

US EPA ARCHIVE DOCUMENT

Environmental Technology Protocol Verification Report

Emissions of VOCs and Aldehydes from Commercial Furniture

Prepared by



Research Triangle Institute

Under a Cooperative Agreement with



U.S. Environmental Protection Agency

US EPA ARCHIVE DOCUMENT

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This document has been subjected to the U.S. Environmental Protection Agency's quality assurance and administrative reviews and has been approved for publication.

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The appendices are not included in the electronic version of this report. They contain raw data, a draft copy of the test protocol, and an EPA quality analysis report. Those interested in obtaining this information may contact

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Environmental Technology Protocol Verification Report

Emissions of VOCs and Aldehydes From Commercial Furniture

Prepared by

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EPA Cooperative Agreement No. CR 822870-01

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Abstract

As part of a U.S. Environmental Protection Agency (EPA) Environmental Technology Verification (ETV) program, the Research Triangle Institute (RTI) developed a test protocol for measuring volatile organic compounds (VOCs) and aldehydes in a large chamber. RTI convened stakeholders for the commercial furniture industry for advice and review of the protocol. In October 1998, a protocol verification test was performed using office chairs. Three laboratories participated in the test. This report gives information on the emissions from the chairs, interlaboratory comparisons, and intralaboratory comparisons. The emissions from the chairs were very low, thus providing a rigorous test of the protocol.

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Abbreviations and Acronyms

AQS	Air Quality Sciences, Inc.
ASTM	American Society for Testing and Materials
DNPH	2,4-dinitrophenylhydrazine
DQI	Data quality indicator
EPA	Environmental Protection Agency
ETL	Enviro-Test Laboratories
ETV	Environmental Technology Verification
MDL	Minimum detection limit
NIST	National Institute of Standards and Testing
QA	Quality assurance
QAPP	Quality Assurance Project Plan, specifically, Environmental Technology Verification Quality Assurance Project Plan for Emissions of VOCs and Aldehydes from Commercial Furniture, (draft dated 9/98 was used for protocol verification testing)
QC	Quality control
Protocol	Environmental Technology Verification Large Chamber Test Protocol for Measuring Emissions from VOCs and Aldehydes (draft dated 8/98 was used for protocol verification testing)
RD ₅₀	Concentration which depresses the respiratory rate (mice) to 50%
RH	Relative humidity
RSD	Relative standard deviation
RTI	Research Triangle Institute
TVOC	Total volatile organic compound
VOC	Volatile organic compound
σ_{est}	Estimated standard deviation

1.0 Introduction

1.1 Project Overview

The U.S. Environmental Protection Agency (EPA) established the Environmental Technology Verification (ETV) Program in 1995. The goal was to accelerate the entrance of new technologies in the marketplace. Through 12 pilot programs, environmental performance of technology was verified by the evaluation of objective and quality assured data. The focus was on commercial-ready technologies and there was no attempt to rank, approve or disapprove any technologies. The pilots verified technologies used in indoor air products, air pollution control, drinking water systems, pollution prevention, metal finishing, climate change, monitoring, etc. EPA selected a partner organization for each pilot. Partners came from both the public and private sectors including federal laboratories, states, and private sector research facilities. The partners performed and reported verification activities based on testing and quality assurance protocols developed with input from stakeholder/customer groups. Research Triangle Institute (RTI) had a pilot for indoor air products. This report discusses the verification testing for chemical emissions from commercial furniture.

1.2 Background

Over the last several years considerable work has been reported on emission chamber testing. The available emissions information has been reviewed for furnishings (1). An ASTM guide (2) for testing products with a small chamber is available. For commercial furniture, a large chamber is needed and specific test methods are needed including defining the required quality procedures.

In the last few years, the State of Washington (3) and the U.S. EPA (4) have required emissions testing data for bids to supply office furniture to new office buildings. The State of California currently has guidelines for low emitting materials and furnishings for office buildings (5). The trade organization for the commercial furniture industry, BIFMA International, was approached by the U.S. General Services Administration to discuss an effort to harmonize the emissions testing requirements. A single test protocol with wide acceptance would reduce the effort required by purchasing organizations to prepare specifications, reduce duplication of testing, and improve the quality of information available to the purchasing community.

