5 L) and indoors in open office spaces (3 L) at near steady-state conditions with the ventilation system operating in three different modes: 100% outside air, exhaust fans off; 100% outside air, exhaust fans on (ventilation rate =  $5.2 \text{ h}^{-1}$ ); and recirculation with  $\sim 16\%$  outside air (ventilation rate =  $0.84 \text{ h}^{-1}$ ).

## RESULTS AND DISCUSSION

The UNACON<sup>®</sup> concentrates the sample components while eliminating much of the water retained by the sampler. However, the traps are heated over a period of  $\sim 21 \text{ sec}$ , and because of heat transfer effects, they take longer to reach maximum temperature and then cool slowly. As a result, analyte vapors enter the column as a broad band. At an initial GC oven temperature of  $1^\circ \text{ C}$  and without the use of the cryogenic focusing attachment, the peaks of low-boiling compounds are broad and poorly resolved (Figure 1a). At the same initial oven temperature, the use of the cryogenic focusing attachment effectively recondenses the analyte vapors at the inlet of the column. Peak resolution is greatly enhanced, and peak area response increases by an average of 13% (Figure 1b). No early emerging peaks are observed, indicating that little of the analytes escapes recondensation.<sup>14</sup> However, by decreasing the oven temperature to  $-30^\circ \text{ C}$  with cryogenic focusing, another similar increase in peak area response can be achieved.

The pressure drop across samplers containing Tenax<sup>®</sup>, Ambersorb<sup>®</sup> and charcoal (TAC) and samplers containing only Tenax<sup>®</sup> and Ambersorb<sup>®</sup> (TA) was investigated as a function of sampling rate. The pressure drop increased substantially over a flow rate range of  $50 \text{ to } 250 \text{ cm}^3 \text{ min}^{-1}$  and was highly variable among samplers (Table II). Since a large pressure drop is impractical for field sampling and may also result in the vacuum desorption of trapped analytes<sup>15</sup>, a flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$  was selected for most sampling applications. This is near the optimal rate for samplers of this geometry<sup>6</sup>.

Water vapor uptake by TAC and TA samplers at a sample gas flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$  and a water vapor concentration of  $9.52 \text{ g m}^{-3}$  ( $20^\circ \text{ C}$ ,  $760 \text{ mm Hg}$ ) in the chamber air, or 55% relative humidity, is shown in Table III. As expected, samplers containing charcoal retain the most water. At a sample volume of 10 L, TAC and TA samplers retain 20 and 15 mg of water, respectively. This represents 21 and 16%, respectively, of the total amount of water passing through the samplers. Since the design of the UNACON<sup>®</sup> allows much of the water to be vented while the sample is transferred to the first analytical trap, the system can tolerate up to 25 mg of water retained on a sampler before ice blockage of the capillary column occurs during trap to column transfer with cryogenic focusing. While Tenax<sup>®</sup> degradation

products can increase when sampling at high relative humidity,<sup>15</sup> the effect of water on TAC and TA sampler blanks is expected to be moderate since the samplers contain a relatively small volume of Tenax®.

Breakthrough volume has been defined as the volume at which a significant amount of a constant atmosphere of an adsorbate drawn through a sorbent tube appears in the tube effluent.<sup>6</sup> The method of direct measurement of breakthrough volume using backup samplers collected at various volume intervals was used because it allows simulation of important field sampling parameters such as air temperature, presence of other compounds, and water vapor concentration. Breakthrough volumes were only measured for representative low-boiling compounds. Breakthrough volumes for higher boiling compounds can be estimated since, for most compounds, there is a good correlation between breakthrough volume and boiling point.<sup>6</sup> Breakthrough volume can be related to the more commonly measured retention volume, which is defined as the volume at which the peak maximum for a single injection emerges from a sorbent tube<sup>6</sup>, from a knowledge of sampler theoretical plates.<sup>16</sup>

In Table IV, breakthrough volumes for ten low-boiling compounds on TA and Tenax® samplers are compared at conditions of 21° C, ~50% relative humidity and 100 cm<sup>3</sup> min<sup>-1</sup> sample flow rate. Significant breakthrough is defined as a loss of more than one percent of an analyte. For the ten compounds, breakthrough volumes on Tenax® alone are generally small, with half of the compounds having breakthrough volumes of less than one liter. These volumes are similar to safe sampling volumes (retention volumes + 2) reported for samplers of the same internal diameter containing 130 mg of Tenax-GC®.<sup>6</sup> Such small volumes are inadequate for the intended application, since sample volumes of 10 L may be required. The use of much larger amounts of Tenax® to increase breakthrough volumes can necessitate more rigorous cleanup procedures to ensure acceptable sampler blanks. In addition, increases in breakthrough volumes may be lower than expected if sampler geometry is changed in a way that reduces theoretical plates.

