



Project Summary

Intercomparison of Sampling Techniques for Toxic Organic Compounds in Indoor Air

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Because people spend a major fraction of their time indoors, concern exists over exposure to volatile organic compounds present in indoor air. This study was initiated to compare several VOC sampling techniques in an indoor environment. The techniques compared include distributive air volume sampling, high and low rate passive sampling, and whole air collection in canisters. The study focussed on ten target compounds:

chloroform	benzene
1,1,1 trichloroethane	toluene
tetrachloroethylene	styrene
bromodichloro-	p-dichloro-
methane	benzene
trichloro-	hexachloro-
ethylene	butadiene.

Altogether, ten separate 12-hour sampling experiments were conducted. Two experiments sampled the background air of the residence. For the other eight experiments, the indoor air was spiked with the target compounds. Three different spike levels were utilized to cover a range of target compound concentrations. The nominal spike concentrations were 3, 9, and 27 ng/l for each of the ten target compounds. Statistical analysis of the sampling results indicates generally high correlation coefficients (greater than 0.90) between the methods. The most notable exception was benzene, which had lower correlation coefficients. In general, the distributed air volume sampling technique and the low rate passive technique measured concentrations less than or equal to the canister method.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is an increasing need to measure volatile organic compounds in air. This need has been especially great for hazardous organic species in indoor air. A variety of approaches have been utilized for collection and analysis of hazardous organic pollutants in air. One of the most widely used sampling techniques is collection on Tenax* solid adsorbent. This study employed an active Tenax sampling technique, in which four samples are collected simultaneously at different flow rates. This technique is called distributed air volume sampling.

Collection of whole air samples in passivated canisters is another technique which has been employed for volatile organic species sampling. This study employed a canister sampling procedure using passivated 6 liter stainless steel sampling canisters and a constant flow sampling system.

Passive collection of volatile organic chemicals is a very attractive means of sampling, especially for human exposure studies. Small stainless steel cylinders containing Tenax adsorbent be-

*Mention of trade names or commercial products does not constitute endorsement or recommendations for use.

hind a diffusion barrier have proven to be very successful for sampling a wide range of compounds, when used under appropriate conditions. Both high-sampling-rate and low-sampling-rate devices were employed in the present study.

All of the techniques noted above have been employed for ambient air sampling, and some have been used to sample indoor air. The study reported here compared these methods for the first time in an indoor environment, with emphasis on a number of hazardous organic chemicals observed in indoor air.

Overview of Study Design

The intercomparison of volatile organic compound sampling techniques was carried out in an unoccupied residence. The techniques compared included distributive air volume sampling, high- and low-rate passive sampling, and whole air collection in canisters. Samples were collected in duplicate for each technique except the canister procedures; each canister sample was analyzed twice, to provide an estimate of analytical precision for this sampling medium. All samples were analyzed within three days of collection by GC/MS. The study focussed on ten target compounds:

chloroform	benzene
1,1,1 trichloroethane	toluene
tetrachloroethylene	styrene
bromodichloro-	p-dichloro-
methane	benzene
trichloro-	hexachloro-
ethylene	butadiene.

Altogether, ten separate 12-hour sampling experiments were conducted. Two experiments sampled the background air of the residence. For the other eight experiments, the indoor air was spiked with the target compounds. Three different spike levels were utilized to cover a range of target compound concentrations. The nominal spike concentrations were 3, 9, and 27 ng/l for each of the ten target compounds. Spiking was accomplished by vaporizing an initial charge of the ten-compound mixture into the furnace blower duct to achieve the approximate spike concentration. Throughout the remainder of the 12-hour period, the target compounds were continuously introduced into the duct from a gas cylinder at a rate calculated to make up for dilution caused by infiltration. Continuous operation of the house furnace blower and

several oscillating fans located throughout the house was used to provide thorough mixing, and also to provide the air velocity required for efficient operation of the passive devices.