1.3 Stakeholder Process

RTI convened a meeting of those interested in the Indoor Air ETV pilot in Washington, D.C. on December 16, 1996. Penny Hansen, head of the EPA's ETV program and Les Sparks, project officer for the indoor air pilot discussed the background and goals for the EPA program. Dave Ensor presented an overview of RTI's vision for the indoor air pilot. Linda Sheldon from RTI and Marilyn Black from Air Quality Sciences presented issues related to emissions chamber testing such as would be required for commercial furniture. Other testing programs were also discussed. At that time, Brad Miller from BIFMA International said that their industry was willing to work with RTI on this program.

RTI then invited people to participate in a stakeholder group for commercial furniture. Represented groups (in 1999) included:

- Industry - BIFMA International, American Seating Company, Geiger International, Inc., Global Upholstery Co. Limited, Haworth, Herman Miller, Inc., Hon Industries, Inc., Kimball International, Knoll, Inc., Steelcase, Bodycote Technitrol, Teknion Furniture Group
- Buyers - U.S. EPA, GSA
- Government - California Air Resources Board, Canadian National Research Council, U.S. EPA,
- Other - Air Quality Sciences, American Lung Association, Composite Panel Association, NSF International, Underwriters Laboratories

Meetings were held on February 26, 1997, June 18, 1997, September 24, 1997, February 25, 1998 and February 23, 1999. Summaries of these meetings are available on both RTI's web site <http://etv.rti.org> and EPA's ETV web site <http://www.epa.gov/etv/>. The stakeholders discussed issues related to the test protocol. They also received early drafts of the protocol and provided comments back to RTI.

An initial draft protocol was issued in August 1997 and a final draft protocol was issued in August 1998. The 1998 version was used for the testing and can be found in Appendix 1. Changes were made in the protocol based on the verification testing, and a final version was released in August 1999 (6). The test protocol is available on Web sites both at RTI (<http://etv.rti.org/iap/furniture/index.html>) and at the EPA (http://www.epa.gov/etv/05/05_prot.htm).

2.0 Test Program

2.1 Participating Laboratories

Three laboratories participated in the study:

- Air Quality Sciences (AQS)
Marietta, GA
- Enviro-Test Laboratory (ETL)
Edmonton, Alberta
- Research Triangle Institute (RTI)
Research Triangle Park, NC

All three laboratories took part in an EPA performance audit prior to the protocol verification testing. Appendix 4 gives details of this audit. RTI and AQS had taken part in an earlier EPA-sponsored large chamber study where emissions from office equipment was measured (7).

Analysis was performed at all three laboratories, however only two of the laboratories had emission chambers used in the study.

2.2 Test Objectives

The protocol verification test was intended to exercise the protocol prior to final release of the document. This allowed RTI to modify the protocol where necessary while still in draft. Results of emissions from the test chairs are being made publicly available in this report. Interlaboratory and intralaboratory comparisons are presented.

2.3 Test Facilities and Equipment

Emission chambers at two laboratories were used for measuring the emissions from the sample furniture. One chamber was 22.7 m³ (10 x 10 x 8 ft) and was constructed of aluminum and stainless steel. The other chamber was a medium scale environmental chamber measuring 5.9 m³ in volume. This second chamber was smaller than the chamber size specified in the Protocol.

2.4 Test Furniture

Four identical office chairs were ordered through a vendor in Raleigh, NC. The vendor worked with the manufacturer to ensure that all four chairs were manufactured on the same day. The chairs were desk chairs with arms, composed primarily of steel and plastic with nylon fabric. Two chairs were shipped to each of the laboratories whose chambers were used. Standard shipping procedures were used. Even though care was taken so that the chairs were manufactured identically, there is no assurance that the emissions were identical. Two chairs were used in each chamber in an attempt to create quantifiable emissions.