With TA samplers and a sample volume of 10 L, trichlorofluoromethane (Freon-11®) and, to a smaller extent, dichloromethane are the only compounds not quantitatively sampled. The charcoal layer in TAC samplers increases the breakthrough volume for trichlorofluoromethane to >5 L while breakthrough volumes for the other compounds exceed 10 L. Thus, the addition of a backup layer of Ambersorb® increases breakthrough volumes for many low-boiling compounds to at least the maximum sample volume required for the intended application. Addition of a charcoal layer may be necessary for the quantitative sampling of very low boiling compounds such as Freons®, but, as noted above, has the disadvantage of increasing water vapor retention.

Adequate retention volumes simplify the calculation of limits of quantitation. A value of ten times the standard deviation of instrumental noise and signal measurements has been recommended for the instrumental limit of quantitation.<sup>17</sup> By this criterion, the limit

of quantitation for compounds used in this investigation is 0.1 - 0.5 ng. With a sample volume of 10 L and no breakthrough, the limit of quantitation for the method is expected to be 10 - 50 ng m<sup>-3</sup> for most compounds. In practical terms, no attempt has been made to quantify concentrations much below 0.4 µg m<sup>-3</sup> with a 5-L sample volume.

The precision and accuracy of the method for the analysis of the ten compounds used in the study of breakthrough volume is demonstrated in Table V. Three replicate samples were collected with the TA sampler from the environmental chamber before and after the addition of known concentrations of the compounds. At background concentrations near 1 ppb, the precision of the method is better than 5%, with the exception of the analysis of pentanal which was more variable. At concentrations of 45-77 ppb, the precision for all compounds is better than 3.5%. Comparison of prepared and measured chamber concentrations indicates that the accuracy of the method for seven of the ten compounds is ±5% or better. The concentration of benzene is 7% too high, and the concentration of pentanal is 12% too low for undetermined reasons. The high measured concentration of trichlorofluoromethane is probably caused by the offgassing of this compound from the polyurethane foam used to insulate the chamber. Calibration curves are typically linear with coefficients of determination (r<sup>2</sup>) of >0.99.

The accuracy of an analysis for VOC is strongly impacted by the potential for contamination and the formation of artifacts. For example, benzene and toluene are present in Tenax® as impurities which are difficult to remove,<sup>18</sup> and benzaldehyde, acetophenone and phenol are known decomposition products of Tenax®.<sup>15</sup> On the other hand, Ambersorb XE-340® has few contaminants in the boiling point range between 100-300° C.<sup>8</sup> Blanks for TAC and TA samplers probably derive from Tenax® since they typically consist of benzene (3-7 ng), toluene (2-6 ng) and benzaldehyde (> 10 ng). Water vapor and oxidants, such as ozone and oxides of nitrogen, can produce decomposition products from Tenax® and from analytes adsorbed on Tenax®. As examples, benzaldehyde, acetophenone and phenol have been shown to increase in magnitude when sampling air with high humidity, and cyclohexene collected on Tenax® reacted with ozone to produce cyclohexadiene, three isomers of C<sub>6</sub>H<sub>10</sub>O and benzene.<sup>15</sup> Artifacts can also be formed on carbonaceous sorbents. Terpenes, for example, have been observed to undergo degradation reactions when thermally desorbed from carbon black and a sorbent similar to Ambersorb XE-340®.<sup>9</sup> Although artifact formation was not specifically investigated, α-pinene is the only compound analyzed to date which clearly undergoes some degradation.

