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Determination of Formaldehyde and Toluene Diisocyanate Emissions from Indoor Residential Sources

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

Determination of Formaldehyde and Toluene Diisocyanate Emissions from Indoor Residential Sources

Final Report

Contract Number 93-315

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ABSTRACT

Building materials and consumer products found in California residences were subjected to chamber testing to determine the emission rates of formaldehyde (HCHO) and of toluene diisocyanates (TDI). The emissions of formaldehyde were determined from bare urea-formaldehyde (UF) and phenol-formaldehyde (PF) wood products, UF wood products with vinyl, paper, and other coatings, and from decorative laminates, permanent press fabrics, fiberglass insulation, paper goods, paints, cosmetics, and acid-cured coatings. Other compounds determined along with HCHO included acetaldehyde, propionaldehyde, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). A separate set of polyurethane (PU) products, including PU foam carpet padding, furniture cushions, sheet foam, PU varnishes, caulks and sealants, and a commercially-applied water stop product for concrete, were tested for emissions of toluene diisocyanate (TDI).

Testing of products for emission of formaldehyde and the other target carbonyl compounds was conducted simultaneously at two sets of test conditions, using twin 1.43 m^3 chambers. Both an integrated method and a sensitive real-time continuous method for formaldehyde were used. Quality assurance efforts included duplicate sampling with the integrated method, performance of confirmatory analyses by an outside laboratory, comparison of the real-time and integrated results for formaldehyde, duplicate chamber tests on 10 products, and testing of two products in both large and small chambers to assess comparability. Formaldehyde emission rates ranged from about 1 to over 1,000,000 $\mu g/m^2/hr$. Among the dry products tested, bare UF wood products showed the highest formaldehyde emissions, followed by new permanent press fabrics, then by coated UF products, bare PF products, insulation, and decorative laminates, with no significant emissions from paper goods. Emissions from permanent press fabrics decreased by 60 percent after a single washing. An acid-cured floor finish and an acid-cured coating on cabinet doors exhibited high formaldehyde emissions. Cosmetics exhibited relatively high initial formaldehyde emissions, but low total amounts of emissions because of the small area of use. HCHO emissions greatly exceeded those of acetaldehyde and propionaldehyde from nearly all products; no emission of MEK or MIBK was observed from any product.

The PU products were screened under elevated temperature and chamber loading conditions, using both an integrated method specific for TDI and a continuous but non-specific real-time monitor for isocyanates. The screening procedure was sensitive to TDI emission rates corresponding to indoor lifetime cancer risks from TDI of about 1×10^{-6}. None of the products normally found in residences showed a positive response in the screening tests. Only the commercially-applied water stop product, containing up to 4 percent TDI by weight, gave a positive response in the screening test. Final testing of that product at realistic temperatures showed initial TDI emission rates of about 300,000 $\mu g/m^2/hr$, with emissions lasting only one hour or less.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

Page

LIST OF TABLES

Page

LIST OF FIGURES

SYMBOLS AND ACRONYMS

A	product surface area, m^2
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BA	San Francisco Bay Area
C	concentration, in $\mu g/m^3$
C_{max}	maximum concentration during emission from a wet product
CAAA	Clean Air Act Amendments of 1990
CARB	California Air Resources Board
CPSC	Consumer Product Safety Commission
DNPH	2,4-dinitrophenyl hydrazine
DQO's	data quality objectives
E or ER	emission rate in $\mu g/m^2/hr$
E_o	initial emission rate in $\mu g/hr$
EPA	U.S. Environmental Protection Agency
GC	gas chromatography
HAPs	hazardous air pollutants
HCHO	formaldehyde
HPLC	high performance liquid chromatography
IP	industrial particleboard
L	product loading in m^2/m^3
L/min	flow rate in liters per minute
MDF	medium density fiberboard
MDI	methylene diphenyl diisocyanate
MEK	methyl ethyl ketone
MFR	manufacturer supplied product for testing

SYMBOLS AND ACRONYMS (Continued)

MIBK	methyl isobutyl ketone
N	air exchange rate (hr^{-1})
NBPA	N-(4-nitrobenzyl)-N-n-propylamine hydrochloride
NPA	National Particleboard Association
ORNL	Oak Ridge National Laboratory
OS	outside the state of California
PF	phenol-formaldehyde product
PP	permanent press fabrics
PU	polyurethane product
PVC	polyvinyl chloride
Q	air flow rate
QAPP	Quality Assurance Project Plan
R_o	initial emission rate of a wet product, in $\mu g/m^2/hr$
RET	retail vendor
RH	relative humidity
RSD	relative standard deviation
SAC	Sacramento area
SC	Southern California
t	time
t_{max}	time of occurrence of maximum concentration during emission from a wet product
T, E	Typical and Elevated test conditions
TAC	toxic air contaminant
TDA	toluene diamine
TDI	toluene diisocyanate
TD-80	mixture of 80% 2,4-TDI and 20% 2,6-TDI

TABLE OF CONTENTS (Continued)

SYMBOLS AND ACRONYMS (Continued)

TLD-1	model number of continuous TDI monitor
U	total estimated uncertainty
UF	urea-formaldehyde product
UV	ultraviolet light
V	chamber volume, in m^3
VOC's	volatile organic compounds
WH	wholesale vendor

1.0 SUMMARY AND CONCLUSIONS

1.1 Objectives and Study Design

Formaldehyde (HCHO) is one of the most intensively studied indoor air pollutants. It is a common component in building materials and numerous consumer products, and may be released to indoor air. Formaldehyde is of interest because of its status as a suspected human carcinogen and an irritant. Reconstituted wood products (e.g., particleboard, plywood) made with urea-formaldehyde (UF) resins have previously been identified as major sources of formaldehyde to indoor air. However, as production changes have reduced the emissions of such products, attention has shifted to the numerous other products that may also be sources of HCHO in homes. Emissions from those products must also be considered to adequately establish the extent and causes of human exposures to HCHO indoors. Unfortunately, although many studies have addressed the emission of HCHO from individual products, very few have addressed a realistically broad set of products (Pickrel, et al., 1982,1983,1984).

Toluene diisocyanate (TDI) is a carcinogenic compound and a potent irritant and sensitizer, used in the manufacture of some polyurethane (PU) products, generally as a mixture of its 2,4- and 2,6-isomers. Despite its toxicity, TDI has received little attention as a potential indoor air contaminant, largely because of its expected reactivity and consequent minimal concentrations in finished PU products. Although PU products are common in homes in the form of carpet padding, furniture cushions, wood varnishes, caulks and sealants, very few prior emission data are available on TDI-containing products (CPSC, 1993; Mahanama and Hodgson, 1995).

The overall goal of this study was to provide HCHO and TDI emission rate data on products currently used in California homes. Those data can then be used to assess the contributions of the various products to human exposures in homes.

The specific objectives of this study were:

1. To select and obtain from the California market samples of commonly used materials or products that may emit HCHO or TDI to indoor residential air.
2. To determine the relative importance of diverse materials and products as TDI sources, by appropriate screening tests.
3. To determine the emission rates of the known major and potential TDI and HCHO sources, under typical and exaggerated indoor conditions, by chamber tests conducted with appropriate conditions and sampling/analytical methods.
4. To report the emission rate results along with sufficient supporting data to allow use in models that predict indoor concentrations and exposures.

Three additional features of this study are noteworthy. First, the chamber testing for HCHO emissions also included four other carbonyl compounds listed in the 1990 U.S. Clean Air Act Amendments or in the California Proposition 65 toxic chemicals list (i.e., acetaldehyde, propionaldehyde, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK)). These chemicals were included because they could readily be determined along with HCHO. Second, a Battelle-developed real-time continuous monitor for HCHO was used in all HCHO emission tests. The monitor was used to confirm achievement of steady state emissions, to follow the rise and fall of HCHO emissions from wet products, and as a check on HCHO levels determined by an integrated sampling method. Third, the comparability of results from this study to those from large chamber tests performed routinely by the wood products industry was assessed for two UF wood products, by testing simultaneously in both large and small chambers.

Testing for emissions of HCHO and the other carbonyl compounds was conducted in twin 1.43 m^3 chambers, each maintained at a different set of test conditions that represented those expected in California homes. The "Typical" conditions were temperature = 70°F, air exchange rate = 1.0 per hour, and 50 percent relative humidity. The "Elevated" conditions were temperature = 80°F, air exchange rate = 0.3 per hour, and 50 percent relative humidity. These two sets of conditions were chosen to bracket likely conditions in California homes, not expressly to investigate the effects of temperature and air exchange on emission rates. Testing on each product was carried out simultaneously in the two chambers. For 10 products duplicate samples were obtained and tested, to assess the reproducibility of the test procedures. Two other products were also tested both in the twin chambers and in a 17.3 m^3 chamber, to assess comparability with the standard large chamber test procedures conducted by the wood products industry (ASTM, 1990a). Both the continuous HCHO monitor and an integrated method that determined all five target carbonyl compounds were used in all tests. Emissions from dry products such as particleboard, plywood, paper, etc., were determined at steady state conditions (i.e., emissions steady with time). For products that underwent a drying or curing stage after application (i.e., emissions changing rapidly with time), the real-time monitoring data were fitted using the curve-fitting equation of Colombo et al. (1990), to allow calculation of the initial and final emission rates and the total amount of HCHO emitted over the test period.

Excellent performance was achieved with the real-time continuous HCHO monitor. In a comparison of real-time and simultaneous time-integrated HCHO results, a linear regression showed Real Time HCHO = 0.992 (Integrated HCHO) + 0.14 ppbv, with $r^2 = 0.973$, for 385 data pairs ranging from 0.3 to over 1,800 ppbv. The monitor provided rapid measurements of changing HCHO levels during application and drying of wet products by sampling alternately from the two test chambers at 5 minute intervals. The resulting emission curves were easily modelled to determine initial emission rates and total emitted quantities of HCHO.

Good agreement was found between the results of simultaneous tests in the 1.43 m^3 chambers and in a 17.3 m^3 chamber at the same product loading rates. For a sample of 5/8 inch particleboard underlayment, an emission rate of 182 $\mu g/m^2/hr$ was found in the small chamber, and a rate of 213 $\mu g/m^2/hr$ was found in the large chamber. For a sample of 3/4 inch hardwood plywood, the corresponding emission rates were 13.0 $\mu g/m^2/hr$ and 10.4 $\mu g/m^2/hr$, respectively. These results confirm the comparability of the present results to those obtained in standard large chamber tests performed routinely by the wood products industry. This extends the usefulness of the present study by validating the data reported here against the large body of data from tests by industry.

Since little was known about potential TDI emissions, PU products were initially screened for TDI release as a way to streamline testing and reduce costs. Screening tests for TDI were conducted at elevated temperature (120°F) and with exaggerated product loadings in a 9 L glass chamber. Both an integrated sampling/analysis method that specifically determined the two TDI isomers, and a continuous monitor sensitive to isocyanates in general, were used. The screening procedure was designed to be sensitive to TDI emission rates that would correspond to estimated indoor lifetime cancer risks from TDI of about 1×10^{-6} to 1×10^{-5}. Products that gave a positive screening result were then subjected to final tests at realistic temperatures and lower product loading rates. The TDI emission curves determined in the final tests were also modelled using the approach of Colombo et al. (1990).

Specific summaries and conclusions related to each of the study objectives are presented below.

1.2 To select and obtain from the California market samples of commonly used materials or products that may emit HCHO or TDI to indoor residential air.

A survey of production and use information and previous emission tests on both HCHO and TDI products was conducted at the start of this study. That survey was the basis for selection of product types for testing. The aim of product selection was to choose a realistic cross-section of samples from all of the product types likely to emit HCHO or TDI in California homes. The selection of samples was weighted toward those products that were likely to be the most important indoor sources. To accomplish that, information was evaluated on the emission rates of products, the amounts of different products sold by manufacturers, the amounts found in various parts of a home, and the likely severity of a person's exposure to any emissions. More samples were chosen of products ranking high on these factors than of products ranking low, however, a wide variety of products were included, and some products were chosen in part simply because there was very little previous information on their emission rates. The products selected were not a statistically representative sampling of the materials and products present in California homes, nor were they intended to be. Rather, the products selected were a carefully chosen, diverse set of samples characteristic of what a California resident would use, purchase, or be exposed to in his home.

The process of actually obtaining the samples for testing was also designed to be realistic. The great majority of samples were purchased in California from common retail outlets, or from wholesale outlets that sell materials to the building industry or to furniture manufacturers. Materials were obtained at normal prices, in common sizes, and with the usual packaging, and atypical samples were avoided. Product samples were purchased at intervals between May 1995 and February, 1996, predominantly in the Los Angeles, Sacramento, and San Francisco Bay regions of the state. For some products more than one sample was obtained. In such cases the samples were obtained from different vendors, usually in different parts of the state. Care was also taken to obtain the most common brands of products; in some cases that meant obtaining a sample of more than one brand of the same type of product. For certain wood products, samples were obtained from both domestic and foreign (i.e., Mexican) manufacturers, since both products are present in the California market. The end result of this process was a set of samples that would be easily recognizable by California residents as products commonly found in homes.

In addition, some products were obtained directly from manufacturers serving the California market. HCHO products obtained in that way included cabinet doors made of medium density fiberboard (MDF), with and without a manufacturer-applied acid-cured finish; mobile home decking (flooring) with and without a waterproof coating normally applied in kitchen and bath areas; industrial particleboard with and without paper and vinyl laminate coatings, commonly used in shelving, furniture, and cabinets; and a commercially-applied two-coat acid-cured finish for residential wood floors. For TDI, the one product obtained that way was a commercially-applied water stop product for concrete. This product is applied to concrete to prevent water leakage or to stop active leaks. It is not normally available to the public, and is generally used in commercial rather than residential construction, but was obtained as a useful benchmark product because of its known TDI content. These products allowed comparisons that would not have been achievable otherwise. Not all of the common PU products in the California market were found to contain TDI, but to assure representative coverage of the products common in residential use a variety of PU products were purchased, even when it was not confirmed that they contained TDI.

The products tested for HCHO and other carbonyl emissions included 19 samples of bare UF wood products, 14 of coated UF wood products, 3 of decorative laminates, 3 of fiberglass insulation products, 4 of permanent press fabrics, 4 of bare phenol-formaldehyde (PF) wood products, 3 paper products, 2 latex paints, 3 cosmetics products, and the base and top coats of the acid-cured floor finish. Products tested for TDI emission included 9 samples of PU foam carpet padding, 10 of mattress foam, sheet foam, or furniture cushions, 12 of PU varnishes for wood, 2 of water sealers for concrete and 3 of water sealers for general surfaces, one PU caulk, one mastic adhesive, and the commercially-applied water stop product for concrete. A summary table is included in Section 4.1.2 of this report that lists all of the samples tested, along with their typical uses in a home and information on their origin.

1.3 To determine the relative importance of diverse materials and products as TDI sources, by appropriate screening tests.

Screening tests were conducted on all the TDI products obtained, either alone or in groups of similar products. The overall strategy was to use extreme conditions to maximize any TDI emissions, so that the likelihood of identifying emitting products was increased. The screening test procedures allowed detection of emission rates as small as 0.018 $\mu g/m^2/hr$ of TDI from dry products, and as small as 0.22 $\mu g/m^2/hr$ from wet products, both adjusted to room temperature. The minimum detectable emission rates differ for the two types of products because of slightly differing procedures for the screening tests. These minimum detectable rates take into account the loss rate of TDI to the chamber walls, which was determined in chamber characterization tests prior to the screening tests. The sensitivity of the screening tests was such that the minimum detectable emission rates correspond to indoor TDI levels associated with lifetime cancer risks of less than about 1×10^{-6}.

None of the common residential PU products produced a detectable TDI emission in any of the screening tests. Because the isocyanate monitor used was not specific for TDI, the absence of response in the screening tests also indicates that emissions of any other isocyanates present must be low, i.e., below about 0.76 $\mu g/m^2/hr$, assuming equal response for all isocyanates. This result is of interest because other isocyanates are increasingly being used in place of TDI in many products. Only the commercially-applied water stop product produced a positive response in the screening tests, and was subsequently tested further to obtain quantitative emission data.

1.4 To determine the emission rates of the known major and potential TDI and HCHO sources, under typical and exaggerated indoor conditions, by chamber tests conducted with appropriate conditions and sampling/analytical methods.

The main results of HCHO testing in this study are summarized in Tables 1 and 2, which show the HCHO emission results from dry and wet products, respectively. All emission rates are in $\mu g/m^2/hr$. Both Tables 1 and 2 show results from both the Typical and Elevated test conditions. Table 1 shows the dry product emission rates determined after 20 to 24 hours in the test chambers. Table 2 shows the initial emission rate at the time of product application, the final emission rate (15-22 hours after application), and the total amount of HCHO released, for each wet product. Products are numbered for clarity in Table 1. Also indicated in the tables are those products for which duplicate tests were performed; for brevity only the average emission rate in each test condition is shown here.