3.0 Test Protocol

3.1 Approach

The test protocol was written by RTI with input and review from the stakeholder group. The draft version used can be found in Appendix 1. The current (final) version (6) was modified, based on this verification testing. RTI followed a test plan developed for the protocol verification testing (8).

The test objects were ordered through a retail distributor, then packaged and shipped to the test laboratory using the manufacturer's routine practices. Acquisition, packaging and shipping were discussed in Appendix A of the draft Protocol. For commercial furniture, Appendix A was specified, and is copyrighted by BIFMA International. Currently, BIFMA is updating the information, thus Appendix A is not included in the final version of the Protocol.

The test used the measurement of emissions of aldehydes and volatile organic compounds (VOCs) from products under conditions designed to simulate product use in the indoor environment. Formaldehyde and total volatile organic compounds (TVOCs) were measured in addition to a range of other aldehydes and individual VOCs. Emissions levels were determined by placing the test objects into a large environmental test chamber under specified test conditions, then measuring chamber air concentrations of aldehydes and VOCs at selected time intervals. Product-specific emission factors were calculated from the chamber air measurements.

Aldehydes in chamber air samples were collected on 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel cartridges. The DNPH-aldehyde derivatives on the cartridges were eluted with acetonitrile then analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. The general procedures outlined in EPA Method TO-11 (9) and EPA Method IP-6A (10) were followed.

VOCs in chamber air samples were collected on sorbent cartridges (tubes). VOCs trapped on the cartridges were thermally desorbed then analyzed by gas chromatography/mass spectrometry (GC/MS). Results of these analyses were used to estimate both individual and TVOC concentrations in chamber air samples. General procedures for the use of sorbent cartridges outlined in EPA Methods TO-1 and TO-17 (9) and EPA IP-1B (10) were followed.

Table 1 provides a list of the VOCs and aldehydes included in the survey. Any additional compounds seen at high levels were also to be reported. The response factor of toluene was used to estimate mass concentration of individual VOCs and the TVOC mass.

Table 1 Potential VOC and Aldehyde Emissions from Office Furniture¹

1-Butanol	Decane
1,1,1-Trichloroethane	Dimethylethanolamine
1,2,3-Trimethylcyclohexane	Dodecane
1,2,4-Trimethylbenzene	Ethanol
2-Butanone	Formaldehyde ²
2-Butoxythanol	Hexanal ²
2-Ethyl-1-hexanol	Hexane
2-Methylhexane	Limonene
2-Methylpropanol	Methanol
3-Methyldecane	Naphthalene
3-Methylhexane	Nonanal
3,7-Dimethyl-1-octanol	Pentanal
4-Ethyltoluene	Phenol
Acetaldehyde ²	Pinene
Acetic acid	Propyl benzene
Acetone	Styrene
Butanal ²	Toluene
Butyl acetate	Undecane
Cyclohexanone	Xylenes
Decanal	

¹ Compounds appearing in >50% of test data.

² Included in list for DNPH method for aldehydes.

Table information provided by Marilyn Black of Air Quality Science.

3.2 Experimental Design

The stakeholder group discussed the merits of designing a test protocol that would require multiple samples to be tested. However, it was decided that the expense was too high when the cost of the office furniture samples and the length of the test were considered. As the protocol does not require multiple furniture samples, the protocol verification test used a single sample (two chairs) in each of two chambers.

4.0 Experimental Program

4.1 Sampling Procedures

Emission samples were taken as specified in the test protocol: aldehydes and VOCs at time 0, 4, 8, 24, 48, 72, 96 and 168 hours. They were collected as discussed in the approach with each laboratory using its own cartridges.

4.2 Measuring Procedures

Environmental conditions (temperature, relative humidity and air flow) were monitored throughout the experiment as specified in the Protocol. This is discussed further in Section 4.5.