For the distributive air volume technique, one blank was run for each sample (i.e., per set of four tubes). The blanks transported to the field were not opened or handled prior to analysis. Duplicate samples were collected using a second distributive air volume collection system, and both the high- and low-rate passive samples were collected in duplicate. Temperature, relative humidity, and air exchange rate were monitored during each experiment.

All samples and blanks were analyzed on the same GC-MS system to minimize the uncertainty in the analytical portion of the measurements so that the comparison can focus on the sampling techniques.

Experimental

The residence used for these experiments is located in the Upper Arlington suburb of Columbus, OH, approximately 10 km northwest of downtown. The test house was unoccupied during this study, and has been used for the past year for heating, ventilation, and air infiltration experiments. The house is a three-bedroom, two-bath ranch constructed in 1963. All sampling was conducted in the living room of the residence.

Sampling Methodology for Target Organic Compounds

Distributed Air Volume Sampling

Sampling with Tenax adsorbent tubes was accomplished with the system shown in Figure 1. For experiment 1 through 4, the mass flow controller:

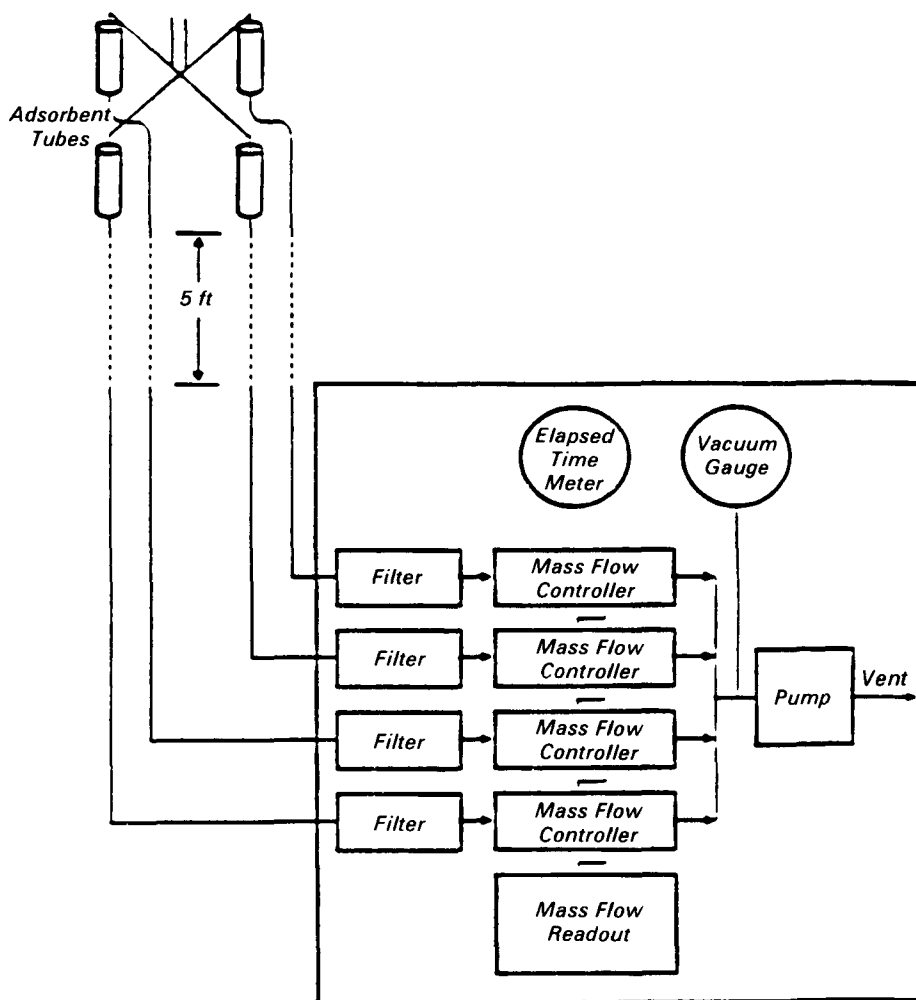


Figure 1. Diagram of distributive air volume sampler.