Table 1 shows that emission rates of dry products varied widely both within and between product categories, with the general ranking bare UF wood products > new permanent press fabrics > coated UF wood products, decorative laminates, fiberglass products, and bare PF wood products > paper goods. The uncertainty in individual emission rates in Table 1 is such that results that differ by about 40 percent or less are not significantly different. The ranking of product categories is based on the range and median of all values in each category, and differences between some categories were large relative to the uncertainties

TABLE 1. SUMMARY FORMALDEHYDE EMISSION RATES FROM DRY PRODUCTS ($\mu g/m^2/hr$)

No.	Product Group and Identity	Test Conditions Typical	 Elevated	
	Bare Urea-Formaldehyde (UF) Wood Products			
1	1/4" UF particleboard	1580	1170	
2	5/8" Particleboard underlayment	508	393	
3	Bare MDF cabinet doors	364	535	
4	3/4" Medium density fiberboard (MDF)	258	254	
5	5/8" Industrial particleboard (I.P.)	237	311	
6	5/8" MDF	272	352	dup
7	1/4" Prefinished hardwood plywood wall panelling	181	140	
8	5/8" Mobile home decking	174	241	
9	1/2" Hardwood veneer plywood	170	154	
10	3/4" Industrial particleboard	145	156	dup
11	5/8" Industrial particleboard	144	168	dup
12	3/4" Industrial particleboard	147	153	
13	5/8" Particleboard underlayment	119	134	
14	3/4" Industrial particleboard	117	177	
15	5/8" Industrial particleboard	104	110	
16	1/2" Stock hardwood plywood	103	147	
17	1/4" Stock hardwood plywood	101	71	
18	3/4" Stock hardwood plywood	71	67	dup
19	3/4" Stock hardwood plywood	8.6	6.8	
	Coated UF Wood Products			
20	MDF cabinet doors w. white acid-cured finish	460	1300	
21	5/8" I.P. black textured non-recoatable paper laminate	55	120	
22	5/8" I.P.recoated white ice paper waterborne topcoat	48	83	
23	5/8" Mobile home decking w. waterproof coating	35	52	
24	3/4" I.P. melamine laminate (imported)	23	65	dup
25	5/8" I.P. w. red cherry paper laminate	26	29	
26	3/4" I.P. melamine laminate (imported)	21	18	
27	5/8" I.P. w. rigid vinyl bonanza oak laminate	16	31	
28	5/8" I.P. vinyl coated	8.6	2.9	
29	Interior door w. particleboard core	7.0	15	
30	5/8" I.P. vinyl coated	3.4	1.5	dup
31	3/4" I.P. melamine laminate (domestic)	4.6	2.7	dup
32	5/8" I.P. w. electron-beam cured acrylic coating	< 2.7	5.7	
33	3/4" I.P. melamine laminate (domestic)	< 2.7	4.6	
	Permanent Press Fabrics			
34	Permanent press draperies	215	173	
35	Permanent press shirts (unwashed)	107	77	
	" " " (washed once)	42	33	
36	Permanent press shirts	45	55	
37	Permanent press sheets	42	53	
	Decorative Laminates			
38	20 mil cabinet liner decorative laminate	51	59	
39	50 mil rigid general purpose laminate	14	15	
40	50 mil general purpose laminate	4.1	6.1	dup

TABLE 1. (Continued)

No.	Product Group and Identity	Test Conditions Typical	 Elevated
	Fiberglass Products		
41	Fiberglass R-19 roll insulation	32	31
42	Fiberglass ceiling tiles	23	18
43	Fiberglass ceiling tiles	16	11
	Bare Phenol-Formaldehyde (PF) Wood Products		
44	1/4" Perforated PF hardboard	9.2	9.5
45	3/4" Softwood plywood	8.0	6.9
46	3/4" Oriented strandboard	6.8	16
47	3/4" Softwood plywood	4.1	13
	Paper Products		
48	Paper grocery bags	< 0.5	0.7
49	Paper towels	< 0.6	< 0.2

Typical: Results obtained in the chamber held at 70 F, 50 % RH, 1.0 air change per hour.
Elevated: Results obtained in the chamber held at 80 F, 50 % RH, 0.3 air change per hour.
Test results indicate steady state emission rates after 20 to 24 hours in the test chamber.
dup: Results shown are average of rates determined in duplicate chamber tests.

TABLE 2. FORMALDEHYDE EMISSION RESULTS FROM WET PRODUCTS

Product	Test Condition(a)	Initial HCHO Emission Ro, $\mu g/m^2/hr$	Final HCHO Emission $\mu g/m^2/hr$	Total HCHO Emitted, μg(b)
Lower quality latex paint	T	591(c)	9.0(c)	698(c)
	E	648(c)	8.8(c)	559(c)
Higher quality latex paint	T	326	9.8	901
	E	494	5.3	611
Wallpaper	T	691	27	1,689
	E	--	--	--
Fingernail hardener	T	215,500(c)	298(c)	855(c)
	E	323,500(c)	435(c)	719(c)
Nail polish	T	20,700	--	53.7
	E	62,600	--	52.8
Commercially applied floor finish				
Base coat	T	1,050,000	10,800	7,780
	E	1,247,000	17,100	9,100
Top coat	T	421,000	4,660	5,950
	E	799,000	13,600	7,500

(a) T = Typical conditions, E = Elevated conditions.
(b) Test duration 22 hours, except lower quality latex paint 18 hours; wallpaper 15.5 hours, nail polish 10.5 hours.
(c) Value shown is average of duplicate tests.

in individual data. Thus bare UF wood products and permanent press fabrics clearly exhibited generally higher emissions, and paper goods lower emissions, than the other product categories. These emission rankings are on a per unit area basis (i.e., $\mu g/m^2/hr$), and it must be noted that the actual emissions from a product in a home depend not only on its emission rate, but also on how much exposed surface area of the product is present in the home. The highest emitting dry products were the 1/4" UF particleboard (product 1 in Table 1) and the MDF cabinet doors with a commercially-applied acid-cured coating (product 20). Product 1 was an inexpensive product, made by a less rigorous process than that used to make particleboard for furniture and flooring. As a result, it did not meet HCHO emission standards pertinent to those other common products (ANSI, 1993).

Comparison of the bare UF and coated UF categories indicates that several surface coatings substantially reduce the HCHO emission from bare UF materials. The lone exception was the MDF cabinet doors with acid-cured coating, which had higher emission rates than identical doors without the coating (product 3).

Although exploration of temperature and air exchange rate effects on HCHO emission was not a goal of this study, a notable feature of the results in Table 1 is that emission rates under Elevated conditions were usually quite similar to those under Typical conditions. The median Elevated/Typical ratio for all emission rates in Table 1 was 1.08, and the average was 1.36. This observation is due to the counteracting effects of the higher temperature in Elevated conditions (which tends to increase emissions) and the lower air exchange rate (which tends to restrict emissions, due to higher chamber HCHO concentrations at steady state). As a result, the HCHO emissions of many products are relatively constant over the range of indoor conditions in this study.

Direct product-to-product comparisons can be made for only a few dry products, one set of which is the manufacturer-supplied coated/uncoated MDF cabinet doors noted above. In addition, products 21, 22, 25, and 27 are of the identical particleboard as product 5 (Table 1). Comparison of those products confirms that paper and vinyl coatings reduce HCHO emissions by from 60 to over 90 percent. A similar reduction of about 80 percent is evident from comparing the waterproofed mobile home decking (product 23) versus identical bare decking (product 8). Finally, permanent press shirts (product 35) showed a 60 percent reduction in HCHO emission after a single washing. These emission differences are all substantial, even when the uncertainties in the emission results are considered.

Table 2 shows that both components of the commercially applied floor finish were high emitters of HCHO, in terms of both emission rates and total amount emitted during the test period. Fingernail hardener and nail polish also showed high initial emission rates. (A "formaldehyde-free" nail hardener was also tested and found to emit no detectable HCHO.) Latex paints and wallpaper emitted significant total amounts of HCHO, despite relatively low initial emission rates. This result is due to the product loadings used: for paints and wallpaper the product loading was 1.04 m^2/m^3, whereas for the cosmetics and floor finish the loadings ranged from 0.0047 to 0.0084 m^2/m^3. An unrealistically low loading of 0.0047 m^2/m^3 was required for the floor finish, to keep maximum HCHO concentrations in the chambers within the normal range of the real-time monitor (i.e., below about 2 ppmv). The final emission rates shown in Table 2 are generally only a few percent of the corresponding initial rates, and with the exception of those for the floor finish are comparable to the emission rates found from dry products (Table 1).

Acetaldehyde and propionaldehyde emissions were detected from some products, but at rates far below those of HCHO. The maximum acetaldehyde emission rate was 56 $\mu g/m^2/hr$, and that of propionaldehyde 18 $\mu g/m^2/hr$. Both were found with bare PF wood products. No emission of MEK or MIBK was detected in any test.

Emission rate results for TDI products were limited to those for the commercially-applied concrete water stop product, which produced a large positive response in the screening tests. That product was subjected to final tests, in duplicate at 70 °F and once at 80 °F. At 70 °F, initial emission rates of 319,000 $\mu g/m^2/hr$ and 257,000 $\mu g/m^2/hr$ were determined, averaging 288,000 $\mu g/m^2/hr$, and the total emitted amounts of TDI in the two tests were 35 and 38 μg. TDI emissions at that temperature became undetectable within about one-half hour. At 80 °F, an initial emission rate of 360,000 $\mu g/m^2/hr$ was determined, and a total of 179 μg of TDI was emitted in about one hour before emissions became undetectable. These total emitted amounts are about 1 percent, and about 5 percent, respectively, of the total TDI content of the samples used.

The TDI content of the water stop product was up to 4 percent by weight. Although not of direct significance for residential use, this product may be a useful benchmark for estimating TDI emissions from other products. Clearly this product has the potential to cause substantial TDI exposures to those using or applying the product.

1.5 To report the emission rate results along with sufficient supporting data to allow use in models that predict indoor concentrations and exposures.

The emission rates for the tested products are presented in this report along with the chamber test conditions and extensive information on the reproducibility and uncertainties of the results. In addition, Appendix A includes data on actual product loading rates in homes for many products. Together these data are directly applicable to modelling of multiple sources of HCHO indoors.

Calculation of the total measurement error in the determination of the HCHO emission rates gave a result of 12.3 percent. The variability of emission rates determined for duplicate samples was larger than this value, indicating that sample-to-sample variability plays a substantial role in the overall variability of HCHO emission results.

The rates of HCHO emission from wood products such as particleboard and plywood in this study were generally in the low end of results reported for such products in most previous studies. This is not unexpected, since changes in production methods have substantially reduced the amount of excess formaldehyde present in such products. Furthermore, mandatory and voluntary HCHO emission standards now exist for some wood products. Industry sources report that nearly all currently produced material meets those standards, and that statement is borne out by this study for nearly all the wood products tested. This study also confirmed that a variety of surface coverings are effective at reducing HCHO emission from bare wood products. For many of the other products tested in this study (laminates, fabrics, fiberglass products, paints, cosmetics, etc.), very few previous data exist with which to make comparisons. The present data generally compare well with the few previous results, and comprise an important addition of high quality emission data for these products.

The TDI results reported here indicate that indoor emissions of TDI from common products are negligible, and thus that modelling of indoor TDI sources is probably not necessary. However, the emission characteristics of the commercially-applied water stop product may be valuable as a basis for estimating TDI emissions from other products.

1.6 Consumer Perspective on Results

Several results of this study may be valuable to California consumers who wish to minimize their residential exposure to HCHO and other carbonyls. First, the use of bare composite wood products should be avoided, even in enclosed areas such as cabinets. The bare wood products for which HCHO emission standards apply almost always met those standards, but this study showed that paper, vinyl, acrylic, or decorative laminate surface coverings on those products sharply lowered HCHO emissions. Second, the emission characteristics of wood products may vary, probably because of differences in manufacturing, storage, and the time between manufacture and purchase. Differences in HCHO emission rates are generally not readily apparent from the appearance of products at the point of sale. However, bare wood products which meet the manufacturers' voluntary emission standards can generally be identified from imprinted labelling on the product. Very low HCHO emissions may be achieved by using products that are made with PF resins. Residential exposure can also be lowered by using cosmetics, paints, and other products with ample ventilation, especially during the application stage. Washing permanent press fabrics before use greatly reduces HCHO emissions. These products may emit HCHO for shorter time periods than do wood products, but the potential for exposure is significant because of the way in which the products are used.

The screening tests in this study showed no detectable emission of TDI from common polyurethane products. Nevertheless, as with all chemicals, caution is recommended in using PU products such as varnishes, caulks, and sealants. Commercially applied products that contain TDI may emit TDI into the air for relatively short periods after application, but those products are not ordinarily available to consumers.

2.0 RECOMMENDATIONS

2.1 Long-Term HCHO Emission Rates

The present study determined the emission rates of HCHO and other compounds from numerous products, under conditions simulating the way in which those products would enter a residence. However, the emission rates determined must be considered to represent initial indoor rates. Further testing would be valuable to determine the long-term decay of HCHO emissions from these products. Among the products for which long-term emission data would be most valuable are unwashed permanent press fabrics (such as draperies), cabinets and furniture that have acid-cured coatings, and the commercially-applied acid-cured floor finish. The latter two products, while not directly used or applied by a resident, may contribute substantially to indoor formaldehyde levels when new, based upon their emissions in the present tests. The rates at which emissions from these products decline will have a strong effect on their overall contributions to indoor exposures to formaldehyde.

2.2 Realistic User Activity Testing

For several of the products tested in this study the extent of formaldehyde emission, and the severity of user exposure, depend on the behavior of the user during use of the product. Examples include cosmetics (fingernail hardeners and polishes), paints, and wallpaper. With these products emissions occur in close proximity to the user, rather than into the bulk volume of the residence. It is recommended that realistic testing be conducted of the emissions and user exposures from these products. Such testing should involve measurements with a rapid time response, preferably both in air in the test room and in the breathing zone or actual breath of the subject.

2.3 Modelling of Multiple Indoor Sources

The emission rates of formaldehyde determined in this study cover a wide range, representing the actual variety of emission characteristics of products found in a residence. The continuous emissions from dry products such as building materials clearly differ from the episodic and rapidly changing emissions from wet products such as cosmetics or paints. To assess the relative impacts of these widely varying source types and strengths on indoor air quality, modelling is needed that includes a realistic simulation of these diverse source characteristics. Inclusion of combustion sources not within the scope of this study, such as gas ranges and tobacco use, would also be necessary for complete evaluation of indoor formaldehyde sources.

2.4 TDI Surface Chemistry

This study and previous studies have shown the tendency for TDI to adsorb on common surfaces. Such adsorption may minimize any potential human exposure to TDI by inhalation, but may also lead to exposure to TDI or its reaction products on surfaces or in house dust. At present, little is known about the chemical fate of TDI on surfaces. An investigation for the presence of TDI or likely reaction products (e.g., toluene diamine, TDA) on common surfaces would be of interest. Laboratory testing in controlled conditions, followed by sampling of realistic surfaces, would be a reasonable approach.

2.5 Listing of TDI Isomers as Toxic Air Contaminants

Although the 2,4-isomer of TDI is listed as a Group I Toxic Air Contaminant by the California Air Resources Board, the 2,6-isomer is not listed. This study confirmed previous results from workplace environments showing that most of the TDI emitted to air is the 2,6-

isomer, even though the 2,4-isomer predominates in the original product formulation. Given the apparent tendency of 2,6-TDI to be less reactive and more readily emitted, it seems probable that 2,6-TDI will also dominate personal exposures to TDI in air. As a result, it is recommended that the 2,6-TDI isomer be considered for listing as a Toxic Air Contaminant.

3.0 INTRODUCTION

3.1 Background

Numerous studies have demonstrated that the levels of many toxic chemicals in indoor air are higher than the corresponding levels in outdoor air. Since most people spend the great majority of their time indoors, individual exposure to indoor air contaminants may often be larger than that to outdoor air contaminants. To assess and minimize the exposure of California residents to indoor air pollutants, the California Air Resource Board (CARB) has undertaken a program of Indoor Air Quality/Exposure Assessment. Among the activities in that program are the identification and quantitation of indoor sources of toxic chemicals. The present study addressed indoor sources of formaldehyde (HCHO) and other aldehydes and ketones, as well as indoor sources of toluene diisocyanates (TDI, including both the 2,4- and 2,6-isomers). Both HCHO and TDI may be important indoor contaminants, however the states of knowledge concerning their respective indoor sources are vastly different.

Formaldehyde is arguably the most intensively studied indoor air pollutant. It is known to be released in substantial quantities from materials formerly or currently used in home construction, such as urea-formaldehyde foam insulation, and reconstituted wood products e.g., particle board, plywood, and paneling. The importance of such materials in homes has led to numerous sampling programs in test chambers, and in both mobile and conventional homes, the latter assessing indoor HCHO levels as a function of type of construction, age of the home, season, geographic area, time of day, air exchange rate, etc. Valuable reviews of these studies are provided by (e.g.) Otson and Fellin (1992), and Godish (1988). In general, indoor HCHO levels in new homes have been found to average up to several hundred ppbv (ppbv = 1×10^{-9} v/v, = 1.24 micrograms per cubic meter ($\mu g/m^3$) HCHO), and to decline with increasing age of the home. Direct testing results of HCHO emission rates from construction materials have also been reviewed to evaluate the effects of temperature and humidity on emission rates (Myers, 1984; ASTM, 1990a). Such testing is typically done in laboratory chambers of various sizes. Procedures for such testing are now well established (but not completely standardized) (e.g., NPA, 1983; Tichenor, 1989; ASTM, 1990a), and emission standards for some products are now set on the basis of those tests (e.g., ANSI, 1993, 1994).