4.3 Data Analysis

Analyses of the samples followed procedures discussed in the Approach Section 4.1 of the Protocol. For each sample, the laboratories provided information as requested in the protocol: aldehydes and VOCs found from Table 1 as well as others found in significant quantities. Calculations were made for TVOCs.

4.4 Results

All three laboratories submitted their results to RTI. Laboratories 1 and 2 analyzed both aldehydes and VOCs, while Laboratory 3 analyzed only VOCs. The laboratory reports can be found in Appendices 2, 3 and 4.

For the aldehydes, only one sample per time point was taken at each of the chambers. For chamber A, Laboratory 1 took the measurements found in Table 2. Formaldehyde, acetaldehyde and hexanal are listed in the table as they were reported and specified for measurement by DNPH method in Table 1. Appendix 2, Table 2-5 gives the complete results for Chamber A, Laboratory 1, also using the DNPH method. Formaldehyde data from Chamber B, Laboratory 2 are shown in Table 3 and in Appendix 3, Table 3-2. The highest formaldehyde emission concentration for two chairs was $4.6 \mu\text{g}/\text{m}^3$, found by Laboratory 2 at time of 8 hours in Chamber B. This was below the program minimum detection level (MDL) of $6.3 \mu\text{g}/\text{m}^3$ specified in the Protocol, thus all of the values should be reported as zeros and no further analysis was performed. They are given here for completeness since individual laboratories had lower quantitation levels and reported values above their own thresholds. An irritation threshold for formaldehyde has been estimated at $0.15 \text{ mg}/\text{m}^3$, based on using $0.03 \times \text{RD}_{50}$ (11). The same

reference gives the odor threshold as 1.1 mg/m³. Thus, the values found were significantly less than irritation or odor rates.

Table 2. Aldehyde Emissions from Chamber A

Time	Emission Factor (mg/chair · hr)		
	Formaldehyde	Acetaldehyde	Hexanal
0	BQL ^a	0.32	0.022
4	0.028	0.34	0.032
4 (duplicate)	0.030	0.32	0.026
8	0.042	0.34	0.069
8 (duplicate)	0.026	0.33	0.047
24	0.025	0.33	0.030
48	0.020	0.26	0.070
72	BQL ^a	0.32	0.031
96	0.020	0.34	0.020
168	BQL ^a	0.34	0.065

^a BQL = below quantitation limit of 1.6 µg/m³ (chamber air concentration)

Table 3. Aldehyde Emissions from Chamber B

Time	Emission Factor (mg/chair · hr)
	Formaldehyde
0	0
4	0.013
8	0.014
24	0.011
48	0.007
72	0.007
96	0.008
168	0.008

For the VOC emissions, each laboratory provided information on the spectra they saw at each sampling time. For this protocol verification report, undecane and TVOC are discussed, as these occurred in samples taken from both chambers and analyzed by all three laboratories. Table 4 shows the emission factors found in both chambers. The same data are plotted in Figure 1, with error bars shown that are 40% of the mean value (i.e., the data quality indicator goal). It should be noted that the emissions were very small and any errors represent large percentages of the values. The protocol MDLs are 2 mg/m³ for toluene, *n*-decane, cyclohexane and 1-hexanol. No MDL was given for undecane. The highest chamber concentration of undecane was 0.2 mg/m³ for two chairs. Therefore, although the values given in Table 4 are above the detection or quantitation levels for the individual laboratories, they are below the project MDL, assuming that the MDL for undecane would be similar to the other values.

Table 4. Undecane Emissions

Time Point (hours)	Undecane Emissions Factor (mg/chair · hr)				
	Chamber A	Chamber A	Chamber A	Chamber B	Chamber B
	Lab 1	Lab 2	Lab 3	Lab 1	Lab 2
0	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
4	0.31	0.21	0.23	0.21	0.11
8	0.31	— ^b	— ^b	— ^b	0.10
24	0.22	0.13	0.14	0.06	0.06
48	0.14	— ^b	— ^b	— ^b	0.04
72	0.10	0.06	0.08	0.05	0.05
96	0.07	— ^b	— ^b	— ^b	0.04
168	0.04	— ^b	— ^b	— ^b	0.03