The applicability of the method for the quantitation of VOC is demonstrated by samples taken outdoors and indoors at the site of a five-month-old, large office building. Forty-two individual compounds were detected in these samples. Approximately half of the detected compounds were identified, and many of the remaining compounds were partially classified. The identified compounds are ubiquitous components of urban outdoor and indoor air. The majority of identified compounds are hydrocarbons including 11 aromatic hydrocarbons, four n-alkanes, two branched alkanes, and one C<sub>n</sub>H<sub>2n</sub> hydrocarbon. In addition, there are four oxygenated compounds and

three halocarbons. Sixteen of the compounds were quantified using multipoint calibration curves (Table VI). Precisions for average concentrations in duplicate samples collected with the ventilation system set at 100% outside air with exhaust fans on range from <1% to 5.5% RSD. With this level of precision, it is possible to detect real differences in concentration with location and ventilation rate. For all compounds, except benzene and benzaldehyde, indoor concentrations consistently exceeded outdoor concentrations. When operating with 100% outside air, deactivation of the exhaust fans decreased ventilation efficiency and increased the concentrations of all compounds except benzaldehyde. Although concentrations are blank-corrected, inconsistencies with benzaldehyde may be due to a variable sampler blank. Reduction of ventilation to ~16% outside air for 3.5 h resulted in increased concentrations for eight of the 16 compounds. An internal source strength was estimated for the 16 compounds using a single-equation, mass balance ventilation model.<sup>19</sup> The model assumes perfect air mixing. For simplicity, the penetration of the compounds into the building from outside air was taken to be unity, and removal mechanisms other than ventilation were ignored. The resulting composite source strength for the compounds was approximately 5 g h<sup>-1</sup> for the entire building.

## SUMMARY

We have assembled the instrumental components and developed procedures for an analytical method to quantify ppb concentrations of a broad range of VOC in ambient and indoor air. The method uses a multisorbent sampler in combination with a thermal desorption system for sample concentrating and inletting, a GC equipped with an on-column cryogenic focusing attachment, and a mass spectrometer. The sampler contains a series of Tenax®, Ambersorb XE-340® and, in some cases, activated charcoal. Sampler breakthrough volumes for representative low-boiling compounds are ≥ 10 L. With a 10 L volume, limits of quantitation are < 1 ppb. Overall precision is normally better than 5% at analyte concentrations ranging between one and several tens of ppb. Accuracy for representative low-boiling compounds is typically ± 5%. With this level of precision and accuracy, it is possible to detect real differences in concentrations of VOC in indoor air, with location and ventilation rate. This was demonstrated by analyses made at a large office building.

## ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building and Community Systems, Building Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The use of trade and product names does not imply endorsement.

## REFERENCES

1. A.R. Hawthorne, R.B. Gammage, C.F. Dudney, B.E. Hingerty, D.D. Schuresko, D.C. Parzyck, D.R. Womack, S.A. Morris, R.R. Westley, D.A. White and J.M. Schrimsher, "An indoor air quality study of forty East Tennessee homes", Oak Ridge National Laboratory Report ORNL-5965, Oak Ridge, TN (1984).
2. E. Lebret, H.J. van de Wiel, H.P. Bos, D. Noij and J.S.M. Boleij, "Volatile hydrocarbons in Dutch homes", In *Indoor Air*, V. 4, pp 169-174, Swedish Council for Building Research, Stockholm, Sweden (1984).
3. M. De Bortoli, H. Knöppel, E. Pecchio, A. Peil, L. Rogora, H. Schaunenburg, H. Schlitt and H. Vissers, "Measurements of indoor air quality and comparison with ambient air: A study of 15 homes in northern Italy", Commission of the European Communities Report, EUR 9656 EN, Directorate-General for Science, Research and Development, Joint Research Centre, Ispra, Italy (1985).
4. L.A. Wallace, E.D. Pellizzari, T.D. Hartwell, C.M. Sparacino, L.S. Sheldon and H. Zelon, "Personal exposures, indoor-outdoor relationships and breath levels for 355 persons in New Jersey", *Atmos. Environ.* 19: 1651 (1985).
5. K.J. Krost, E.D. Pellizzari, S.G. Walburn and S.A. Hubbard, "Collection and analysis of hazardous organic emissions", *Anal. Chem.* 54: 810 (1982).
6. R.H. Brown and C.J. Purnell, "Collection and analysis of trace organic vapor pollutants in ambient atmospheres", *J. Chromatogr.* 178:79 (1979).
7. G. Holzer, H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield and H.M. Liebich, "Collection and analysis of trace organic emissions from natural sources", *J. Chromatogr.* 142:755 (1977).
8. G. Hunt and N. Pangaro, "Potential contamination from the use of synthetic adsorbents in air sampling procedures", *Anal. Chem.* 54:369 (1982).
9. V.A. Isidorov, I.G. Zenkevich and B.V. Ioffe, "Methods and results of gas chromatographic-mass spectrometric determination of volatile organic substances in an urban atmosphere," *Atmos. Environ.* 17:1347 (1983).
10. L.D. Ogle, R.C. Hall, W.L. Crow, E. Jones and J.P. Gise, "Development of preconcentration and chromatographic procedures for the continuous and unattended monitoring of hydrocarbons in ambient air", *Preprint extended abstract, Division of Environmental Chemistry, American Chemical Society Conference, September 1982, Kansas City, MO.*