Indoor HCHO sources other than construction materials have also been identified. Combustion sources such as gas ranges, kerosene heaters, fireplaces, and tobacco products are substantial indoor sources (Otson and Fellin, 1992). In addition, formaldehyde is among the many toxic chemicals that may be emitted from a variety of consumer products (Pickrell et al., 1983, 1984; Tichenor and Mason, 1988; Otson and Fellin, 1992). However, HCHO emissions from products such as fabrics, paper goods, cosmetics, and fiberglass insulation have not been studied as extensively as those from construction materials. For example, even in the study by Pickrell et al. (1983), which focused on HCHO emissions from a wide range of products, tests were conducted only at 100 percent RH and a constant (and not necessarily realistic) product loading. The subsequent study (Pickrell et al. 1984) evaluated the effects of test conditions, but for only a very few consumer products. There also has been no thorough testing aimed specifically at products obtained from the California market. As a result, much of the HCHO emission information of particular interest to CARB has not previously been obtained. Up-to-date emission data are needed for a variety of consumer products at realistic indoor conditions and loading rates. Independently measured emission data for wood products are also of interest as a check on the emission rates reported from the industry's own testing programs.

For TDI, much less information is available. Like HCHO, TDI is designated as a Group I toxic air contaminant (TAC) under the CARB review program. However, only the 2,4-TDI isomer is listed; the 2,6-isomer is not addressed. The reactivity of TDI in air with water vapor, ozone, ammonia, and other chemicals has been tested, (Holdren et al., 1983, 1984, 1985) but indoor exposure data are lacking. In a previous CARB-supported study, Hodgson and Wooley (1991) compiled information on 47 air pollutants either not yet under review (Category IIB) or having insufficient data on health effects to support review (Category III). Although TDI is known to be used in production of common polyurethane products such as foams, coatings, varnishes, adhesives, and sealants, Hodgson and Wooley found that no data exist on TDI concentrations in air other than in industrial environments, and no data exist on emission of TDI from indoor sources. Thus it is not clear what indoor sources may be most important for TDI, much less what their indoor emission rates are.

The present study was aimed at filling gaps in the information available on indoor HCHO and TDI sources.

3.2 Overall Project Objectives

The overall objectives of this project are:

1. To select and obtain from the California market samples of commonly used materials or products that may emit HCHO or TDI to indoor residential air.
2. To determine the relative importance of diverse materials and products as TDI sources, by appropriate screening tests.
3. To determine the emission rates of the known major and potential TDI and HCHO sources, under typical and exaggerated indoor conditions, by chamber tests conducted with appropriate conditions and sampling/analytical methods.
4. To report the emission rate results along with sufficient supporting data to allow use in models that predict indoor concentrations and exposures.

3.3 Additional Project Features

The emissions testing included four other carbonyl compounds: acetaldehyde, propionaldehyde, methyl ethyl ketone (MEK), and methyl iso-butyl ketone (MIBK), because they could readily be determined along with HCHO. These compounds are of interest because of the potential for their emission from products that emit formaldehyde, and because of their potential toxicity. Acetaldehyde is one of the 189 Hazardous Air Pollutants (HAPs) listed in the 1990 Clean Air Act Amendments (CAAA, 1990), and is also listed as a carcinogen in California's "Proposition 65" chemicals list (Proposition 65, 1991). Propionaldehyde, MEK, and MIBK are all in the CAAA 189 HAPs list. These five target compounds were determined in all testing of products for formaldehyde emission.

Real-time monitoring of formaldehyde, using a Battelle-developed continuous analyzer (Kelly, 1992; Kelly and Fortune, 1994) was carried out during all tests of formaldehyde-emitting products. Use of the monitor was originally planned only for monitoring of "wet" product emissions, i.e., those products that exhibit a peak and subsequent decay in formaldehyde emissions, due to the drying or curing of the product after application. However, real-time monitoring was implemented during all tests to document achievement of steady-state formaldehyde levels in the test chambers, and to allow a comparison to integrated sampling results for formaldehyde.

The comparability of results from this study with those from previous tests by industry or other researchers was also of interest. This issue was addressed in two ways. First, for two wood products emission testing was carried out in both small test chambers and in a standard large chamber procedure (ASTM, 1990a), to allow direct comparison of the present results to those from procedures used by industry. Also, results from previous testing of some product categories were compared to the present test results, to assess the degree of similarity.

4.0 EXPERIMENTAL METHODS

4.1 Product Selection and Handling

The aim of this study was to evaluate the emissions of materials and products found in California residences. As a result, samples were obtained from retail and wholesale sources in California, or directly from manufacturers supplying the California market. Samples were then packaged and shipped to Battelle for testing. The following subsections describe how the samples were chosen, obtained, and handled prior to testing. It must be noted that combustion sources such as gas ranges, heaters, and tobacco products were not included within the scope of this study.

4.1.1 Product Review

Selection of products for testing in this study was based on a review of information about products containing or made from HCHO and TDI. The summary report on that effort is included as Appendix A of this report. The aim of that review was to select a reasonable cross section of samples from all the likely categories of indoor residential HCHO and TDI sources. An extensive information gathering effort was conducted as the basis for product selection, relying on literature surveys and electronic literature searches, reviews of reports and other documents, telephone inquiries to government and industrial representatives, and formal written requests for information.

The selection of samples was weighted, so that more samples were selected from the most common and highest-emitting product groups, and fewer samples from likely less important groups. Weighting of sample selection was made as quantitative as possible, by considering four criteria: (1) market share or quantity of production of the material , (2) extent of use in a home, (3) likely or demonstrated product emission rate, and (4) the potential intensity of user exposure that might result from any emissions. Data pertinent to the first three criteria for HCHO products are listed in Tables 1 to 3, respectively, of Appendix A. The fourth criterion was a qualitative factor relating to the manner of use of the product: for example, proximity of the user to any emissions during application of a paint or cosmetic product could enhance any resulting exposure. Information on all four criteria is summarized for HCHO products in Table 4 of Appendix A. For TDI, no emission rate data exist, so product selection was based on the other three criteria. The available information for TDI products is summarized in Table 6 of Appendix A. A wide variety of products were included, and some products were included in part simply because there were few previous data on their emissions. The products selected were not intended to be a statistically representative sampling of all materials and products sold in California, but rather a carefully chosen, diverse set of samples characteristic of what a California resident would purchase, use, or be exposed to in his home.

4.1.2 Product Acquisition

The samples actually obtained and tested in this study followed the initial sample selections described in Appendix A quite closely, but with adjustments due to unavailability of some samples, changes in product formulations or use, and unexpected opportunities for obtaining other samples.

Nearly all of the products tested in this study were obtained from retail or wholesale sources in California by staff of KKO Labs, of Fremont, California. KKO was retained as a subcontractor by Battelle for this purpose. At Battelle's direction, KKO purchased the required samples, cut purchased materials as needed to sizes appropriate for shipping and testing, sealed all samples by wrapping in plastic film, and shipped the samples to Battelle. The sample sizes shipped by KKO were established by Battelle to achieve the required sample sizes for chamber testing, which in turn were based on the chamber volumes, and on in-home loading rates found in the product selection process (Appendix A). For convenience, wood products and decorative laminates were cut into 2 ft x 2 ft pieces for shipment to Battelle, and then cut down to the slightly smaller sizes needed to achieve the desired loading rates in Battelle's test chambers (see Appendix B). For two wood products, larger than normal quantities were obtained, to allow testing of the products in a large chamber for comparison to the small chamber results. All products purchased in packaged form were kept in their original packaging until shortly before testing at Battelle. Wood and laminate sheet pieces (2 ft x 2 ft) were sandwiched between extra sheets of the identical product before wrapping in film for shipping.

KKO used a Sample Identification Sheet, supplied by Battelle, to document all samples obtained. The form used for HCHO products is shown in Figure 1; that used for TDI products was very similar. Each Sample Identification Sheet was given a consecutive number, and the product obtained was identified by its number from the appropriate product selection listing in Appendix A. The forms include spaces for description of the product, identification of the vendor and manufacturer, product characteristics, sample size, indication of single or duplicate sample, and dates of purchase, shipping, receipt, and testing. A Sample Identification Sheet was enclosed with every sample obtained by KKO.

Samples were obtained at intervals between May 1995 and February 1996, primarily in three areas of the state of California: the Los Angeles Basin, the Sacramento Area, and the San Francisco Bay Area. These areas were chosen to represent densely populated areas of the state in which consumer products and building materials were moving actively through the marketplace. When appropriate, KKO purchased samples directly from common retail outlets, at normal prices, in common sizes, and in the usual packaging. For some materials, such as industrial particleboard and other wood products, it was necessary to contact wholesalers to obtain samples. In all cases, KKO took steps to obtain samples that were representative in terms of emission characteristics. Primarily this was done by avoiding samples that had obviously been exposed, aged, or damaged. For example, in obtaining wood and laminate samples, sheets were obtained from the center of product stacks, rather than from the top. For some product types more than one sample was obtained, from different vendors in different parts of the state. The most common brands of products were obtained, and in some cases that required obtaining more than one brand of the same kind of product. Samples of both domestically- and Mexican-produced laminate-covered particleboard were obtained, since both products are present in the California market.

SAMPLE IDENTIFICATION SHEET FOR CARB PRODUCTS

(To be completed for each product sample obtained, and enclosed with each sample shipped to Battelle. KKO should retain a copy.)

Consecutive Sheet Number (1,2,3,...): ______

Sample Number (1-38): ____________

Sample Identity: ____

Single Sample or Duplicate (S/D): _______

Date Sample Obtained: ________________

Vendor Identity: _________________________________

Vendor Address: ____

Sample Characteristics (e.g., Manufacturer product number; Lot number; Vendor stock number; Date of manufacture; other characteristics): _______

____

____

____

Other Comments: ____

____

Quantity of Sample Purchased: ______________________________________

Quantity of Sample Shipped: ____

Date Sample Shipped: ____________________________

Date Sample Received at Battelle: __________________

Date Sample Tested: _____________________________

Date Duplicate Tested (if applicable): _______________________

FIGURE 1. SAMPLE IDENTIFICATION SHEET USED TO DOCUMENT HCHO-CONTAINING PRODUCTS

During the product acquisition process, a few products were found to be unavailable or no longer representative of the current market. For HCHO, such products were exterior PF particleboard, and MDF with a UV-cured filler coating. Unavailable or non-representative products were dropped from the sample list, and additional contacts were made with industry representatives to identify possible alternative products. Those discussions identified sources of important HCHO-containing materials that would not ordinarily be available through retail or wholesale outlets. These were products that ordinarily would be incorporated into finished products, such as furniture or cabinets, before reaching the consumer or that are used commercially rather than by a private consumer. With the cooperation of industry sources, samples of such materials were provided for testing. These samples provided a unique opportunity to test the emission characteristics of realistic materials. HCHO products obtained directly from the manufacturer in this way included particleboard with and without paper and vinyl laminates (used in furniture, shelves, and cabinets); particleboard mobile home decking (i.e., flooring), with and without a waterproofing coating normally applied in kitchen and bath areas; cabinet doors of medium density fiberboard (MDF), with and without a fresh manufacturer-applied white acid-cured finish; and a commercially-applied two-coat finish for wood floors. A Sample Identification Sheet was filled out, for each sample received directly from the manufacturer, immediately upon receipt at Battelle.

Product acquisition was difficult for TDI products, due to increasing use of other isocyanates, use of isocyanate "pre-polymers" in formulations, or adoption of non-isocyanate formulations. That is, not all of the common polyurethane (PU) products found in California actually contain monomeric TDI. Nevertheless, in order to assure broad coverage of potential TDI sources, a wide variety of the common polyurethane products available to Californians was obtained. The samples obtained and tested focussed on the flexible foams in which TDI is known to be used, but also included product categories such as wood coatings, sealants, and adhesives for which TDI is less commonly used (Brydson, 1982). As was the case for HCHO products, certain types of samples planned for testing were found not to be representative of the current market. Discussions with manufacturers disclosed that PU-coated fabrics are no longer commonly found in residences, having been largely replaced in raincoats and other clothing by more "breathable" waterproofing treatments. As a result, PU-coated fabrics were not included in the TDI testing. Similarly, foam-backed carpeting was found to be uncommon in current residential use, and was excluded from testing. In order to obtain as wide a range of TDI products as possible, further contacts were made with industry during the acquisition of TDI products in California. That effort identified commercially-applied concrete sealers generally used in commercial construction as an additional category, and led to testing of one such product known to contain up to 4 percent by weight of monomeric TDI.

Overall, of the HCHO products tested, 44.6 percent were obtained in the San Francisco Bay area, 42.9 percent in southern California, 8.9 percent in the Sacramento area, and 3.6 percent directly from manufacturers selling in California but located outside the state. For TDI products tested, the corresponding percentages were 51.3 percent from the Bay area, 46.2 percent from southern California, and 2.6 percent from manufacturers located outside the state.

It must be pointed out that a few of the samples tested represent industrially- or commercially-applied treatments that ordinarily cannot be carried out by a consumer. For HCHO, two such samples were: (1) a commercially-applied acid-cured floor finish, and (2) the manufacturer-applied acid-cured coating on cabinet doors. For TDI, the one sample of this type was a commercially-applied concrete water stop product. (This product is applied to concrete to prevent water leakage, or onto wet surfaces to stop existing leaks. Because of its TDI content, application may be performed only by trained commercial contractors.) The emission rates determined for these samples probably overestimate the rates consumers would be exposed to, because of the time lag between commercial application and consumer exposure. In addition, several samples of bare (i.e., uncoated) wood products were tested, although most residences contain little or no bare surface area of particleboard and plywood. These products are virtually always covered with carpeting or other floor coverings, paint, or various laminate coatings. Nevertheless, testing of bare wood products provides valuable comparisons to previous emission data, and to test results for coated wood products.

Table 3 shows a listing of all the products tested for HCHO and for TDI, indicating the geographic location where the product was obtained, the type of vendor, and typical uses of

TABLE 3. ORIGIN AND NATURE OF PRODUCTS TESTED

No.	Product Group and Identity	Location	Vendor	Use in Home
DRY PRODUCTS TESTED FOR HCHO EMISSION				
	Bare Urea-Formaldehyde (UF) Wood Products			
1	1/4" UF particleboard	SC	WH	Cabinet backs, drawer bottoms
2	5/8" Particleboard underlayment	SC	WH	Flooring in conventional homes
3	Bare MDF cabinet doors	OS	MFR	
4	3/4" Medium density fiberboard (MDF)	SC	WH	Furniture, cabinet doors
5	5/8" Industrial particleboard (I.P.)	SC	MFR	Furniture, shelving, cabinets
6	5/8" MDF	SC	MFR	Furniture, cabinet doors
7	1/4" Prefinished hardwood plywood wall panelling	SC	WH	Interior wall panelling
8	5/8" Mobile home decking	BA	MFR	Flooring in mobile homes
9	1/2" Hardwood veneer plywood	SC	WH	Cabinets, furniture
10	3/4" Industrial particleboard	SC	WH	Furniture, shelving, cabinets
11	5/8" Industrial particleboard	SC	WH	Furniture, shelving, cabinets
12	3/4" Industrial particleboard	BA	RET	Furniture, shelving, cabinets
13	5/8" Particleboard underlayment	BA	RET	Flooring in conventional homes
14	3/4" Industrial particleboard	SAC	RET	Furniture, shelving, cabinets
15	5/8" Industrial particleboard	BA	RET	Furniture, shelving, cabinets
16	1/2" Stock hardwood plywood	SC	WH	Cabinets, drawers,furniture
17	1/4" Stock hardwood plywood	SC	WH	Cabinets, drawers
18	3/4" Stock hardwood plywood	SC	WH	Cabinets, drawers,furniture
19	3/4" Stock hardwood plywood	BA	RET	Cabinets, drawers,furniture
	Coated UF Wood Products			
20	MDF cabinet doors w. white acid-cured finish	OS	MFR	
21	5/8" I.P. black textured non-recoatable paper laminate	SC	MFR	Furniture
22	5/8" I.P.recoated white ice paper waterborne topcoat	SC	MFR	Furniture
23	5/8" Mobile home decking w. waterproof coating	BA	MFR	Flooring in mobile homes
24	3/4" I.P. melamine laminate (imported)	SC	WH	Furniture, shelves, countertops

TABLE 3. (Continued)

No.	Product Group and Identity	Location	Vendor	Use in Home
25	5/8" I.P. w. red cherry paper laminate	SC	MFR	Furniture
26	3/4" I.P. melamine laminate (imported)	SC	WH	Furniture, shelves, countertops
27	5/8" I.P. w. rigid vinyl bonanza oak laminate	SC	MFR	Furniture
28	5/8" I.P. vinyl coated	BA	RET	Shelving, cabinets
29	Interior door w. particleboard core	BA	RET	Bedroom/bathroom door
30	5/8" I.P. vinyl coated	SC	WH	Shelving, cabinets
31	3/4" I.P. melamine laminate (domestic)	SC	WH	Furniture, shelves, countertops
32	5/8" I.P. w. electron-beam-cured acrylic coating	SC	WH	Furniture, stereo cabinets
33	3/4" I.P. melamine laminate (domestic)	SC	WH	Furniture, shelves, countertops
	Permanent Press Fabrics			
34	Permanent press draperies	BA	RET	
35	Permanent press shirts	BA	RET	
36	Permanent press shirts	SAC	RET	
37	Permanent press sheets	BA	RET	
	Decorative Laminates			
38	20 mil cabinet liner decorative laminate	BA	RET	Cabinet interior surfaces
39	50 mil rigid general purpose laminate	BA	RET	Countertops, table tops
40	50 mil general purpose laminate	BA	RET	Countertops, table tops
	Fiberglass Products			
41	Fiberglass R-19 roll insulation	BA	RET	Ceiling and wall insulation
42	Fiberglass ceiling tiles	BA	RET	Drop ceilings
43	Fiberglass ceiling tiles	SAC	RET	Drop ceilings