^a ND - not detected

^b no measurement taken

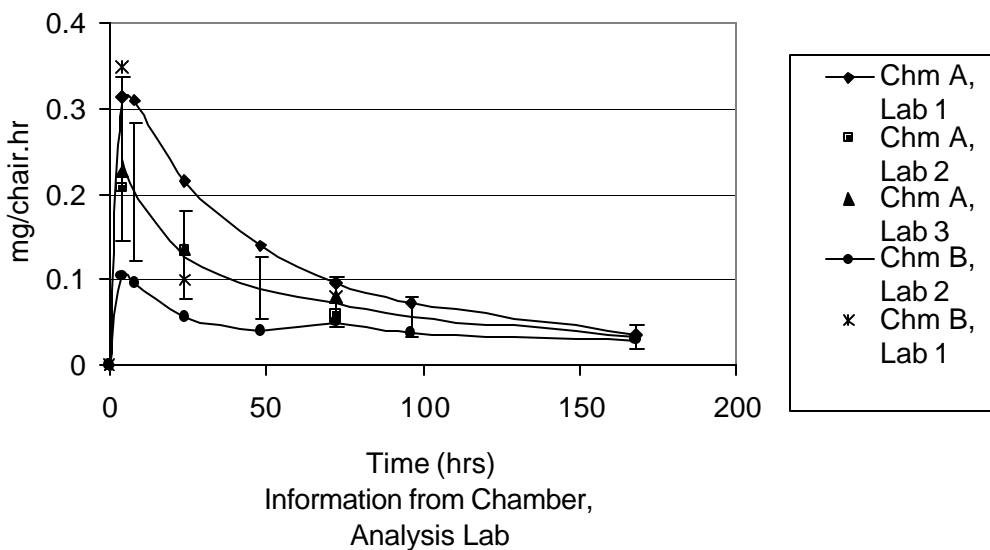


Figure 1. Undecane Emissions

(Error Bars - Target (Goal) - 40% of Mean Value)

Table 5 provides interlaboratory comparisons, including a mean and estimate of standard deviation for each chamber. Because the number of measurements was so small (2 or 3), the range was used as an estimate of population standard deviation σ_{est} , according to Section 2-2.22 of Experimental Statistics Handbook 91, page 2-6 (12). This value was very close to the calculated standard deviation, but for those cases where there are only two values, σ_{est} was larger in most cases. The percentage of means was calculated using the values reported in the table, rather than the values calculated directly from the reported chamber concentrations since only two significant figures were reported in most cases.

Table 5. Undecane Interlaboratory Comparisons

Chamber A

Emission Factors

Time - Hours	Lab 1	Lab 2	Lab 3	Mean	σ_{est}
4	0.31	0.21	0.23	0.25	0.06
24	0.22	0.13	0.14	0.16	0.05
72	0.10	0.06	0.08	0.08	0.02

% of mean

Time - Hours	Lab 1	Lab 2	Lab 3	σ_{est}
4	124%	84%	92%	24%
24	138%	81%	88%	33%
72	125%	75%	100%	30%

Chamber B

Emission Factors

Time - Hours	Lab 1	Lab 2	Mean	σ_{est}
4	0.11	0.21	0.16	0.09
24	0.06	0.06	0.06	0.00
72	0.05	0.05	0.05	0.00

% of mean

Time - Hours	Lab 1	Lab 2	σ_{est}
4	67%	133%	57%
24	97%	103%	5%
72	99%	101%	2%

There were duplicate measurements reported from one of the laboratories, so intralaboratory comparisons were also made as seen in Table 6. Again, σ_{est} was estimated from the range and the percentages were based on values reported in the table.