were adjusted so that nominal air volumes of 5, 10, 15, and 20 liters were collected over the 12-hour sampling period. For experiments 5 through 11, nominal sample volumes of 5, 10, 20, and 40 liters were collected. Actual volumetric flow rates were measured before and after each experiment. Duplicate sets of Tenax adsorbent tubes were collected during all ten experiments. These tubes consisted of packed glass cartridges as used with the Volatile Organic Sampling Train (VOST) System developed by EPA for stack sampling. Tenax for the VOST-type cartridges was purchased from Alltech Associates. The Tenax was extracted in a Soxhlet apparatus with methanol followed by pentane, and dried in a vacuum oven. The clean material was then transferred to the individual glass cartridges. Forty-eight hours before use, the sampling cartridges were further cleaned by heating (240°C) under a helium purge (50 ml/minute). When not being used for sampling or analysis, all Tenax cartridges were stored at room temperature in one-gallon metal cans containing a layer of charcoal.

A sample blank was carried along with each set of four Tenax cartridges. The blank cartridge was not removed from its storage container; it simply accompanied the four adsorbent tubes to the test site and then back to the laboratory for analysis.

Canister Sampling

Six-liter stainless steel canisters (Demaray Scientific Instrument, Ltd.) were used for collecting integrated whole air samples. A stainless steel pump (Metal Bellows Corp., Model-158) directs flow to the sample canister. The sampling rate is controlled with a mass flow controller (Tylan, FC-260). A stainless steel tube restrictor (0.03-inch inner diameter by 6-inch length) was positioned upstream of the mass flow controller to prevent pump oscillations from affecting the mass flow. The sample flow was set so that a final canister pressure of 10 psig was achieved (i.e., 10 cc/min for a 12-hour sample period).

In preparation for sampling, the canister was sequentially filled (15 psig) and evacuated (25 in. of Hg) five times using zero air (Aadco, Inc.) as the flushing gas. After the fifth evacuation, the canister was sealed, transferred to a higher vacuum system and pumped down to 0.1 torr. A liquid nitrogen trap was utilized in this system to prevent contamination from the pump oil. An

oven (100°C) was also used to bake out the canisters during evacuation.

Passive Device Sampling Procedure

Two types of passive sampling devices (PSDs) were utilized in this study. Both types are stainless steel cylinders filled with 0.4 g Tenax GC. The device shown schematically in Figure 2 was designed to have a relatively high sampling rate for organic compounds. This device employs a 200-mesh stainless steel screen as the diffusion barrier.

The second type of device is similar to that shown in Figure 2, except that the 200-mesh screen is replaced by a stainless steel plate with a single 0.5 mm hole in the center. This device was designed to have a reduced sampling rate.

The sampling rates for PSDs employing reversible adsorption are dependent on the specific design of the device as well as the retention volume of each organic compound with respect to Tenax. Based on the design specifications of these devices and the 12-hour exposure time used in this study, the effective sample volumes for each target compound are shown in Table 1. A time-weighted average sampling rate was used to compute the volumes for the high rate PSD, because the rate decreases with time for some compounds over the 12-hour sampling period.

Before sampling, the PSDs were cleaned by baking at 200°C for at least two hours in an oven designed to hold ten PSDs. During bakeout, the PSDs were exposed to a flow of 100 ml/min of hydrocarbon-free N₂. Following cleanup, the PSDs were stored in a stainless steel cylinder which was purged with hydrocarbon-free N₂ and pressurized through a quick-connect fitting. With this device, the PSDs were transported to and from the testing residence. The blank PSDs were kept in the cylinder during sampling at the residence.

Three high-rate and three low-rate PSDs were employed for each experiment. Two devices of each type were analyzed; the third was collected as a backup. One of each PSD type was transported to the residence for use as a blank. These PSDs were not removed from the transfer cylinder.

Efficient operation of the PSDs requires movement of air around the device to replenish the boundary layer, which is depleted by sampling. The furnace blower and three oscillating fans were operated in the living room during each experiment, providing linear velocities of 25-35 ft·min⁻¹ at the location of the PSDs.