TABLE 3. (Continued)

No.	Product Group and Identity	Location	Vendor	Use in Home
	Bare Phenol-Formaldehyde (PF) Wood Products			
44	1/4" Perforated PF hardboard	SC	WH	Tool organization ("Pegboard")
45	3/4" Softwood plywood	SC	WH	Exterior walls, roof
46	3/4" Oriented strandboard	BA	RET	Exterior walls
47	3/4" Softwood plywood	BA	RET	Exterior walls, roof
	Paper Products			
48	Paper grocery bags	BA	RET	
49	Paper towels	BA	RET	
WET PRODUCTS TESTED FOR HCHO EMISSION				
	Lower quality latex paint	BA	RET	Interior walls and ceiling
	Higher quality latex paint	SAC	RET	Interior walls and ceiling
	Paper-based wallpaper	BA	RET	Interior walls
	Fingernail hardener	BA	RET	
	Fingernail hardener "formaldehyde free"	BA	RET	
	Fingernail polish	BA	RET	
	Commercially applied floor finish	SAC	MFR	Applied to wood floors by contractor,
POLYURETHANE PRODUCTS TESTED FOR TDI EMISSION				
	Polyurethane carpet padding (3 products, 3/8" thick)	BA	RET	Placed under wall-to-wall carpet
	Polyurethane carpet padding (1 product, 7/16" thick)	BA	RET	Placed under wall-to-wall carpet
	Polyurethane carpet padding (5 products, 1/2" thick)	BA	RET	Placed under wall-to-wall carpet

TABLE 3. (Continued)

No.	Product Group and Identity	Location	Vendor	Use in Home
	Mattress and sheet foam (2 products, 4 1/2" mattress)	BA	RET	Mattresses, pads, waffle foam
	Mattress and sheet foam (1 product, 5" mattress)	BA	RET	Mattresses, pads, waffle foam
	Mattress and sheet foam (1 product, 4" mattress)	BA	RET	Mattresses, pads, waffle foam
	Mattress and sheet foam (1 product, 1" sheet)	BA	RET	Mattresses, pads, waffle foam
	Mattress and sheet foam (1 product, 1" waffle pad)	BA	RET	Mattresses, pads, waffle foam
	Furniture cushion foam (2 products, foam chair pads)	BA	RET	Pillows, furniture cushions
	Furniture cushion foam (1 product, sofa cushions)	BA	RET	Pillows, furniture cushions
	Furniture cushion foam (1 product, pillows)	BA	RET	Pillows, furniture cushions
	Spray polyurethane varnishes (4 products)	SC	RET	Spray-on coatings for wood
	Brush-on polyurethane varnishes (8 products)	SC	RET	Brush-on coatings for wood
	General purpose water sealers (3 products)	SC	RET	Sealant for wood, concrete, etc.
	Concrete-only water sealers (2 products)	SC	RET	Sealant for concrete surfaces
	Mastic construction adhesive	SC	RET	Used during home construction
	High performance caulk	BA	RET	Long-lasting caulking compound
	Commercially applied water stop product	OS	MFR	Prevents water leaks, or stops active leaks, on concrete

Location: SC = southern California; BA = San Francisco Bay area; SAC = Sacramento area, OS = outside the state.
Vendor: WH = purchased from wholesale dealer; RET = purchased from retail dealer; MFR = direct from manufacturer.

Multiple products indicated for polyurethane product types were obtained from different vendors in the areas shown. For example, the 3 samples of 3/8" foam carpet padding were obtained from 3 different vendors in the Bay area.

the product in a home. The terminology used for wood products in Table 3 follows current industrial practice, as embodied, for example, in voluntary standards for particleboard and MDF (ANSI, 1993, 1994). Note that as terminology has changed with time, earlier compilations of wood product terminology (e.g., ASTM, 1993) have become partly contradictory to modern usage.

4.1.3 Product Documentation and Storage

Upon arrival at Battelle, each sample package was opened sufficiently to remove the Sample Identification Sheet. The date of sample receipt was noted on each sheet, copies were made, and a copy was replaced into the sample package. Each sample was then re-wrapped in plastic film until close to the date of chamber testing. Information on the Sample Identification Sheets was then entered into a spreadsheet program documenting each sample received, and recording any comments or notes about the sample shipment.

All samples were stored in a vacant office, maintained at 70(±3)°F and 50(±5) percent relative humidity (RH), and ventilated by means of a standing fan which operated continuously. The intent of sample storage and handling was to preserve the emission characteristics that the samples would normally have upon introduction into a residence. Samples that ordinarily would be enclosed until use were kept in their original packaging until just before placement in the test chamber. Paints, coatings, cosmetics, some paper products, and permanent press fabrics were the HCHO products handled in this way. Paints, coatings, sealants, and adhesives were TDI products handled in the same way. All other products were unwrapped, separated from extra protective sample sheets, and allowed to air out in the storage room for two to seven days before testing. The edges of all wood product samples were sealed with sodium silicate solution as suggested in the ASTM small chamber guidelines (ASTM, 1990b).

4.2 Testing Procedures

All products were tested for emissions of the target compounds while held in enclosed test chambers under controlled conditions. This section describes the chamber facilities and test procedures used for testing of HCHO products, and for initial screening and final testing of TDI products.

4.2.1 HCHO Chamber Tests

Products were tested for emissions of HCHO and other carbonyls at two different test conditions, as shown in Table 4. The two sets of conditions, designated "Typical" and "Elevated", were chosen to cover the range of expected indoor conditions. The Elevated conditions differ from the Typical conditions in the higher temperature and lower air exchange rate (N). Both conditions included a relative humidity of 50 percent; as a result the absolute concentration of water vapor in the Elevated conditions was about 40 percent greater than that in the Typical conditions.

TABLE 4. CHAMBER CONDITIONS USED FOR TESTING OF HCHO AND OTHER CARBONYL EMISSIONS

Condition	Typical	Elevated
Temperature	21.1°C (70°F)	26.7°C (80°F)
Air Exchange Rate	1.0 hr^{-1}	0.3 hr^{-1}
Relative Humidity	50 percent	50 percent

All HCHO products were tested simultaneously at the two sets of test conditions, using identical twin chambers, each of 1.43 m^3 volume, and made of stainless steel and glass. Figure 2 shows a schematic of the twin chamber facility. This figure shows that air was supplied to the two chambers from an Aadco pure air generator, with a reservoir to stabilize the air supply. The air supplied to each chamber was made up of a dry and a humidified flow,

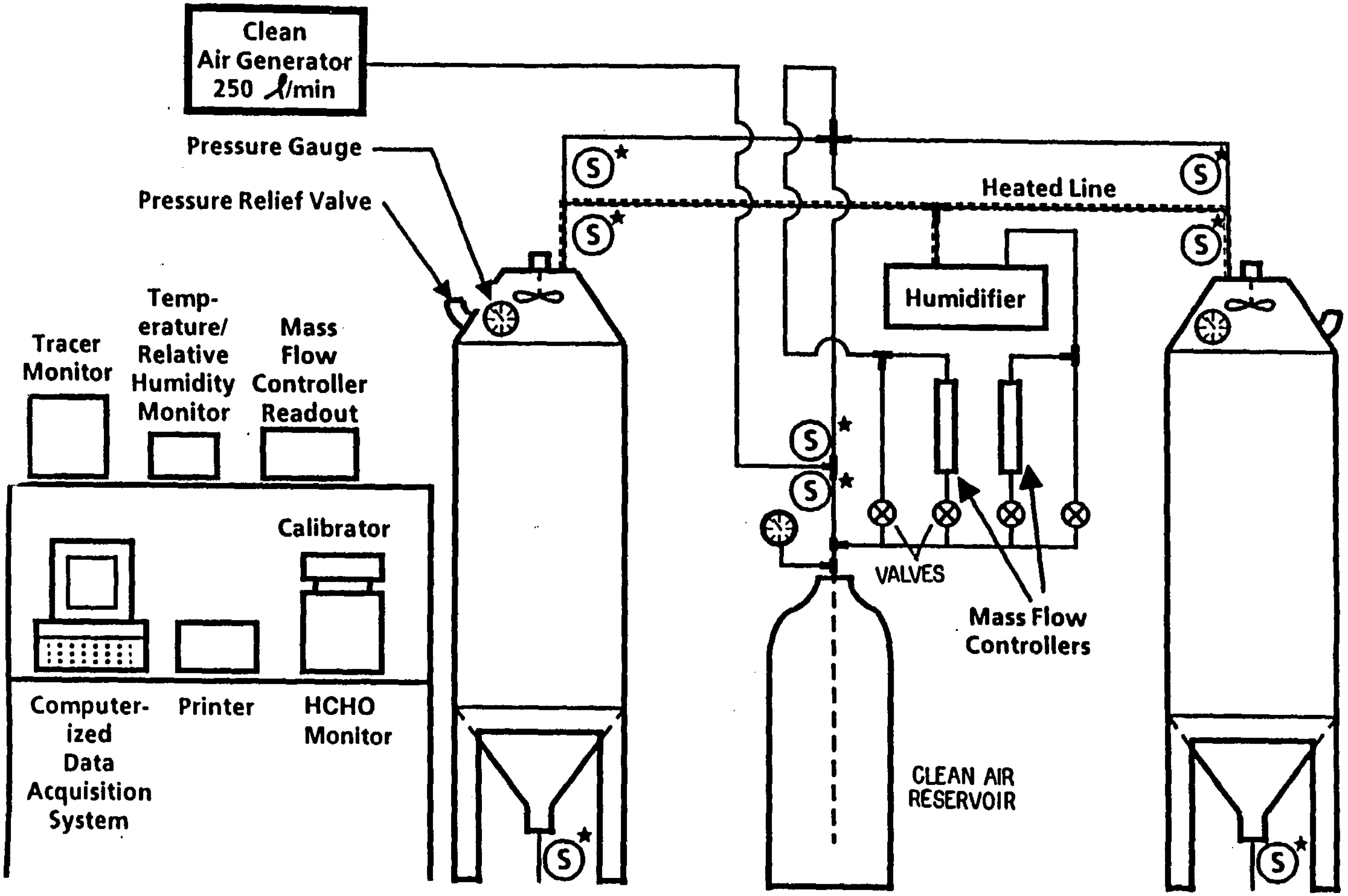

FIGURE 2. HCHO TEST CHAMBERS

★Ⓢ = SOLENOID VALVE

which were mixed at the inlet of the chamber to achieve the desired humidity. Each of these flows to each chamber was controlled by an electronic mass flow controller located upstream of the humidifier. For clarity, Figure 2 shows a single humidification system supplying both chambers, but in fact each chamber was connected to separate flow controllers and a separate humidifier. Thus, the two chambers were completely independent in flow control and humidification. The left chamber in Figure 2 was operated at the Typical conditions. Total volume flow through this chamber was 23.8 L/min, to achieve an N of 1.0 hr^{-1}. The temperature of this chamber was maintained at 70°F by controlling the temperature of the laboratory in which the chambers are installed. The right chamber in Figure 2 was operated at the Elevated conditions. Total volume flow through this chamber was 7.2 L/min, to achieve an N of 0.3 hr^{-1}. The temperature of this chamber was maintained at 80°F by heat lamps located around the base of the chamber, and controlled by an electronic temperature controller. This chamber was insulated by 1" thick styrofoam, including a removable panel of insulation over the chamber door.

Testing of HCHO products was conducted by placing identical samples of a product in each of the two chambers simultaneously. The sample sizes (i.e., product loadings) were established based on realistic product loadings in residences and on expected emission rates (Appendix A), and are specified in test protocols prepared for dry and wet HCHO products (Appendices B and C, respectively). Product loadings were occasionally adjusted, to accommodate very low or very high emission rates in the actual tests. Emission rates were calculated based on the actual exposed surface area of product tested (e.g., both sides of a board or laminate sheet exposed in the chamber). The actual product loading rates used in each test are specified in Section 6, along with the test results. Wet products were applied to substrate materials outside the test chambers, and the substrates were then immediately placed into the chambers. Substrate materials in HCHO tests were gypsum wallboard, for paints and wallpaper; oak flooring, for floor finish; artificial fingernails, for fingernail polish; and aluminum foil over a wooden support, for fingernail hardener. The HCHO content of each chamber was monitored throughout all tests using a continuous monitor (see Section 4.3.1), and quantitation of all five target compounds was accomplished by integrated sampling with a standard method employing 2,4-dinitrophenylhydrazine (DNPH). In general, the chamber background air was sampled in the morning, then the product was loaded into each chamber and maintained at test conditions overnight (i.e., for 18 to 24 hours). Depending on the type of product, duplicate DNPH samples were taken the morning after the start of the test, or at a suitable time as indicated by the continuous HCHO monitor. Appendices B and C present further detail on the test procedures.

Data acquisition was accomplished using Lab Tech Notebook software on a personal computer located in an adjacent laboratory. Temperature and RH data from both chambers, and the output of the real-time HCHO monitor, were recorded during each test.

4.2.2 TDI Screening Tests

All TDI products were subjected to a screening test under conditions chosen to exaggerate any TDI emissions. Screening tests were conducted according to a detailed test protocol, which is included as Appendix D of this report. The screening tests were conducted in a 9 L glass chamber. This chamber was found to be far superior to larger steel or polymer enclosures in terms of the stability of TDI in the vapor phase. Efforts to characterize the glass chamber, including determination of the TDI loss rate to the chamber walls, are described in Section 5.5. This glass chamber was maintained at about 50°C (120°F) by placing it inside a 0.44 m^3 steel and glass chamber, which was heated by internal electric heaters. The outer chamber air was continually mixed by an internal fan to assure uniform temperature. Screening tests were conducted with minimal air flow through the 9 L test chamber. Air exchange rates during the TDI screening tests of dry products were zero throughout each test, except for the last 20 minutes of the test, when sample withdrawal increased N to 10 hr^{-1}. In screening of wet TDI products, continuous monitoring of the chamber air caused a continuous air exchange rate of about 3 hr^{-1}. As a result, the minimum detectable TDI emission rate for dry products differed from that for wet products. TDI concentrations in the screening chamber were determined both by a commercial continuous monitor and an integrated sampling technique (see Section 4.3.2). Plywood was used as a substrate in TDI testing of varnishes and caulks, and bare concrete was used for testing of concrete sealers. These products were applied to pieces of the substrates, which were then immediately placed into the 9 L chamber.

Some of the TDI screening tests were conducted on groups of similar products, as described in Appendix D. For example, samples of several carpet padding products were placed in the test chamber together. In this way, entire product categories could be ruled out or targeted for further testing. An indication of TDI above the chamber background level was taken as a positive indication of TDI emission in the screening tests. Section 4.4.3 documents the sensitivity of the screening procedures for identifying TDI-emitting products.

4.2.3 TDI Final Tests

Only one product showed TDI emission in the screening tests. For that product (the commercial water stop product for concrete), final testing was done using the 9 L glass chamber, in a manner based upon the screening procedure in Appendix D. However, final testing was performed at realistic temperatures and with lower product loading rates in the chamber, relative to the screening tests. The water-stop product is not normally available to residential users, but is applied by contractors, primarily in commercial buildings. It reacts with liquid water to form a polymer film or plug that seals any water leakage path. The means of use of the product depends on the amount of water present at the point of use: the product may be injected below the surface of standing water at the leakage point, or may be applied to wet concrete where it reacts with available moisture, or may even be applied to dry concrete and then flooded with water to promote reaction. Maximum TDI release is expected when the product is exposed to air without reaction with water, i.e., as when applied to dry concrete. As a result, to best simulate the actual conditions of use, the product was tested in that manner in both the screening and final tests.

Several trial runs were conducted with the product before a final test procedure was established that allowed the entire TDI emission and decay curve to be followed with the continuous TDI monitor described in section 4.3.2. That final procedure involved applying 90 mg (± 5 mg) of the product dropwise from a glass pipet onto a 3.6 cm^2 area of the concrete substrate, producing a realistic application rate of 25 mg/cm^2, and immediately placing the substrate into the test chamber. The resulting product loading was 0.040 m^2/m^3. The TDI emission curve was determined continuously using the TLD-1 monitor, and an integrated TDI sampling method was also used after the peak of the emission curve had passed. Final TDI testing was conducted in duplicate at 70°F and once at 80°F. The chamber air flow was 8 L/min through all final tests, and the relative humidity of the test air was 50 percent. The test was ended when the chamber TDI level fell below the 2 ppbv detection limit of the TLD-1 monitor. The product reacted rapidly even with the humidity in the air, so the final TDI tests were ended within one hour or less.