Table 6. Undecane Intralaboratory Comparison, Chamber A, Laboratory 1

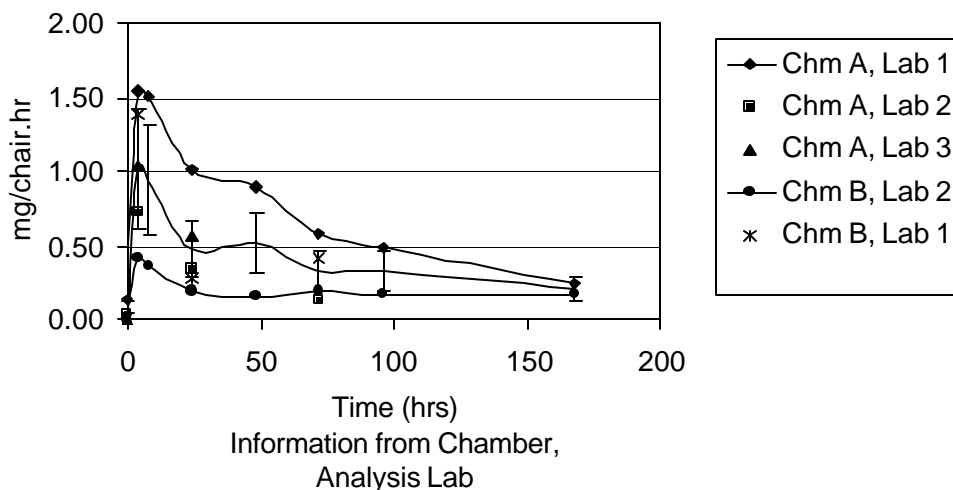
Time Hours	Emission Factor	% Mean
8	0.31	103%
8 Duplicate	0.28	93%
8 Mean	0.30	
8 σ_{est}	0.03	10%
96	0.07	140%
96 Duplicate	0.03	60%
96 Mean	0.05	
96 σ_{est}	0.04	80%

All laboratories reported TVOC measurements, with the values given in Table 7 and Figure 2.

Table 7. TVOC Emissions

Time Point (hours)	TVOC Emissions Factor (mg/chair · hr)				
	Chamber A Lab 1	Chamber A Lab 2	Chamber A Lab 3	Chamber B Lab 1	Chamber B Lab 2
0	0.14	0.04	— ^b	ND ^a	ND ^a
4	1.55	0.72	1.03	1.38	0.41
8	1.50	— ^b	— ^b	— ^b	0.36
24	1.01	0.34	0.57	0.27	0.19
48	0.89	— ^b	— ^b	— ^b	0.15
72	0.58	0.13	— ^b	0.41	0.19
96	0.49	— ^b	— ^b	— ^b	0.16
168	0.25	— ^b	— ^b	— ^b	0.17

^aND - not detected



^b no measurement taken

Figure 2. TVOC Emissions
 (Error Bars - Target (Goal) - 40% of Mean Value)

Table 8 provides interlaboratory comparisons of TVOCs, with σ_{est} calculated from the range.

Table 8. TVOC Interlaboratory Comparisons

Chamber A					
Emission Factors					
Time	Lab 1	Lab 2	Lab 3	Mean	σ_{est}
0	0.14	0.04	– ^a	0.09	0.09
4	1.55	0.72	1.03	1.10	0.49
24	1.01	0.34	0.57	0.64	0.57
72	0.58	0.13	– ^a	0.36	0.4

% of Mean					
Time	Lab 1	Lab 2	Lab 3	σ_{est}	
0	156%	44%	– ^a	100%	
4	141%	65%	94%	45%	
24	158%	53%	89%	89%	
72	161%	36%	– ^a	111%	

Chamber B				
Emission Factors				
Time	Lab 1	Lab 2	Mean	σ_{est}
4	0.41	1.38	0.90	0.69
24	0.19	0.27	0.23	0.06
72	0.19	0.41	0.30	0.15

% of Mean			
Time	Lab 1	Lab 2	Range
4	46%	153%	113%
24	83%	117%	30%
72	63%	137%	67%

^a no measurement taken

Table 9 provides intralaboratory comparisons.