Additional measurements which were made to complement the organic species sampling intercomparison in-

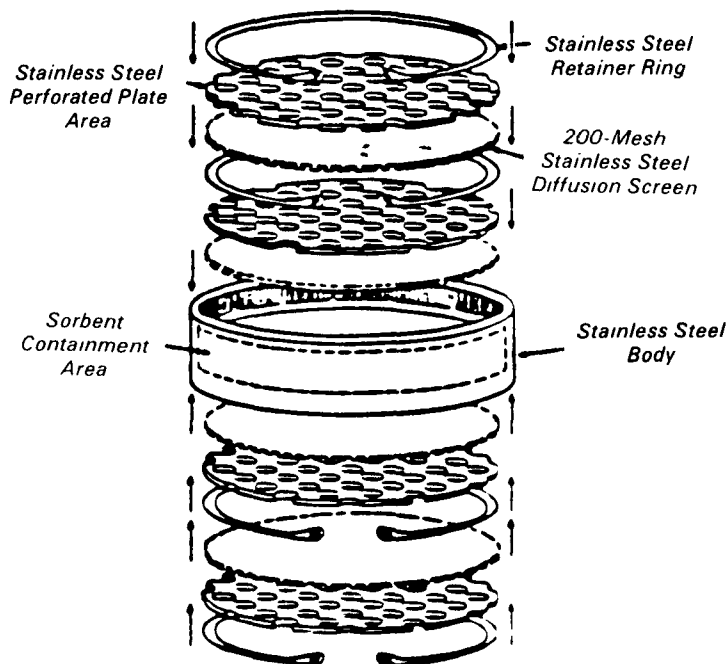


Figure 2. Thermally desorbably passive sampling device.

Table 1. 12-Hour Sample Volumes for High Rate and Low Rate Passive Sampling Devices

Target Compound	High Rate PSD Volume (l)	Low Rate PSD Volume (l)
chloroform	8.28	1.80
1,1,1-trichloroethane	5.19	1.53
tetrachloroethylene	36.2	1.86
bromodichloromethane	28	1.70
trichloroethylene	16.6	1.89
benzene	17.9	2.01
toluene	40.3	1.92
styrene	46	1.81
p-dichlorobenzene	41	1.53
hexachlorobutadiene	31.4	1.25

cluded temperature, relative humidity, NO/NO_x, and air infiltration rate. These measurements were made in the living room simultaneously with the organic species sampling. Temperature and relative humidity were monitored with an EG&G Model 911 unit. The concentrations of NO and NO_x were monitored with a CSI Model 2200 portable chemiluminescence instrument. Readout from both of these instruments was recorded on two Weather/Measure dual channel recorders.

Air infiltration rate was measured by the decay method, using SF₆ as the inert tracer. The concentration of SF₆ was measured every 30 minutes throughout each 12-hour experiment with a Hewlett Packard Model 5790 electron capture gas chromatograph with a 1 cc sampling loop and automated gas sampling valve.

Analysis Methods

The instrumentation used in this effort consisted of an Extranuclear Simulscan quadrupole mass spectrometer interfaced to a Hewlett Packard 5710A gas chromatograph. Data acquisition and reduction was performed with an on-line Finnigan INCOS 2300 data system. Sample analyses were performed by thermal desorption of the adsorbent (passive and distributive air volume samplers) or direct sampling (canister) into a cryogenic trap. Distributive air samples were desorbed at 200°C for ten minutes while purging with helium at 80 ml/min. Passive monitors were desorbed at 150°C for 15 minutes with an equivalent helium flow. The lower desorption temperature for the passive monitors was selected to minimize thermal degradation of sensitive compounds due to the stainless steel passive monitor housing. The canister was sampled through approximately 1 meter of Nafion tubing resulting in a dry sampling volume of 1.0 liter.