11. S.R. Heller and G.W.A. Milne, "EPA/NIH mass spectral data base", *U.S. Nat. Bur. Stand., Nat. Stand. Ref. Data Ser.* 63, U.S. Govern. Printing Office, Washington, DC (1978).
12. *Eight Peak Index of Mass Spectra*, 3rd ed., The Mass Spectrometry Data Centre, The Royal Society of Chemistry, The University, Nottingham, UK (1983).
13. R.M. Riggin, "Compendium of methods for the determination of toxic organic compounds in ambient air", U.S. Environ. Protection Agency Report EPA-600/4-84-041, Environ. Monitoring Systems Laboratory, Research Triangle Park, NC.
14. J.W. Graydon and K. Grob, "How efficient are capillary cold traps?", *J. Chromatogr.* 254:265 (1983).
15. E. Pellizzari, B. Demain and K. Krost, "Sampling of organic compounds in the presence of reactive gases with Tenax GC," *Anal. Chem.* 56:793 (1984).
16. G.I. Sennum, "Theoretical collection efficiencies of adsorbent samplers", *Environ. Sci. Technol.* 15:1073 (1981).
17. L.H. Keith, W. Crummett, J. Deegan, Jr., R.A. Libby, J.K. Taylor and G. Wentler, "Principles of environmental analysis", *Anal. Chem.* 55:2210 (1983).
18. J.F. Walling, "The utility of distributed air volume sets when sampling ambient air using solid adsorbents", *Atmos. Environ.* 18:855 (1984).
19. G.W. Traynor, J.R. Girman, M.G. Apte, J.F. Dillworth and P.D. White, "Indoor air pollution due to emissions from unvented gas-fired space heaters", *J. Air Pollut. Contr. Assoc.* 35:231 (1985).

Table I. Typical event times and temperatures for sample concentration and inletting with UNACON®.

Elapsed Time (Min:Sec)	Event	Max. Temp. (° C)
0:00 - 1:00	Initial carrier gas flow	
1:00 - 5:00	Tube chamber heating	275
5:00 - 10:00	Secondary carrier gas flow	
10:00 - 10:21	Trap 1 heating	310
10:21 - 12:21	Trap to trap transfer	
12:21 - 12:42	Trap 2 heating	310
12:42 - End	Trap to column transfer	
10:00 - 14:42	On-column cryogenic focusing	

Table II. Pressure drop across samplers versus flow rate.

Flow Rate <sup>a</sup> (cm <sup>3</sup> min <sup>-1</sup> )	Pressure Drop	
	TA Samplers (mm Hg)	TAC Samplers (mm Hg)
50	26 ± 5 <sup>b</sup>	31 ± 6 <sup>b</sup>
100	55 ± 11	65 ± 15
150	87 ± 19	102 ± 26
200	122 ± 29	143 ± 40
250	163 ± 41	191 ± 53

<sup>a</sup> Flow rate at 20° C, 760 mm Hg.

<sup>b</sup> Mean ± standard deviation for 5 samplers.



Table III. Cumulative water vapor retention versus sample volume.

Sample Volume <sup>a</sup> (L)	Cumulative H <sub>2</sub> O Retention <sup>b</sup>	
	TA Sampler (mg)	TAC Sampler (mg)
2	5.1	7.5
4	7.8	11.1
6	10.1	14.2
8	12.4	17.2
10	14.9	20.3

<sup>a</sup> Volume at 20° C, 760 mm Hg.