Table 9. TVOC Intralaboratory Comparison
 Chamber A, Laboratory 1

Time	Emission Factor	% Mean
8	1.51	116%
8 Duplicate	1.08	83%
8 Mean	1.30	
8 σ_{est}	0.38	29%
96	0.49	117%
96 Duplicate	0.34	81%
96 Mean	0.42	
96 σ_{est}	0.13	31%

4.5 Routine Quality Assessment

The quality assurance followed both the Protocol (6) and the Quality Assurance Project Plan (13). Data quality indicator goals as defined in Table 10 were established in the Protocol.

Table 10. Data Quality Indicator Goals for Chamber Test Measurements

Parameter	Precision	Accuracy	Completeness
Temperature	±2.0 °C	±0.5 °C	>90%
Relative Humidity	±5.0% RH	±5.0% RH	>90%
Air Flow Rate	±10.0%	±10.0%	>90%
Chamber Air Concentration			
Aldehydes	±40% RSD	±30%	>90%
VOCs	±40% RSD	±30%	>90%

The two laboratories conducting the chamber experiment reported their conditions as shown in Table 11.

Table 11. Comparison of Actual Measurements and Goals

Parameter	Protocol Specification	Chamber A	Chamber B
Temperature	23.0 ± 2.0 °C	22.7 ± 0.06 °C	23.0 ± 2.0 °C
Relative Humidity	50.0 ± 5.0 % RH	51.5 ± 0.9% RH	50.0 ± 5.0 % RH
Air Flow	1.0 ± 0.05 hr ⁻¹	1.05 ± 0.01 hr ⁻¹	1.00 hr ⁻¹

Each laboratory performed QA/QC on its own data. After the data was sent to RTI, additional QA/QC was performed. There was a question with the data from one of the laboratories, and it was asked to reexamine its data. It found a problem – pentane that also showed up on the blanks -- that was then adjusted in the TVOC values.

5.0 Quality Assurance

5.1 Audit of Analysis Laboratories

Under an earlier RTI/EPA study of chemical emissions from office equipment (7), a single copier was tested in several laboratory emission chambers, including both being used for the commercial furniture verification. The

results of that testing showed good comparisons between chambers. Therefore, EPA determined that it would do an audit of the analysis, rather than the chamber operation.

Nancy Adams of EPA designed the audit. She and Roy Fortmann of Arcadis Geraghty & Miller performed the audit. All three laboratories (AQS, RTI, ETL) participated. Samples contained known chemical compounds. The compounds were

- limonene, a ring with unsaturated branched-chain substitution;
- 2-butoxyethanol, an oxygenated alkane;
- o-xylene, substituted aromatic; and
- n-decane., a straight-chain alkane.

These were provided at three levels: high, low and as blanks, but the actual concentrations were unknown. The chemicals were chosen because they represented four classes of chemicals that have been previously identified in commercial furniture.

Each laboratory sent specially prepared sorbent cartridges to EPA for spiking. The reference lab then spiked the tubes and verified the concentration with its own cartridges. The cartridges were returned to the laboratories, who analyzed and reported on their data. Each lab reviewed and verified its own data, but the RTI ETV program did not perform a separate QA function. The auditors then compared results, provided complete results to the individual laboratories and provided feedback on the bias and precision of the procedures. A report was presented at the February 1999 ETV stakeholder meeting and can be found in Appendix 5.

The spiking solvent (methanol) was incompatible with the sorbent used with one lab's sorbent. When the cause of the discrepancy was found, a second set of sorbent tubes was prepared using a different spiking solvent.

6.0 Conclusions/Summary

The *ETV Large Chamber Test Protocol for Measuring Emissions of VOCs and Aldehydes* was verified using two chairs placed in each of two chambers. Three laboratories participated in the analysis. Samples were taken and analyzed for both VOCs and aldehydes. The test showed that the emissions from chairs were very low, as expected, with the concentrations of both VOCs and aldehydes at or below the program MDLs. The two chambers were able to meet the environmental DQI goals. RTI recommends that additional use be made of the protocol before adjustments of the DQI goals are attempted.

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