The cryogenic trap consists of a 20-cm loop of 1/8 in. OD stainless steel tubing packed with 60-80 mesh silanized glass beads. The trap was maintained at 87°K with liquid Argon during the cryofocussing step. The cryotrap was then heated to 160°C during back flushing with 3 ml/min of helium for a period of seven minutes. The cryotrap eluent was routed to a Hewlett Packard 50 m crosslinked SE 30 wide bore thick film fused silica capillary column using a 6-port valve maintained at 100°C. The initial column temperature was -20°C.

Following cryotrap desorption, the column was temperature programmed at 8°C/min to 200°C. GC/MS acquisition was initiated after a six minute delay. Electron impact ionization was used with the instrument scanning from m/z 46-270 with a 0.5 second cycle time.

Data reduction was performed automatically using in-house developed software. This involved retention driven reverse search for the target analytes followed by integration of characteristic extracted ion current profiles. Quantification was performed by comparison to the chromatographic peak areas of a known standard. Calibration and performance check analyses were done by cryotrap sampling a known volume from an aluminum compressed gas

cylinder containing 1.0 ppm in each of the target analytes. The concentration of benzene in the calibration cylinder was found to be within 6% of the calculated value based on direct comparison with an NBS primary standard cylinder.

Results

The dates of the ten experiments and the nominal spike levels are shown in Table 2. Some of the target compounds were present in the background air in the residence, contributing significantly to the total residence concentration during the spiking experiments.

An example of the results from the 10 intercomparison experiments is provided in Table 3. The table lists the experiment number, date, spike level, measured air exchange rate, average temperature, average relative humidity and the mean NO and NO₂ concentrations over the 12-hour sampling period. Table 3 also reports the sample volumes, blank-corrected concentrations and blank values for the various sampling techniques.

Analysis of Results

The statistical methods were taken from linear regression analysis. The canister method was chosen as the reference method throughout. This means that the results from the three Tenax methods (DAV, high rate PSD, and low rate PSD) were used as the dependent variable and the canister results as the independent variable in the regression. The canister and Tenax means were paired by experiment for each compound. The experimental design for the DAV Tenax was complicated by a number of factors and various types of averaging were done before performing the regression analysis. Details and justification for the regression analysis are given in the Project Report.

Table 2. Nominal Spike Levels for Indoor Intercomparison Experiments

Experiment No.	Date	Nominal Spike Level (ng/l)
1	June 12, 1985	background
2	June 18, 1985	3
3	June 24, 1985	3
4	June 26, 1985	9
5	July 1, 1985	9
6	July 8, 1985	27
7	July 10, 1985	27
9	August 20, 1985	background
10	September 23, 1985	3
11	September 30, 1985	9

Table 3. Results from Indoor Intercomparison Study, Experiment 6

Experiment No. 6
Date: July 8, 1985

Organic Spike Level: High
Measured Air Exchange Rate: 0.045 hr⁻¹

Average Temperature, °C 27°
Average Relative Humidity, percent 37
Average [NO], ppb NA
Average [NO₂], ppb NA