<sup>b</sup> At H<sub>2</sub>O vapor conc. of 9.52 g m<sup>-3</sup> (55% RH).

Table IV. Breakthrough volumes for low-boiling compounds.

Compound	Boiling Point (° C)	Breakthrough Volume <sup>a</sup> (L)	
		Tenax® Sampler	TA Sampler
Trichloroflouromethane	24	<0.5	<4
n-Pentane	36	<0.5	>10
Dichloromethane	40	<0.5	8-10
n-Hexane	69	1-2	>10
2-Butanone	80	1-2	>10
Chloroform	62	1-2	>10
Ethyl acetate	77	>4	>10
1,1,1-Trichloroethane	74	<0.5	>10
Benzene	80	2-4	>10
Pentanal	102	0.5-1	>10

<sup>a</sup> Breakthrough is loss of >1% of analyte.

Table V. Precision and accuracy for low-boiling compounds using TA sampler.

Compound	Concentration in Chamber (ppb)		
	Background	Prepared	Measured
Trichlorofluoromethane	1.75 (0.1) <sup>a</sup>	49.0	58.4 (1.1) <sup>a</sup>
<i>n</i> -Pentane	1.54 (1.5)	76.5	74.5 (2.5)
Dichloromethane	0.95 (1.5)	68.8	65.3 (2.3)
<i>n</i> -Hexane	0.56 (2.5)	66.6	68.8 (3.2)
2-Butanone	0.74 (3.2)	72.9	72.9 (3.4)
Chloroform	--- <sup>b</sup>	54.0	52.4 (3.1)
Ethyl acetate	0.11 (7.5)	65.9	67.3 (2.5)
1,1,1-Trichloroethane	1.11 (4.8)	44.7	46.5 (1.0)
Benzene	1.11 (4.4)	73.8	79.0 (3.0)
Pentanal	0.90 (4.0)	61.6	54.3 (3.0)

<sup>a</sup> Mean and (RSD) for triplicate samples.

<sup>b</sup> Below limit of quantitation.

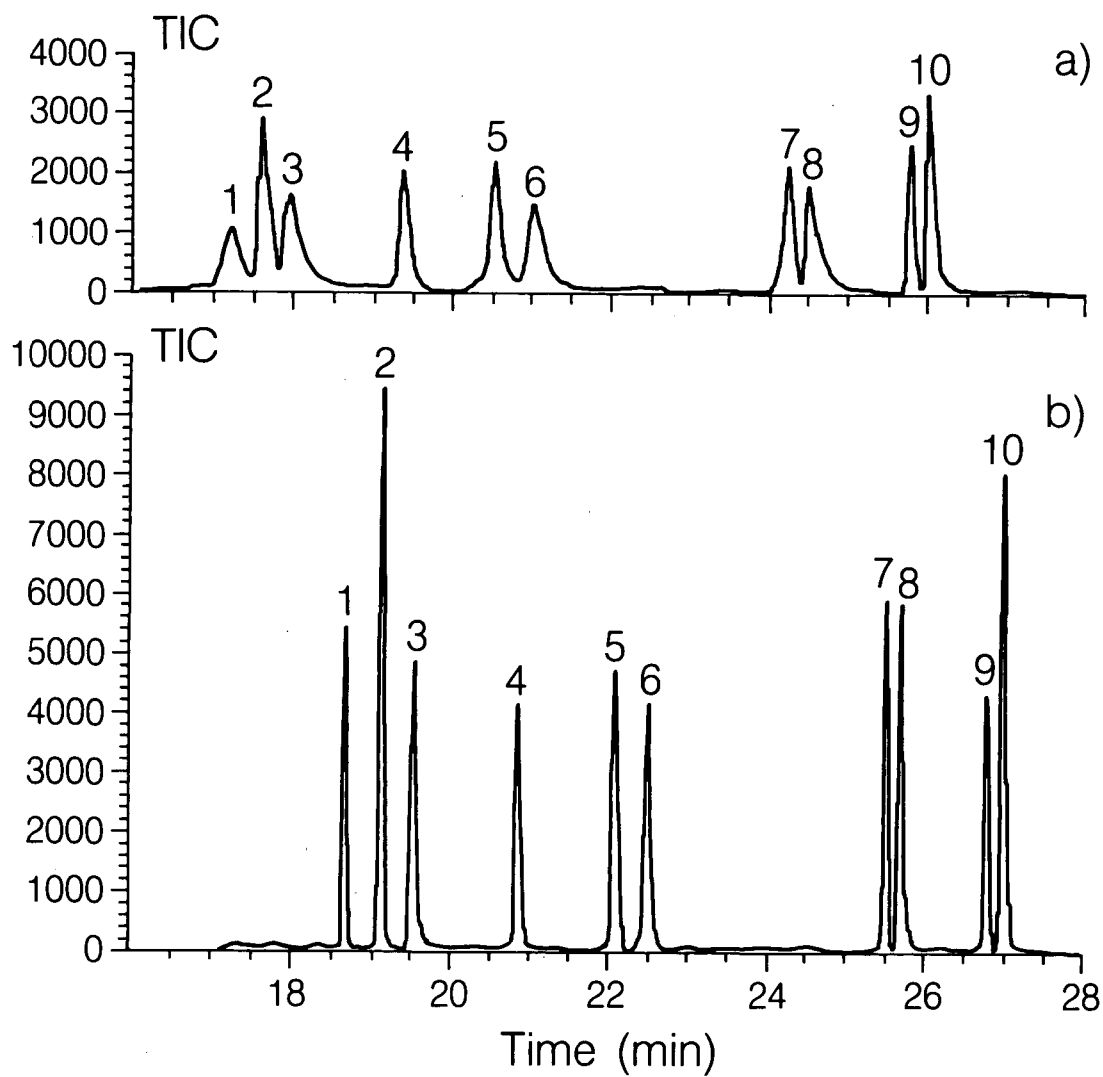
Table VI. Outdoor and indoor concentrations of VOC at a large office building.