4.3 Chemical Measurement Methods

4.3.1 Methods for HCHO and Other Carbonyl Compounds

Two different methods were used to determine HCHO and the other carbonyl compounds (acetaldehyde, propionaldehyde, MEK, MIBK) in this study: a Battelle-developed continuous monitor was used for determination of HCHO (Kelly, 1992; Kelly and Fortune, 1994), and EPA Method TO-5, based on derivatization with 2-4-dinitrophenyl-hydrazine (DNPH), was used for determination of HCHO and the other four target carbonyl compounds (Winberry et al., 1988). The continuous HCHO instrument functions by continuously contacting a flow of 2 L/min of sample air with a flow of about 0.7 ml/min of 0.1 N H_2SO_4 scrubbing solution (Kelly and Fortune, 1994). Formaldehyde in the sample air is rapidly and efficiently absorbed into the scrubbing solution. After separation of the air and scrubber solution flows, a small continuous flow of an aqueous reagent mixture containing 2,4-pentanedione (i.e., acetylacetone) is added to the scrubber flow. The combined aqueous flows then pass through a reaction coil maintained at 95°C (± 1°C), promoting formation of a cyclic derivative in 1:1 stoichiometry with the collected HCHO. The derivative is in turn continuously detected by a commercial fluorometer with a quartz micro-volume flow cell. The instrument used in this study was improved beyond the version previously described (Kelly, 1992; Kelly and Fortune, 1994) by use of a different commercial fluorometer (GTI/Spectrovision FD-100) that allows for automatic zeroing, multiple ranging, and flexibility in selecting sensitivity and time response. The instrument has a detection limit of 0.1 ppbv, a lag time of 90 seconds, and a response time to step changes of about 60 seconds. The instrument responds linearly over a wide range of concentrations. At 1 ppmv of HCHO, the departure from linearity is 3 percent, and at the maximum HCHO levels observed in this study, (about 1.8 ppmv) the departure from linearity is less than 9 percent. HCHO results above 1 ppmv were corrected for non-linearity. The monitor provides highly specific detection of HCHO, to the exclusion of other carbonyl compounds and potential interferents.

The continuous HCHO monitor was used in all tests on HCHO-emitting products. The monitor was set up near the two test chambers, and sampled alternately from the two chambers by means of an automatic valve. For dry products, i.e., those that emit HCHO at a steady rate, the monitor sampled for alternate 30-minute periods from each chamber. For wet products, i.e., those that undergo a peak in emission after application followed by a decrease as the product dries or cures, the cycling time was shortened to five minutes alternately on each chamber. Figure 3 shows an example of the continuous output of the monitor in the five-minute cycling mode. The figure shows the chart recorder trace of the monitor's response to HCHO in each of the two chambers, in the first few hours of a test of nail polish emissions. Sampling of the chamber background HCHO levels is shown at the right of Figure 3, followed by the emission peak and gradual decay of emissions in both chambers. The difference in HCHO concentrations in the two chambers is evident from the cyclic response of the monitor. Note that the maximum HCHO concentration indicated in Figure 3 is only about 25 ppbv. In the test shown in Figure 3, as in all tests, the HCHO monitor continuously sampled the chamber background air before introduction of samples, to distinguish chamber background HCHO levels from product emissions. In testing of dry samples, the continuous HCHO data were used primarily to document stabilization of chamber HCHO levels, and as a check on the HCHO results from the DNPH method. However, for wet products, the continuous HCHO data were the primary measurement, and were used to model the time behavior of emissions from these products, as described in section 4.4.2.

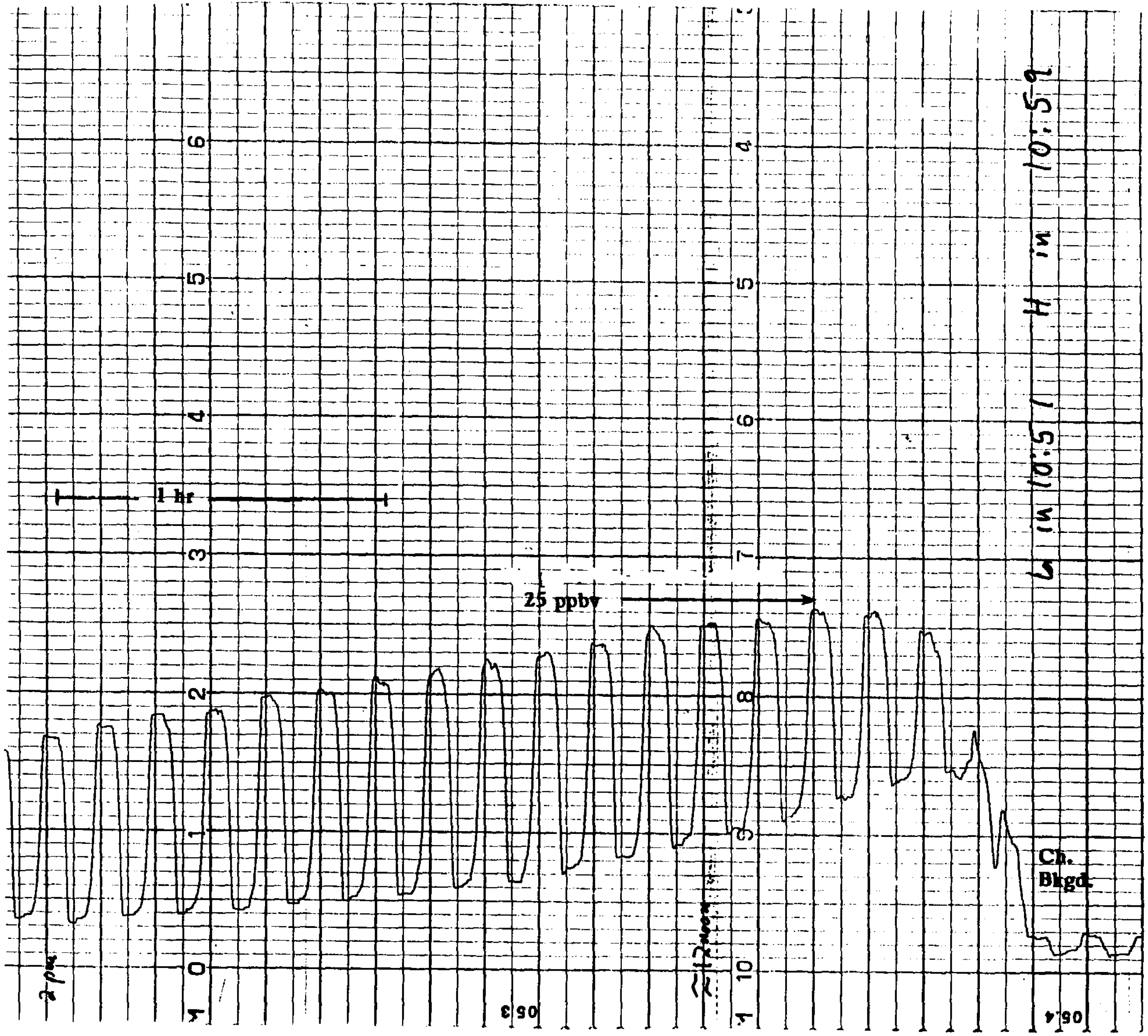

FIGURE 3. EXAMPLE OF REAL-TIME HCHO TRACE

The HCHO monitor was calibrated using 1 x 10^{-6} M to 4 x 10^{-4} M solutions of HCHO, prepared from a 37 percent formalin primary standard (13.3 M) by serial dilution with the 0.1 N H_2SO_4 scrubber solution (Kelly and Fortune, 1994). A continuing standard of 1.33 x 10^{-5} M was run on every day of testing. The characteristics of the monitor lead to a direct relation between the aqueous standard and its equivalent gaseous HCHO concentration (Kelly and Fortune, 1994). For example, the 1.33 x 10^{-5} M solution is equivalent to about 100 ppbv gaseous HCHO. However, the accurate determination of that relation depends on measurement of the sample air and scrubber solution flows in the monitor. The sample air flow was controlled by an electronic mass flow controller built into the monitor. That flow controller was periodically recalibrated during the study using an electronically-sensed bubble flow meter. No adjustments to the flow controller were needed at any time as a result of those calibration checks. The scrubber solution flow rate was measured on every test day, by recording the volume drawn by the monitor from a 10 ml graduated cylinder, over a time period measured with a stopwatch. The monitor's sensitivity thus was determined independently for each test conducted.

EPA Method TO-5 uses DNPH in acetonitrile solution as the collecting and derivatizing medium for HCHO and other carbonyl compounds. DNPH forms a characteristic derivative with each carbonyl compound. Those derivatives are then separated by HPLC and quantified by UV detection (Winberry et al., 1988). The collection medium used in this study consisted of 240 mg of crystalline DNPH per liter of HPLC-grade acetonitrile (Aldrich), acidified by addition of 200 μl of phosphoric acid per liter. Sampling was conducted by drawing air at 1.65 L/min through midget glass impingers containing 20 ml of the reagent solution. For sampling of the background concentrations in the test chambers, a single sampling train with one impinger was used. For sampling of the concentrations released by products in the chambers, duplicate samples were collected using two impinger trains, each of which had two impingers in series. Generally 95 percent or more of the target compounds was found in the first impinger. All background sampling and some product emission sampling was of 60-minute duration. However, the sampling period was shortened to 30 minutes for those products which produced relatively high HCHO levels in the chambers, as indicated by the real-time HCHO monitor.

Calibration of the HPLC analysis was conducted by preparing standard solutions containing 2 μg/ml or 20 μg/ml of the DNPH derivative of each of the five target compounds. Those derivatives were prepared by reaction of DNPH with each of the pure compounds. The 2 μg/ml standard was within the range of the concentrations analyzed, and was run with every batch of DNPH sample analyzed. The 20 μg/ml standard exceeded the highest sample concentrations observed, and was analyzed only when needed with such samples. Linear response was observed over the full calibration range. The stability of the DNPH method was evaluated based on all analyses of the 2 μg/ml standard; those results are presented in section 5.1.2. Average peak areas of the 2 μg/ml standard ranged from 284,000 to 395,000 area counts for the five target compounds. A slight decrease in the peak area for HCHO, due to slow decomposition of that derivative in the standard, triggered preparation of a new standard for that compound about five months into the study.

Based on a minimum detectable peak area of 2,000 area counts, and a 60-minute sampling duration at 1.65 L/min, the detection limit of the DNPH method was 0.16 ppbv (0.20 $\mu g/m^3$) for HCHO; 0.12 ppbv (0.23 $\mu g/m^3$) for acetaldehyde; 0.10 ppbv (0.25 $\mu g/m^3$) for propionaldehyde; 0.11 ppbv (0.31 $\mu g/m^3$) for MEK; and 0.11 ppbv (0.44 $\mu g/m^3$) for MIBK. However, in all tests the convention was adopted that an increase above chamber background of at least 1 ppbv of HCHO, and at least 0.5 ppbv of the other target compounds, was required to initiate calculation of the corresponding emission rates. The higher cutoff level for HCHO was chosen based on the higher chamber background levels of that compound, relative to those of the other four compounds.

The DNPH results were the primary means of quantitation for the target compounds, except for HCHO emitted from wet products, for which the real-time HCHO data were required. Comparisons of DNPH and real-time HCHO data were made to confirm the accuracy of the concentrations found, and comparisons of the duplicate DNPH samples were made to assess the precision of the DNPH results. Those results are presented in sections 5.1.5 and 5.1.4 of this report, respectively.

4.3.2 TDI Measurement Methods

Both a real-time continuous method and an integrated sampling method were used for TDI determination. The real-time monitor was a TLD-1 Toxic Gas Detector (MDA Scientific, Inc.). This monitor relies on a continuous paper tape, impregnated with a reagent that produces a color change upon contact with TDI. The color development is non-specific for TDI; i.e., the monitor will also respond to other isocyanates. The monitor draws air at about 500 cm^3/min with an internal pump, and contacts it with the tape. An optical system measures the color formation and outputs both a digital display (in whole ppbv units) and a 4-20 mA signal readable to 0.08 ppbv. The monitor's detection limit is 2 ppbv, and output equivalent to zero ppbv is indicated at all levels below 2 ppbv. The monitor responds only up to 60 ppbv of TDI. The TLD-1 monitor was used both to provide a continuous display of TDI levels in the chamber, and to provide a warning to prevent exposure of personnel to TDI. The warning level of the instrument was set to 5 ppbv for this study. The calibration of the TLD-1 is built into the instrument, but instrument performance was checked by means of a permeation tube of 2,4-TDI maintained in a commercial permeation oven.

The integrated method for TDI determination was based on derivatization of TDI with N-(4-nitrobenzyl)-N-n-propylamine hydrochloride (NBPA) in toluene solution, followed by reversed phase high performance liquid chromatography (HPLC) separation with UV detection (Dunlap et al., 1976; Holdren et al., 1984). Sampling was conducted by drawing air at 1 L/min for 20 minutes through a midget glass impinger containing 10 ml of 2×10^{-4} M NBPA in toluene. The sample solution was then evaporated to dryness, and then made up to 1 ml volume with acetonitrile. The 2,6- and 2,4-TDI isomers were separated on a 25-cm Zorbax ODS column, using 55/45 acetonitrile/water as the mobile phase at 2 ml/min. The injection volume was 20 microliters, and the 2,6- and 2,4-isomers eluted from the HPLC with retention times of about 7 and 10 minutes, respectively. Detection was by UV absorption at 215 nm wavelength. A detection limit of 0.14 ppbv TDI (1 $\mu g/m^3$) was achieved with a 20 L air sample.

Fresh calibration standards for the NBPA analysis were prepared with each batch of samples by spiking known quantities of TDI into 2 x 10^{-4} M NBPA reagent. The TDI used was commercial "TD-80", i.e., 80 percent 2,4-TDI and 20 percent 2,6-TDI. In order to obtain reliable TDI analyses, care was needed in preparation and analysis with the NBPA method. The NBPA reagent was found to be relatively unstable, i.e., subject to gradual decomposition. This did not affect the collection or derivatization of TDI with the NBPA reagent, but it did lead to the presence of extraneous peaks in the HPLC chromatogram, which were significant because of the low levels of TDI to be detected. As a result, the NBPA reagent was made up fresh at least once a week. This procedure prevented the decomposition product peaks from becoming large enough to interfere with identification and quantitation of TDI peaks. For the same reason, all collected NBPA sample solutions were analyzed within a few days after collection. There was no indication from analysis of standards that the TDI-NBPA derivatives themselves decomposed within that time period.

An additional problem was the gradual degradation of the HPLC column that occurred during analysis of samples. This degradation was evidenced by gradually shifting retention times of the TDI standard peaks. It is believed to have been caused by accumulation of NBPA decomposition products at the head of the column. For a few samples, this problem was addressed by splitting each screening sample, spiking one half with a small amount of TD-80, and analyzing both halves. The spiked sample served to confirm TDI peak locations. Analyzing TDI standards more frequently during sample analysis was also adopted. Subsequently, an analysis procedure was chosen which included flushing the HPLC column with pure acetonitrile between runs. This approach slowed sample analysis somewhat, but maintained good stability of TDI retention times and eliminated the need for sample splitting and spiking.

A permeation source of 2,4-TDI was also used for calibration and intercomparison of the TLD-1 and NBPA methods, and for characterization of the test chamber. The tube had a nominal permeation rate of 250 ng/min. The TDI tube was maintained at 60°C in the permeation oven of a Metronics 340 calibrator. The results of tests using that TDI source are reported in Section 5.5

4.4 Calculation Procedures

4.4.1 Steady-State HCHO Sources

For those products that produced steady-state HCHO concentrations in the test chambers, the following equation was used to calculate the emission rates from each product (ASTM, 1990a):

$$E = \frac{CN}{L} \tag{1}$$

where E = emission rate of target compound in $\mu g/m^2/hr$

C = concentration of the target-compound in the test chamber under steady state conditions, in $\mu g/m^3$, corrected for background concentration at the start of the test

N = air exchange rate in hr^{-1}

L = product loading rate in the chamber, in m^2/m^3.

The steady state concentration (C) was determined by DNPH sampling and analysis near the end of the chamber tests. The DNPH results allowed emission rates to be calculated for any of the five target compounds that were present at levels exceeding their background levels. HCHO was the predominant emission from all products. In a few cases, problems with DNPH sampling or analysis invalidated the DNPH results. In those cases the steady state HCHO concentration determined by the real-time monitor was used in Equation 1. The use of the real-time results in this way is justified by the close agreement found between real-time and DNPH HCHO results (section 5.1.5).

4.4.2 Wet HCHO Sources

For those products that were applied wet and went through a drying or curing stage after application, the real-time HCHO monitor was the means of following the rise and decay of

HCHO emissions from the product. Since the other four target compounds could not be determined in real time, only the time dependence of HCHO emission could be modelled. However, the other target compounds were determined by DNPH sampling at the end of the test.

Initially an attempt was made to fit the emission curves with a simple first-order decay equation, i.e.

$$R_t = R_o \, e^{-kt} \qquad (2)$$

where R is the emission rate in $\mu g/m^2/hr$, t is time, and k is the first order decay constant (ASTM, 1990a). Although this approach provided a reasonable fit to the initial peak in HCHO emissions, it provided a very poor fit to the later decay of HCHO emissions in the chambers. As a result, an alternative modelling approach was chosen based on a review of published information.

The modelling approach adopted was a 4-parameter empirical model (Colombo et al., 1990; Colombo and DeBortoli, 1992; De Bortoli and Colombo, 1993), having the form:

$$C = \boldsymbol{a}(1-e^{-\boldsymbol{b}t}) - \boldsymbol{c}(1-e^{\boldsymbol{d}t}) \quad . \qquad (3)$$

In this equation C is the measured chamber concentration of HCHO in $\mu g/m^3$, at time t (in hours). The coefficients **a** and **c** also have units of $\mu g/m^3$, whereas the exponential coefficients **b** and **d** have units of hr^{-1}. This model is a mathematical form that mimics the emission curves obtained, and is not derived directly from physical principles or characteristics of the sample. However, the parameters of the model can be used to derive important characteristics of the HCHO emission process. For example, the initial HCHO emission rate of the sample (E_o, in $\mu g/hr$) is given by (Colombo et al. 1990):

$$E_o = V\,(\boldsymbol{ab}-\boldsymbol{cd}) \qquad (4)$$

where V is the volume of the test chamber in m^3, and parameters **a-d** are as indicated above. Since the product loading in the chamber (L) is

$$L = \frac{A}{V} \qquad (5)$$

where A is the exposed surface area of the product in m^2, then the initial emission rate per m^2 of product surface may be calculated as:

$$R_o = \frac{E_o}{A} = \frac{(ab-cd)}{L} \qquad (6)$$

where R_o has units of μg/m^2/hr. The total emission of HCHO during each test was determined by integration of the concentration-time curve, multiplication of that result by the air flow rate through the chamber, and addition of the "residual" HCHO present in the chamber at the end of the test (Colombo and De Bortoli, 1992). The time of occurrence and peak concentration of the calculated curve (t_{max}, and C_{max}, respectively) can also be calculated from the fitting results (Colombo et al., 1990).