Sampling Techniques	Sample No	Sample Volume, l	Reported Units	Target Chemicals									
				Chloroform	1,1,1-Trichloroethane	Tetrachloroethylene	Bromodichloromethane	Trichloroethylene	Benzene	Toluene	Styrene	p-Dichlorobenzene	Hexachlorobutadiene
Integrated Canister—Sample 1	C-3	10	ng/l	23.1	21.0	29.5	15.7	15.7	26.4	32.3	11.2	11.3	18.7
Integrated Canister—Sample 2	C-3	10	ng/l	23.8	20.7	30.3	15.9	16.0	27.9	33.7	11.6	11.8	17.0
Distributed Air Volume—System 1	T-20	5.22	ng/l	21.3	21.8	31.6	16.2	16.6	28.1	38.5	13.7	13.5	17.4
Distributed Air Volume—System 1	T-19	10.20	ng/l	22.8	19.8	29.4	15.9	15.5	26.3	36.6	13.4	12.8	18.3
Distributed Air Volume—System 1	T-13	19.60	ng/l	18.9	17.4	22.4	12.9	13.3	24.7	30.1	11.2	10.7	15.9
Distributed Air Volume—System 1	T-14	39.90	ng/l	11.9	15.0	27.6	14.0	13.7	25.5	34.1	12.0	11.6	18.0
Distributed Air Volume—System 2	T-1	4.78	ng/l	21.5	18.6	28.7	14.6	15.4	24.5	34.7	12.7	12.4	15.6
Distributed Air Volume—System 2	T-4	9.10	ng/l	17.7	16.0	24.4	11.1	11.8	21.6	29.7	11.3	11.2	16.5
Distributed Air Volume—System 2	T-8	18.90	ng/l	18.6	17.1	25.7	12.6	13.4	25.1	32.6	11.7	11.2	16.7
Distributed Air Volume—System 2	T-7	39.80	ng/l	10.0	15.1	28.1	13.4	14.9	25.1	31.7	12.1	11.9	18.6
DAV Blank	MCT-1		ng	—	0.3	—	—	—	3.1	0.2	—	0.6	—
DAV Blank	MCT-2		ng	—	0.3	—	—	—	0.5	0.1	0.1	—	—
High Rate Passive Sampler	87	*	ng/l	15.9	57.6	39.2	13.3	19.0	18.9	47.3	16.9	18.5	24.6
High Rate Passive Sampler	90	*	ng/l	15.7	56.7	43.0	13.2	20.3	21.0	50.5	17.5	19.4	31.4
High Rate Passive Sampler		*	ng/l										
HRPS Blank	93		ng	—	26.8	—	—	0.9	0.8	3.4	0.3	—	—
Low Rate Passive Sampler	B208	*	ng/l	14.7	15.5	14.8	11.3	9.9	17.9	14.8	6.6	7.3	11.2
Low Rate Passive Sampler	B206	*	ng/l	15.2	15.5	15.9	11.8	10.7	18.8	15.9	7.1	6.6	<1.1
Low Rate Passive Sampler		*	ng/l										
LRPS Blank	B211		ng	0.1	6.8	0.2	0.1	1.0	1.2	2.0	0.2	0.1	1.8
NA Not available		*Sampling rate for PSDs varies with compound	High Rate PSD	8.3	5.2	36.2	28	16.6	17.9	40.3	46	41	31.4
NR Not reported due to interference or high blank		Sample volume for 12 hour collection period, in liters	Low Rate PSD	1.80	1.53	1.86	1.70	1.89	2.01	1.92	1.81	1.53	1.25

The two statistics of greatest interest from the regression analysis are the slope of the Tenax vs. canister regression line and the correlation coefficient between the canister and Tenax means. The slope is interpreted as a measure of the agreement between the two methods in any comparison. If the intercept is 0, a slope less (greater) than one indicates that the Tenax mean is, generally, lower (higher) than the canister mean. A correlation coefficient close to one indicates that the canister and Tenax means are approximately linearly related over all experiments. That is, the resultant means from the measurements by the two methods show the same relative peaks and valleys over all experiments.

Figures 3, 5, and 6 are summaries of the slope (agreement) for all three Tenax methods, while Figure 4 shows the correlation coefficients for DAV Tenax for all compounds. The compound numbers on the horizontal axis refer to the compounds as listed in the 'Overview of Study Design' section of

the Project Report. The chromatographic retention of the compounds increases from left to right. Several conclusions have been drawn from the statistical analysis illustrated in Figures 3, 4, 5, and 6.

- 1) The slope (agreement) results for DAV are shown in Figure 3. Note that ± one standard error bars are drawn on the figure.
 - a) (9) p-dichlorobenzene and (10) hexachlorobutadiene had slope estimates less than one and the estimates were within two standard errors of one.
 - b) (3) benzene, (6) toluene and (7) tetrachloroethylene had slope estimates greater than one and the estimates were within two standard errors of one.
 - c) The five other compounds had slope estimates less than one and the estimates were more than two standard errors from one.
 - d) (8) styrene was the only one of the ten compounds with an inter-

cept estimate (0.79 ng/l) more than two standard errors from zero.