Compound	Outdoor Concentration Roof (ppb)	Indoor Concentration <sup>a</sup>		
		100% Vent. Exhaust On (ppb)	100% Vent. Exhaust Off (ppb)	16% Vent. (ppb)
<i>n</i> -Pentane	0.29	1.15 (2.5) <sup>b</sup>	2.46	0.59
Acetone	2.08	6.94 (5.5)	10.2	12.6
<i>n</i> -Hexane	--- <sup>c</sup>	0.56 (2.5)	1.14	----
2-Butanone	1.63	6.67 (0.8)	7.65	21.0
1,1,1-Trichloroethane	0.18	0.98 (1.4)	1.20	2.25
Benzene	1.99	2.11 (3.4)	3.65	0.87
3-Methylhexane	0.10	0.33 (2.1)	0.67	----
Trichloroethylene	----	----	----	1.30
Methylcyclohexane	0.14	----	0.63	----
Toluene	1.08	2.96 (2.6)	5.41	3.10
Ethylbenzene	0.20	0.97 (2.2)	1.39	2.28
<i>m</i> -, <i>p</i> -Xylene	0.70	3.85 (1.6)	5.38	9.67
<i>o</i> -Xylene	0.54	1.35 (2.6)	1.94	3.43
Benzaldehyde	1.99	3.06 (1.8)	1.80	0.82
<i>n</i> -Decane	0.39	0.40 (1.8)	0.47	0.60
<i>n</i> -Undecane	----	0.76 (0)	0.80	0.85
Total	9.2	32.1	44.8	59.4

<sup>a</sup> Measured in a single open office space.

<sup>b</sup> Mean and (RSD) for duplicate samples.

<sup>c</sup> Below limit of quantitation.



XBL 863-1063

Figure 1. Total ion current chromatograms for selected ion analyses of: 1. trichlorofluoromethane, 284 ng; 2. *n*-pentane, 159 ng; 3. 2-propanol, 299 ng; 4. dichloromethane 253 ng; 5. 4-methyl-1-pentene, 169 ng; 6. cyclopentane, 189 ng; 7. *n*-hexane, 168 ng; 8. 2-butanone, 153 ng; 9. chloroform, 188 ng; and 10. ethyl acetate, 171 ng. Oven temperature held at 1° C and then, starting between peaks 6 and 7, ramped at 10° C min<sup>-1</sup>. a). without cryogenic focusing and; b). with cryogenic focusing.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*