Modelling using this approach was done using non-linear least squares regression on each data set, using Sigma Plot software. In applying this 4-parameter model, the recommendations of Colombo et al. (1990) were followed. The initial value of **a** was set equal to the observed maximum concentration in the data set. The initial value of **c** was set equal to the difference between that maximum value and the final asymptotic level of the decay curve (Colombo et al., 1990). The initial value of **d** was set equal to the air exchange rate (N) in the chamber (i.e., 0.3 or 1.0 air exchanges per hour), and the initial value of **b** was set to 3, based on experience in trial runs. Convergence of the model generally occurred within five iterations. Trials were also conducted in which **d** was fixed at the value of N; these trials produced poorer fits than those in which N served as an initial value only.

An example of the fits obtained with the 4-component model is shown in Figure 4, which shows the concentration-time curve determined for nail hardener in the Elevated condition chamber. The model-calculated curve is the solid line. Corresponding plots and model fitting results are shown for all wet test results in Appendix F. Close fitting of the initial concentration increase, the timing and magnitude of the peak, and the decay of HCHO

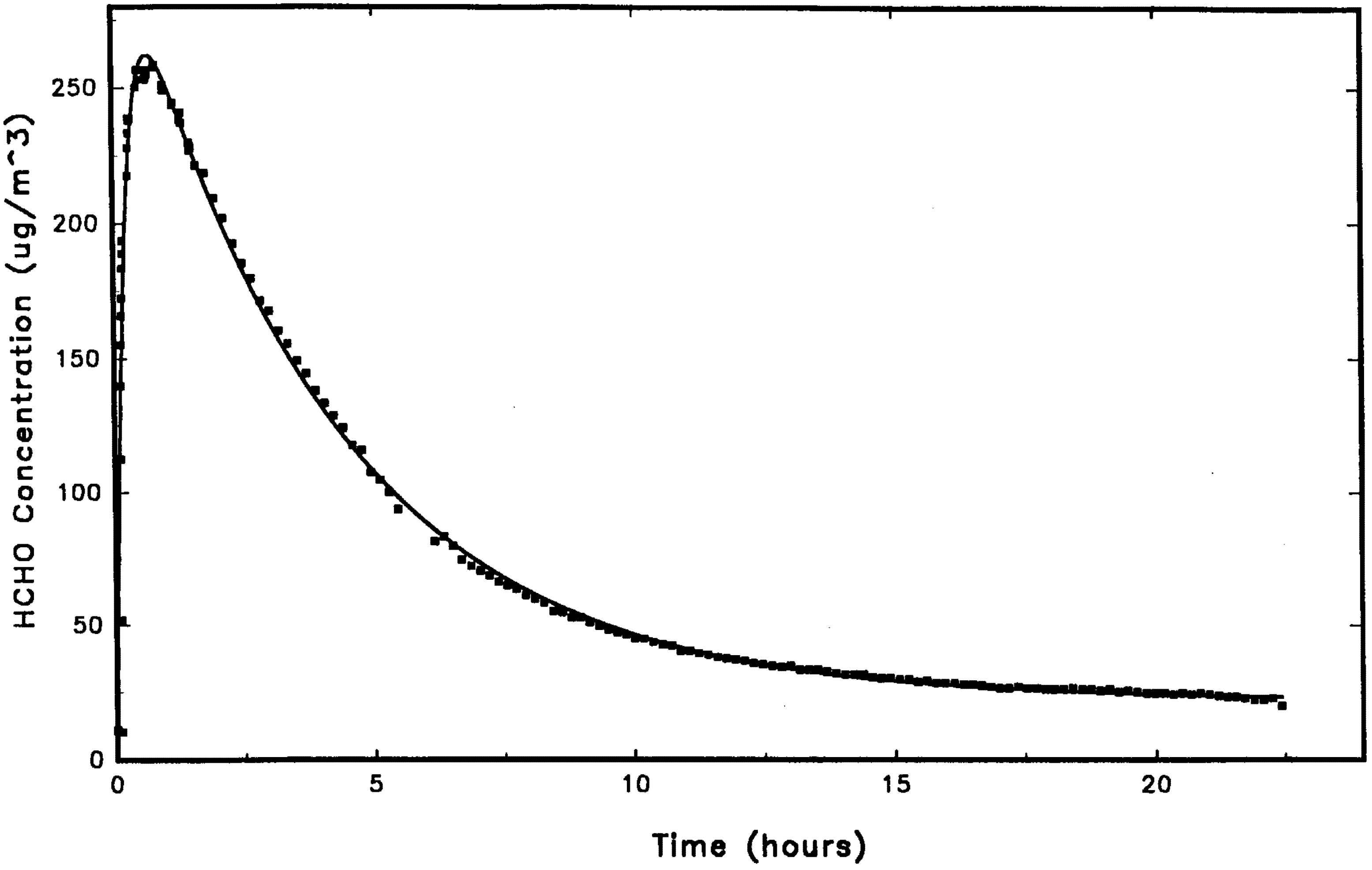

FIGURE 4. EXAMPLE OF MODEL FITS OBTAINED TO WET TEST HCHO DATA

concentrations was observed in all tests. However, it was necessary to carefully account for the lag time in the response of the HCHO monitor, and to accurately record the time of introduction of samples into the chambers, to achieve these results. Accurate fitting of the emission peak, and consequently the determination of R_o, was sensitive to the timing of the initial increase in HCHO. However, the determination of total integrated HCHO emissions during a test was much less sensitive to the shape and fitting of the initial peak. Those products that emitted large amounts of water and relatively little HCHO (i.e., latex paints and freshly applied wallpaper) overwhelmed the humidity control system in the test chambers. For these products the shape of the HCHO peak and decay curves was affected by the varying chamber humidity during the test. As a result, the emission curves for these products were not as smooth, and were more difficult to fit with the model.

Inspection of Figure 4 and of Appendix F shows that in most cases chamber HCHO concentrations in wet product tests achieved or approached a steady state by the end of the chamber test. For such cases it is perfectly acceptable to apply the steady-state emission model embodied in Equation 1 above, to calculate the HCHO emission rate at the end of the test. That final emission rate may be appropriate for characterizing the long term exposure to HCHO that results from a product, as opposed to the initial emission rate calculated as described above, which relates to exposure during use or product application. Equation 1 was applied to those wet products for which a steady state chamber HCHO concentration could be determined. The HCHO emission rates calculated for wet products in this way are denoted as "final HCHO emission rates" in Sections 1 and 6 of this report, and are directly comparable to the steady state emission rates calculated for dry products by means of Equation 1.

4.4.3 TDI Screening Test Calculations

The screening tests were conducted under exaggerated test conditions, with the intent of producing a yes or no indication of the presence of TDI emissions. That is, the screening tests were not intended to provide quantitative emission data. However, given the absence of detectable TDI emissions from all but one of the products in the screening tests, an important issue is how accurately the screening tests identify potential TDI emissions in the home. In assessing the adequacy of the screening protocol, three factors are important: 1) the detectability of any TDI emissions in the screening tests; 2) the relation of emissions under the screening conditions to those under realistic in-home conditions; and 3) the impact of in-home TDI emissions on in-home TDI concentrations and health risks. These factors are discussed below.

The minimum detectable emission of TDI from a product would be that which produces a TDI concentration in the chamber that is just equal to the detection limit of the NBPA measurement method, i.e., 0.14 ppbv, or 1 ug/m^3. For a dry product, screened under static conditions, that emission rate can be estimated by means of Equation 7:

$$ER = CVF_1 \; F_2/tA \tag{7}$$

where

ER = the minimum detectable TDI emission rate of the product or group of products, in μg/m^2/hr,

C = the minimum detectable TDI concentration in the chamber, at the end of the test, i.e., 1.0 μg/m^3,

V = the screening chamber volume (0.009 m^3)

F_1 = a calculated correction factor of 3, to correct for the loss of TDI in the test chamber over the 4-hour test period

F_2 = a correction factor of 3.3, to account for dilution of the chamber contents during sampling (i.e., 10 hr^{-1} for 20 minutes)

t = the time in hours from placing the sample in the chamber to the midpoint of the concentration measurement, i.e., 4 hours

A = the total exposed surface area of the product or products, in m^2.

A typical value of the dry product surface area (A) in the screening tests was 0.124 m^2. As a result, the minimum detectable TDI emission rate for dry products is approximately 0.18 μg/m^2/hr.

A corresponding estimate of the minimum detectable TDI emission rate from a wet product can be made using Equation 1 (Section 4.4.1), with the assumption of steady state emissions from the wet product. In this estimate, a correction factor must be included in the numerator of Equation 1 to account for loss of TDI to the chamber internal surfaces. Based on the TDI exponential loss rate of 0.7 per hour determined in this study (see Section 5.5), and the air exchange rate of 10 per hour during NBPA sampling in the wet product screening tests, this correction factor has a value of about 1.1. With a typical wet product surface loading of 5 m^2/m^3 in the screening chamber, a minimum detectable TDI emission rate of about 2.2 $\mu g/m^2/hr$ results.

Regarding the second criterion stated above, the vapor pressure of TDI is elevated by about a factor of ten at the screening temperature of 50°C, relative to that at 20°C (III, 1980). As a result, the minimum detectable TDI emission rates in the screening tests equate to realistic in-home emission rates about a factor of ten lower. In other words, the screening tests are capable of identifying TDI products that have in-home emission rates as low as 0.018 $\mu g/m^2/hr$ for dry products, and as low as 0.22 $\mu g/m^2/hr$ for wet products.

The likely in-home TDI concentrations and TDI-related health risks that would result from detectable TDI emissions in the screening tests may be estimated by assuming realistic in-home product loadings and air exchange rates. Assuming an in-home air exchange rate of 0.5 per hour, and a product loading of 0.3 m^2/m^3 (typical of carpet padding, the most widely used dry polyurethane product), Equation 1 predicts an in-home steady-state TDI concentration of 0.011 $\mu g/m^3$. Assuming the same air exchange rate, with a product loading of 0.1 m^2/m^3 (typical of a polyurethane wood coating, a common wet product), the minimum detectable in-home emission rate of 0.22 $\mu g/m^2/hr$ would result in an in-home TDI concentration of 0.044 $\mu g/m^3$. By comparison, a TDI concentration of 0.09 $\mu g/m^3$ is associated with a 70-year lifetime cancer risk of about 1×10^{-6}, and a concentration of 0.9 $\mu g/m^3$ is associated with a lifetime risk of about 1×10^{-5} (CAPCOA, 1992). Clearly, the screening protocol used in this study was capable of detecting TDI emissions with sufficient sensitivity to identify products that might convey significant cancer risks in the home. Note, however, that the calculations above are intended only as a gauge of the screening sensitivity, not as a quantitative risk assessment.

Additional factors enhance the preceding evaluation of screening sensitivity. The evaluation presented above assumes that TDI emissions in the home will be in steady state, when in fact emissions are likely to decay with time. Furthermore, the evaluation above neglects indoor loss processes for TDI. Any TDI in air in a home would probably be destroyed rapidly by adsorption and chemical reaction on the numerous surfaces present, thereby reducing the indoor TDI level resulting from any emissions.

Note that a comparable calculation of the screening sensitivity can be done using the detection capabilities of the TLD-1 monitor, which was less sensitive than the NBPA method. That calculation indicates that the TLD-1 monitor could identify dry products responsible for indoor TDI levels as low as 0.15 $\mu g/m^3$, and wet products responsible for indoor levels as low as 0.21 $\mu g/m^3$. Those values are in the range associated with lifetime cancer risks of about 1×10^{-6} to 1×10^{-5} (CAPCOA, 1992). Thus the screening procedure used in this study was sensitive enough to identify products that might convey significant indoor health risks, even if only the TLD-1 monitor had been used.

4.4.4 TDI Final Test Calculations

The TDI emission curves measured in the final tests were modelled using the approach of Colombo et al. (1990), in the same manner as described in Section 4.4.2 for the HCHO curves. The plots of $\mu g/m^3$ TDI versus time, and the corresponding model fitting results, are shown in Appendix G. The final TDI tests were conducted with continuous ventilation of the chamber, with the result that the residence time of emitted TDI in the chamber was short, and consequently the loss of TDI to the chamber walls was estimated to be small (i.e., less than 2 percent). No correction was made for this small effect in calculating TDI emission rates from the final test data. An estimate is presented in Section 5.5 of the overall uncertainty in the TDI emission rates determined in final testing of the concrete water stop product.

5.0 DATA QUALITY

In this section a variety of results are presented that document the quality of the data. These results include comparisons conducted to control and to check the validity of the data, external quality assurance analyses, and achievement of Data Quality Objectives (DQO's). Also included is an uncertainty analysis for the HCHO emission rate measurements.

5.1 Internal Data Quality Efforts for HCHO Tests

In this section the several activities performed to establish data quality are described, and quantitative results are presented. These results are then used in section 5.3 to determine the extent to which the DQO's were met, and in section 5.4 to estimate the overall uncertainty in the emission rate measurements.

5.1.1 Chamber Characterization and Control

An initial step in the data quality effort was characterization of the twin test chambers before testing was conducted. The leakage rate of both chambers was tested by injecting SF_6 as a stable tracer into clean air in both chambers. The SF_6 content of the chamber air was then determined using a gas chromatograph (GC) (Shimadzu Mini-2) with electron capture detector. The GC automatically sampled about 100 cm^3 of air from the chamber every five minutes. There was no air flow through the chambers other than this withdrawal of sample air, but the air within both chambers was mixed by the internal fans. Performance of SF_6 measurements over several hours indicated leak rates of 0.0138 per hour for the chamber maintained at Typical conditions, and 0.0065 per hour for the chamber at Elevated conditions. These values agree well with previous data on the chambers from past studies, and are very small relative to the air exchange rate values of 1.0 and 0.3 per hour, respectively.

In separate tests, the rate of mixing within the chambers was assessed by injecting SF_6 near the wall of the chamber while sampling with the automated GC. These tests showed that complete mixing of SF_6 throughout the chamber occurred within the five-minute cycle time of the GC.

The stability of gaseous HCHO in the two chambers at test conditions of temperature and relative humidity was also tested. HCHO levels of 50-300 ppbv (comparable to levels occurring in the product tests) were prepared in the chambers by using a syringe drive to inject small quantities of 0.01 M HCHO solution through a heated vaporizing probe into the chambers. HCHO concentrations then were determined over several hours using the real-time HCHO monitor. Chamber conditions were static except for the 2 L/min flow withdrawn by the monitor. After correction for chamber leak rates determined previously, and for the 2 L/min sample flow, the loss rates of HCHO to the chamber surfaces were found to be 5 to 6 percent per hour. These loss rates are much smaller than the chamber air exchange rates noted above.

Temperature, relative humidity, and air exchange rate were closely controlled during nearly all tests. The exception was humidity control in testing of latex wall paints and wallpaper. The water released from those products resulted in larger variations in chamber relative humidity than in other tests, particularly under the Elevated test conditions. Temperature and RH were recorded continuously in all tests, and those data were reviewed after the completion of testing to assess the precision and accuracy of temperature and RH control.

The average chamber temperature in the individual tests conducted under Typical conditions ranged from 68.7°F to 71.6°F, averaging 70.0°F, with a standard deviation of 0.75°F (0.42°C). In the Elevated conditions, individual average test temperatures ranged from 78.5°F to 82.1°F, averaging 80.2°F (± 0.59°F (0.33°C)). The standard deviation of average temperatures in Typical conditions (i.e., 0.75°F (0.42°C)) was taken to represent the overall accuracy of temperature control in this study.

The precision of temperature control was estimated from the variation observed in chamber temperature in the individual chamber tests. Under Typical conditions, the standard deviation of chamber temperature in individual tests ranged from 0.34°F to 1.54°F, averaging 0.72°F (0.40°F). Under Elevated conditions the corresponding values were 0.22°F to

2.27°F, averaging 0.60°F (0.33°C). The larger of the average temperature variations, i.e., 0.72°F (0.40°C) in Typical conditions, was chosen to represent the overall precision of temperature control in this study.

The average RH value in individual tests under Typical conditions ranged from 47.5 to 56.2 percent RH, averaging 51.3 (± 1.7) percent RH. Under Elevated conditions, the corresponding range was 44.3 to 66.4 percent RH, averaging 50.2 (± 2.64) percent RH. The larger of the two standard deviations, i.e., 2.64 percent RH in Elevated conditions, was taken to represent the overall accuracy of RH control in this study.

Precision of RH control was evaluated in the same way as was temperature. The standard deviation of RH in individual tests under Typical conditions ranged from 0.63 to 5.48 percent RH, averaging 2.25 percent RH. The corresponding results from individual tests under Elevated conditions were 0.91 to 16.2 percent RH, averaging 2.23 percent RH. The larger value of 2.25 percent RH from Typical conditions was used to represent the overall precision of RH control.