- e) The more detailed statistical analysis indicated that for the DAV Tenax, the slopes for (1) chloroform, (2) 1,1,1-trichloroethane, and (10) hexachlorobutadiene shown in Figure 3 do not adequately represent the experiment and these results should be qualified.
- 2) The low rate PSD slope estimates (Figure 5) show that all slope estimates were less than one and all intercept estimates were within two standard errors of zero. With the exception of (3) benzene, the slope estimates for all compounds were not within two standard errors of one.
- 3) The high rate PSD slope estimates (Figure 6) are as follows:
 - a) (3) benzene had a slope estimate less than one and within two standard errors of one.
 - b) (1) chloroform and (4) bromo-

dichloromethane had slope estimates less than one but these estimates were not within two standard errors of one.

c) The seven remaining compounds had slope estimates greater than one and were not within two standard errors of one.

d) (10) hexachlorobutadiene was the only compound with an intercept estimate (-1.53 ng/l) more than two standard errors from zero.

4) The correlation between Tenax means and canister means was generally large (>0.90) for all Tenax methods. The most notable exception was (3) benzene, which had relatively small correlation coefficients for all Tenax methods.

Precision estimates were obtained for the three Tenax methods by pooling the variance of replicates over all experiments for PSD and DAV and over all nominal volumes for DAV. The precision estimate is taken as the square root of the pooled variance estimate. The compounds that showed precision estimates greater than 2.0 ng/l were:

- (3) benzene for the DAV and low rate PSD Tenax
- (6) toluene for all three Tenax methods
- (7) tetrachloroethylene for the DAV and high rate PSD Tenax
- (10) Hexachlorobutadiene for the low- and high-rate PSD

Precision estimates for the duplicate canister sample analyses were less than 1.2 ng/l for all compounds.

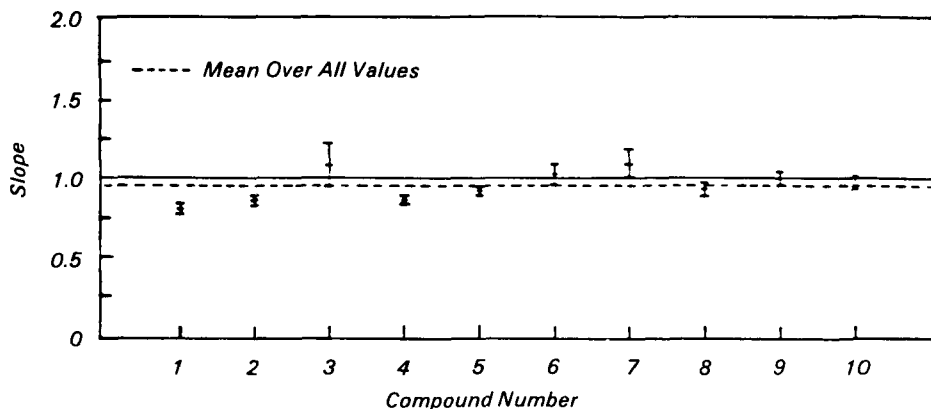


Figure 3. AGREEMENT: Tenax distributed air volume and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