Air exchange rate was controlled by two electronic mass flow controllers on each chamber. Air flows were displayed continuously but were not recorded by the data system. Based on the stability of observed flows and the accuracy of calibrations conducted by Battelle's Instrument Laboratory, precision and accuracy are both estimated to be about 1 percent for each flow controller. As a result, an overall precision of 2 percent and accuracy of 2 percent are estimated for air exchange rate in each chamber.

5.1.2 Chamber Background HCHO Levels

An important factor in obtaining good emission rate data is the cleanliness of the test chambers. The 1.43 m^3 chambers exhibited little memory effect, and in nearly all cases background HCHO levels below the 10 ppbv target level were achieved. In only a few cases was it necessary to wash the interior chamber walls with water, or to purge extensively with clean air, to reduce the chamber background below the 10 ppbv target. In a few instances, chamber background levels above 10 ppbv were tolerated because emissions from the product to be tested were expected (and were subsequently found) to greatly exceed the background level.

A quantitative presentation of the background HCHO levels observed in this study is shown in Figures 5 and 6. Figure 5 shows the histogram of all 131 chamber HCHO background determinations made by the DNPH method, and Figure 6 shows the corresponding histogram of all 140 background determinations made with the real-time monitor. The two data sets are of different sizes because of occasional omissions due to sampling problems, and thus do not represent exactly the same set of tests. However, as shown subsequently the two methods agreed closely on simultaneous measurements. Figure 5 shows that 118 of the 131 DNPH determinations were below the 10 ppbv target level, and all but five were below 14 ppbv. Similarly, Figure 6 shows that 128 of the 140 real-time results were below 10 ppbv, and all but five were below 14 ppbv. These results establish that the test chamber background HCHO levels were maintained at a low level throughout the study.

Chamber background levels of the other four target compounds were lower than those of HCHO. Acetaldehyde background values ranged from 0.14 ppbv to 2.22 ppbv, averaging 0.82 ppbv. Propionaldehyde background values ranged from less than 0.1 ppbv to 5.1 ppbv, averaging 0.26 ppbv. Neither MEK nor MIBK were detected in chamber background samples (i.e., levels were always <0.1 ppbv).

5.1.3 Calibration Standard Checks

At the start of the study, checks were made on the standards for the two HCHO measurement methods. The accuracy of the HCHO content of the 2 μg/ml five-component standard prepared by Battelle was checked by obtaining a new HCHO standard from Radian Corporation. Those two standards were found to agree within 2 percent. Similarly, the 1.33×10^{-5} M HCHO solution used as the continuing daily standard for the real-time monitor was analyzed by the DNPH method, showing agreement with the expected value within 1.6 percent.

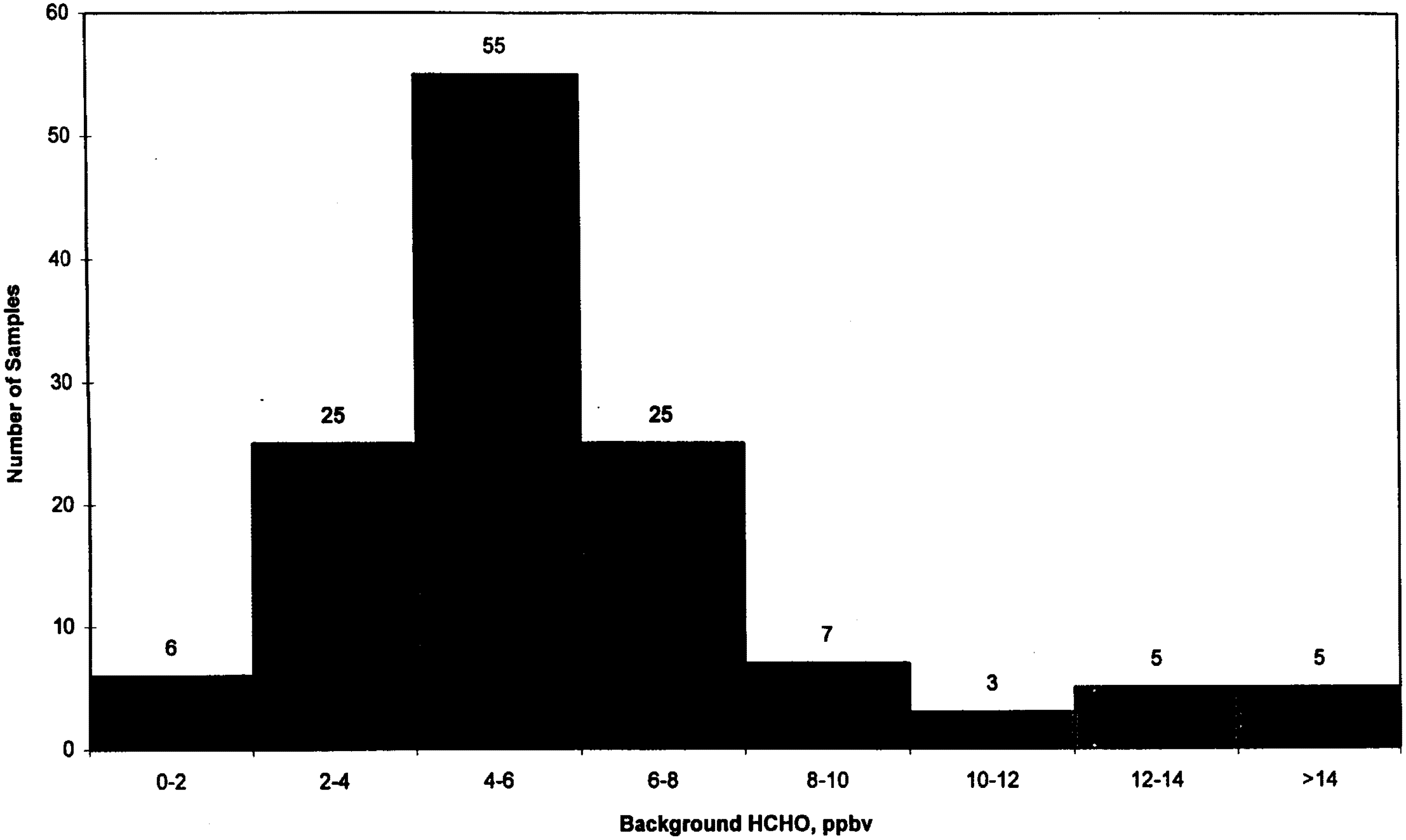

FIGURE 5. CHAMBER BACKGROUND HCHO CONCENTRATIONS BY DNPH METHOD

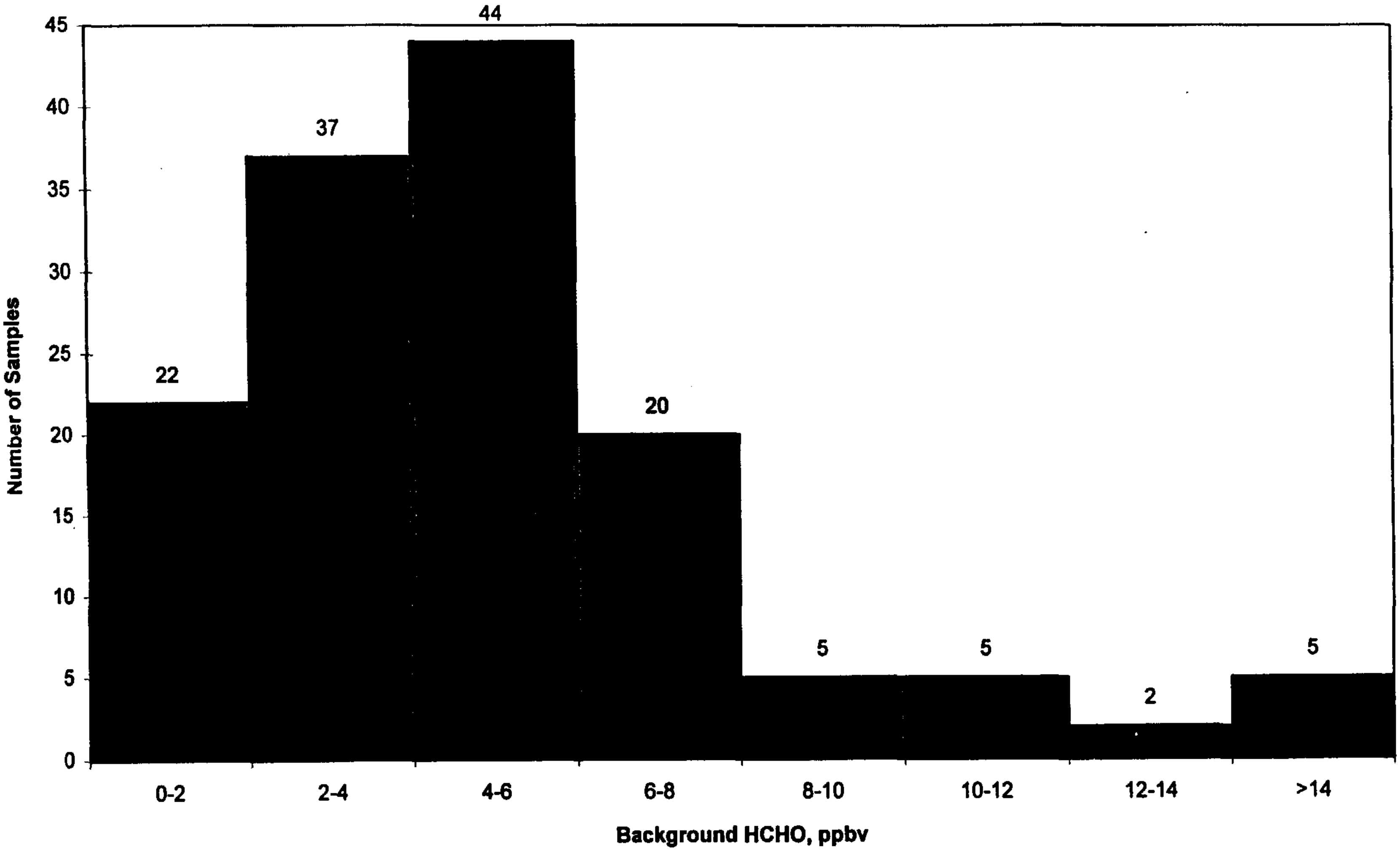

FIGURE 6. CHAMBER BACKGROUND HCHO CONCENTRATIONS BY REAL-TIME METHOD

Records were also kept of all analyses of the five-component 2 μg/ml DNPH standard throughout the study. That standard was analyzed 45 times between June 7 and November 3, 1995 and the peak areas obtained for all five target compounds were recorded. In addition, a standard of 2 μg/ml of the HCHO/DNPH derivative was prepared near the end of the study, as a result of a slight decay of the HCHO peak area in the five-component standard. That standard was analyzed an additional three times. Table 5 lists the results of all analyses of these standards, in terms of the averages and standard deviations of the peak areas.

TABLE 5. SUMMARY OF ANALYSES ON DNPH STANDARD SOLUTIONS[a]

Target Compound	Number of Analyses	Average Peak Area	Standard Deviation of Peak Areas	Relative Standard Deviation (%)
HCHO	48[b]	284,034	16,807	5.9
Acetaldehyde	45	352,218	20,888	5.9
Propionaldehyde	45	395,244	24,255	6.1
MEK	45	367,890	24,298	6.6
MIBK	45	326,679	20,356	6.2

(a) Analyses conducted between June 7 and November 3, 1995.
(b) Forty-five analyses of five-component standard showed 5.98 percent RSD; three analyses of HCHO-only standard showed 1.91 percent RSD.

Table 5 shows that the stability of the DNPH standard was excellent throughout the study. The relative standard deviations (RSD) of all five compound peak areas were 5.9 to 6.6 percent of the mean values obtained over the five months of use of the standard. Note that the actual uncertainty in any individual DNPH analytical result is smaller than the percent RSD values shown in Table 5. This is so because Table 5 shows the total variability of the analysis over the full period of the study, whereas each batch of DNPH samples was referenced only to the calibration standard on the day of analysis. Thus day-to-day variability in the HPLC analysis is accounted for by the standard analyzed with each sample batch.

A corresponding record was kept of the response to the 1.33×10^{-5} M HCHO standards that were analyzed by the real-time monitor on every test day (73 total analyses). The nominal gas-phase equivalent concentration of this aqueous concentration varied from day to day as a result of changes in scrubber solution flow rate, caused by gradual aging of the peristaltic pump tubes in the HCHO monitor. Over the five-month chamber testing period, the gas-phase equivalent concentration ranged from 92.5 ppbv to 111.5 ppbv, averaging 100.2 (± 4.5) ppbv, resulting in an RSD of 4.5 percent. More important, however, is the variation in actual instrument sensitivity that occurred during the study. Measured instrument sensitivity is affected by the reagent solution used, by slight decay of the aqueous standards over a few days of use, and by variations in lamp intensity in the fluorometer. The full scale range of the monitor on the most frequently used sensitivity setting averaged 140.6 ppbv (± 12.8 ppbv), for a percent RSD of 9.1 percent, based on all calibrations over the five-month study period. As noted above for DNPH, the actual uncertainty in real-time HCHO results is less than that, because day-to-day variations are accounted for by the daily calibrations.

5.1.4 DNPH Duplicates

In all chamber tests, two simultaneous DNPH samples were taken from each chamber for determination of product emissions. Comparison of those duplicate results provides an indication of the precision of the DNPH measurements.

Figure 7 shows the comparison of HCHO results from duplicate DNPH samples. This figure shows a total of 134 data points, ranging from 2.2 to over 1,800 ppbv HCHO; the 1:1 line of perfect agreement is also shown. It is apparent that excellent agreement was obtained in duplicate DNPH samples. The linear regression to the data in Figure 7 has the form DUP 2 = 1.013 (DUP 1) - 0.64 ppbv, with an r^2 value of 0.999. The precision of the DNPH HCHO results is indicated by the percent RSD values of the individual duplicate data pairs: those 134 RSD values range from 0.04 percent to 65.4 percent, averaging 4.30 percent. For those 89 percent of the data below 300 ppbv the average percent RSD is 4.59 percent. This comparison shows that very good precision was obtained in HCHO sampling and analysis by DNPH.

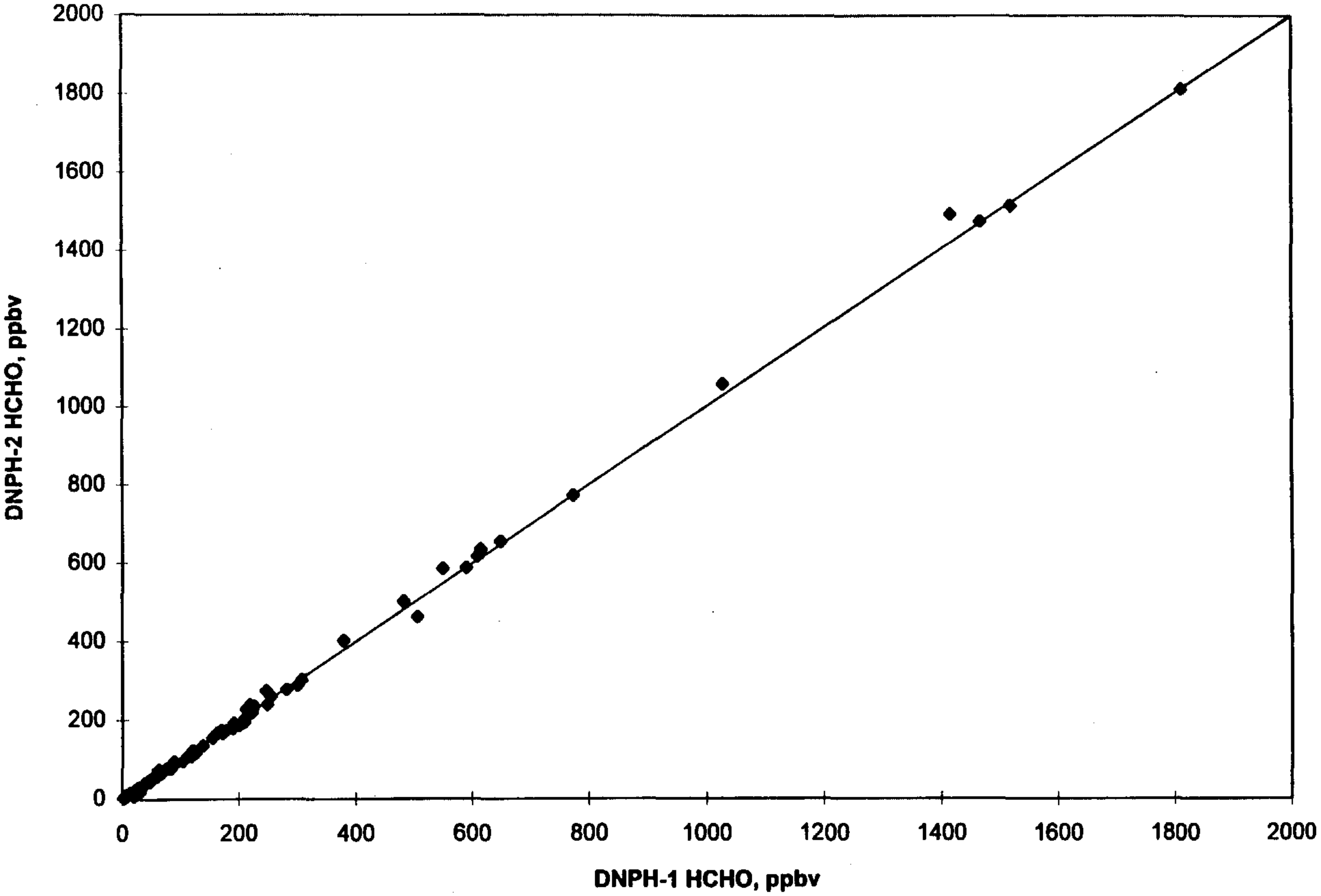

FIGURE 7. DNPH DUPLICATE COMPARISON

Similar agreement was found for acetaldehyde and propionaldehyde in DNPH duplicates. The linear regression of the acetaldehyde data has the form DUP 2 = 0.981 (DUP 1) + 0.11 ppbv, with $r^2 = 0.996$, for 129 data points ranging from <0.1 to 49.9 ppbv. The average percent RSD for all 129 data pairs was 9.1 percent. For propionaldehyde the regression is DUP 2 = 0.995 (DUP 1) + 0.00 ppbv, with $r^2 = 0.997$, for 103 data points ranging up to 11.5 ppbv. The average percent RSD for all 103 data pairs was 16.6 percent. MEK and MIBK were below 0.1 ppbv in all samples.