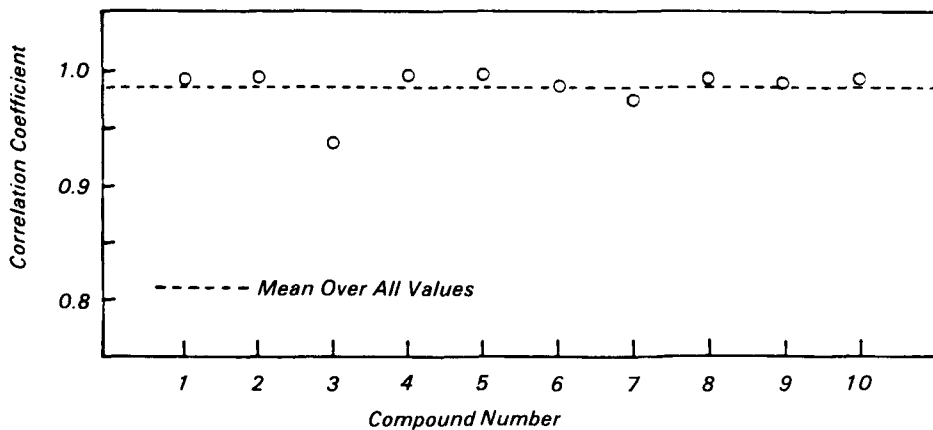


Figure 4. CORRELATION: Tenax distributed air volume and canister correlation of Tenax mean and canister mean.

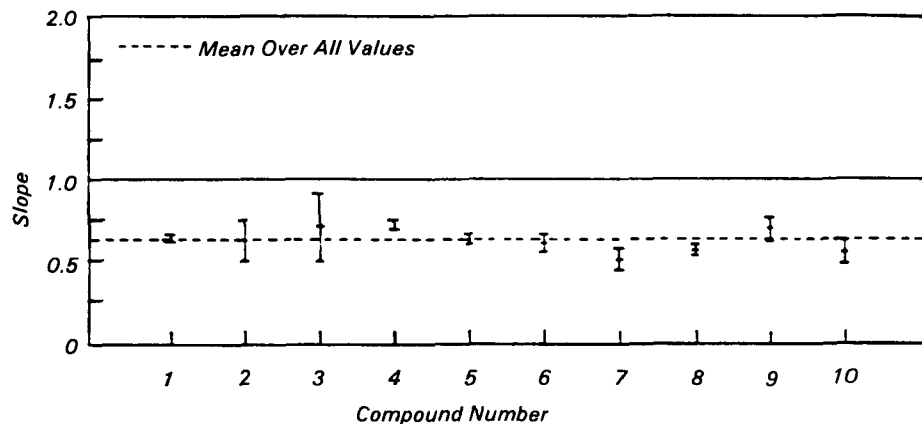


Figure 5. AGREEMENT: Tenax low rate personal sampling and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

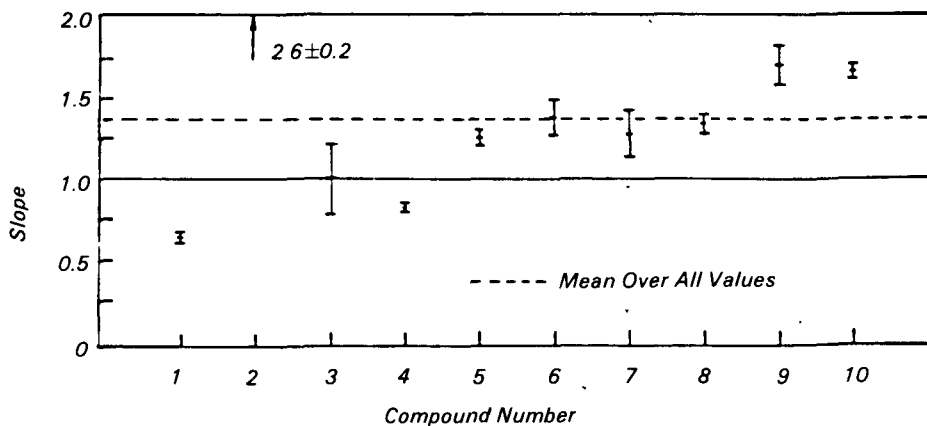


Figure 6. AGREEMENT. Tenax high rate personal sampling device and canister slope plus and minus one standard error from the linear regression of Tenax mean vs canister mean.

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James D. Mulik and William A. McClenny are the EPA Project Officers (see below).

The complete report, entitled "Intercomparison of Sampling Techniques for Toxic Organic Compounds in Indoor Air," (Order No. PB 87-165 262/AS; Cost: \$18.95, subject to change) will be available only from:

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