5.1.5 DNPH/Real-Time Comparison

Averaging of the real-time HCHO data over the periods of collection of DNPH samples allows a direct comparison to be made between the HCHO results from the two methods. The DNPH samples were collected at times when the real-time monitor indicated relatively stable HCHO levels in the test chambers, so little error is introduced by averaging the real-time data for comparison. The two methods were operated and calibrated completely independently, so comparison of the two sets of results provides a valuable assessment of the accuracy of both methods. The comparison of the two methods is shown in Figure 8, which plots the real-time HCHO data versus the corresponding DNPH data. All DNPH samples are treated independently in this figure, i.e., no averaging of duplicate samples has been done. Figure 8 contains 385 data points, including both chamber background samples and product test samples, ranging from 0.3 ppbv to over 1,800 ppbv. The 1:1 line of perfect agreement is also shown in Figure 8.

It is clear from Figure 8 that HCHO results from the two methods agreed closely. The data fall along the 1:1 line over a wide range of concentrations. The linear regression to the data in Figure 8 has the form Real Time HCHO = 0.992 x DNPH HCHO + 0.14 ppbv, with an $r^2 = 0.973$. Over 92 percent of the data points in Figure 8 lie below 300 ppbv; for that subset of the data the linear regression has the form Real Time HCHO = 1.01 x DNPH HCHO - 0.48 ppbv, with an $r^2 = 0.992$. These results establish the accuracy of the HCHO concentration measurements, and in turn the accuracy of the HCHO emission rates based on those data.

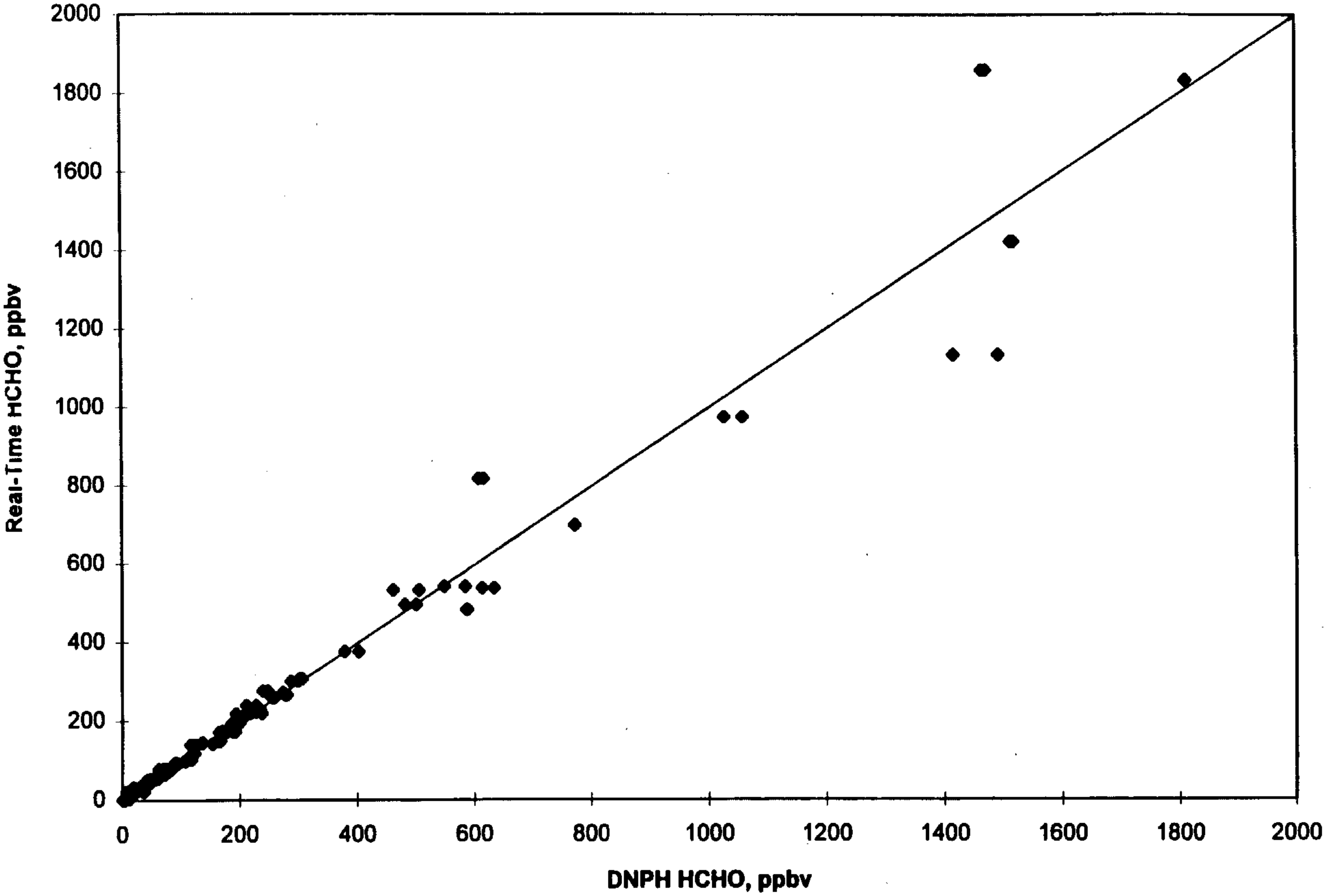

FIGURE 8. REAL-TIME/DNPH COMPARISON

5.1.6 Duplicate Chamber Tests

For 10 products, the chamber tests were run twice on separate samples, to assess the degree of repeatability of the entire test procedure. Of those ten products, eight were dry products (four bare UF wood products, three coated UF wood products, and one decorative laminate), and two were wet products (one latex paint, one nail hardener). The duplicate tests were conducted on successive days, so that sample storage was as nearly identical as possible for the duplicate samples. However, the purpose of this study was to assess emission rates under conditions representative of those in a home. As a result, extensive product conditioning, intended to assure uniformity of emissions across all samples, was not conducted. Such conditioning has been used in detailed studies focussing on inter- and intra-lab variability in test procedures (e.g., Matthews et al., 1987; DeBortoli and Colombo, 1993). Furthermore, in this study duplicate tests were conducted on a variety of products, not on a single highly uniform product as in other studies (Matthews et al., 1987; DeBortoli and Colombo, 1993). Thus the duplicate test results from this study are expected to include the effects of real variability within and between product types, as well as variability due to the test procedures.

5.1.6.1 Duplicate Tests on Dry HCHO Products. The results from the duplicate tests are presented in detail in Section 6 of this report. Figure 9 summarizes the duplicate results for dry samples, showing a comparison of the emission rates (in $\mu g/m^2/hr$) determined in those eight duplicate tests. Each test consists of measurements in both Typical and Elevated conditions, so Figure 9 contains 16 data points. In all cases the second duplicate run is plotted as the y value, and the first run as the x value. The 1:1 line is shown in Figure 9 as the solid line. The data are scattered along the 1:1 line, covering a range from 1 to nearly 400 $\mu g/m^2/hr$. A linear regression to the data has the form DUP 2 = 1.14 (DUP 1) - 6.7 $\mu g/m^2/hr$, with an $r^2 = 0.880$, and is indicated by the dashed line in Figure 9.

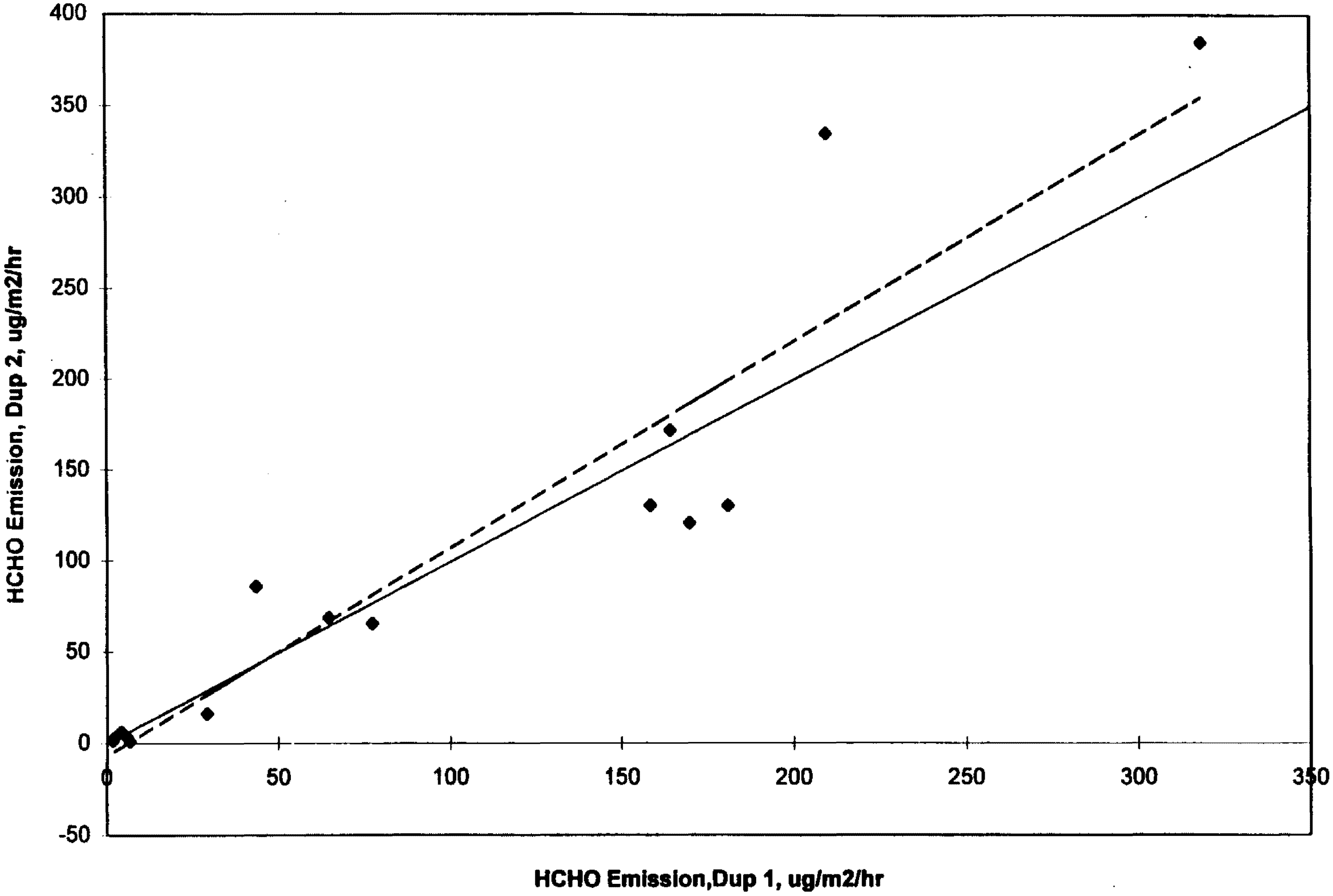

FIGURE 9. DRY PRODUCT DUPLICATE TEST RESULTS

The degree of duplication is also indicated by the percent RSD values of the duplicate data pairs in Figure 9, which range from 3.1 to 46.3 percent, averaging 23.1 percent, with a median of 24.0 percent. (One outlier was excluded from this calculation, a duplicate pair averaging 3.86 $\mu g/m^2/hr$ with an RSD of 105 percent. This pair was judged to be an outlier because 5 other duplicate pairs with means of 1.5 to 5.1 $\mu g/m^2/hr$ showed RSD values of 15.6 to 35.9 percent, averaging 26.6 percent, similar to the entire duplicate set.) Thus, the results in Figure 9 indicate good duplication of chamber tests within the constraints of this study.

Duplicate HCHO test results from other studies, with which to make comparisons to the results in Figure 9, are almost non-existent. However, the study by Matthews et al. (1987) is of interest. That study determined HCHO emission rates from particleboard underlayment in small chambers at two separate labs (EPA and Oak Ridge National Laboratory (ORNL), to test the comparability of small scale chamber results. Matthews et al. report eight cases in which emission rates in $\mu g/m^2/hr$ were measured under identical conditions in the two labs. They report a linear regression of EPA results vs. ORNL results with slope = 1.07, intercept = -15 $\mu g/m^2/hr$, and $r^2 = 0.881$, for eight data points. These regression results are similar to those for the data in Figure 9. For the eight EPA and ORNL data pairs, an average percent RSD of 6.3 percent is calculated.

Although two labs participated in the Matthews et al. (1987) study, great effort was put into assuring comparability of the chambers, test conditions, and measurement methods. Extensive intercomparisons and cross-calibrations of measurement methods were conducted. Thus the two labs were as closely matched as possible in all aspects of the testing. Also, Matthews et al. tested only a single product, using small pieces cut from a single board. Matthews et al. also tested <u>identically the same</u> pieces in the two chambers, by shipping the pieces between labs. The samples tested were stored for several months under laboratory conditions, then equilibrated together under controlled conditions for two months prior to testing. Samples were then also conditioned together <u>at the test conditions</u> for two days prior to the actual tests. These efforts would have the effect of minimizing any sample-to-sample variability or short-term emission changes after obtaining the samples. Furthermore, because only a single material was tested, the ranges of HCHO emission rates in the Matthews study were relatively narrow, i.e., from 88 to 240 $\mu g/m^2/hr$. Nevertheless, despite the extensive efforts to assure sample uniformity, Matthews et al. (1987) reported that sample-to-sample variability was the largest cause of the variation in test results.

Relative to the Matthews et al. study, several factors tend to increase the variability of duplicate test results in the present study. This study deliberately tested different pieces of the products, albeit from the same purchased material, in duplicate runs, and aimed for realism rather than lengthy equilibration in sample storage and conditioning. Furthermore, because of the variety of products tested, the range of emission rates in the present duplicate tests was large. These duplicate tests were also performed at two different test conditions simultaneously, possibly introducing variability due to the added complexity of maintaining two test environments rather than one. In light of these factors, the degree of duplication shown in Figure 9 is good. Given the precision and accuracy in HCHO determination shown in previous sections, it seems likely that sample-to-sample variations in emission rates are an important cause of variability in the duplicate test results.

Similar observations result from two recent studies in which small chamber test methods were intercompared (Crump et al., 1996; Liles et al., 1996). Good agreement was found among three small chamber methods using UF wood products preconditioned for one year (Crump et al., 1996). In contrast, poor agreement was found between two small chamber methods using UF wood products with little preconditioning (Liles et al., 1996). Sample-to-sample variability, partly due to the small sample sizes used, was named as a key factor in the poor agreement found.

Duplicate test results for compounds other than HCHO provide some additional comparisons. Turner et al. (1995) performed triplicate tests of oak-veneered particleboard and plywood in a small test chamber, and reported "semi-quantitative" analyses for a number of volatile organic compounds (VOC). Those preliminary data indicate substantial variability in emission rates in triplicate runs. For example, toluene and xylene emissions show RSD values of about 35 percent and about 20 percent, respectively. Similar results were found in the extensive interlaboratory intercomparison reported by DeBortoli and Colombo (1993). In that study emissions of four VOC's from PVC floor tile samples were measured in 22 laboratories. Analysis of variance in the test results showed that the intra-lab component of variability in PVC tile emission rates ranged from 11.1 percent to 27.7 percent, relative to mean emission rates of 61 to 791 $\mu g/m^2/hr$, for the four target VOC's. Given the range of products and emission rates determined, these results are consistent with the degree of duplication found in this study, and shown in Figure 9.

5.1.6.2 Duplicate Tests on Wet HCHO Products. Table 6 shows the results from the duplicate tests on two wet products. Listed in Table 6 are the product surface area and surface loading, the model fit parameters **a-d**, the initial emission rate R_o of the product, the final steady-state emission rate of the product, and the total quantity of HCHO emitted over the course of the test. Duplicate test results from both the Typical and Elevated chambers are shown. The two wet products were very different: the latex paint applied to gypsum board emitted little HCHO and large amounts of water vapor, whereas the nail hardener applied to an aluminum foil substrate produced substantial HCHO emissions despite a small surface area in the chamber. The C_{max} values measured in the Typical and Elevated conditions were about 80 and 105 $\mu g/m^3$, respectively, for the latex paint, and about 190 and 275 $\mu g/m^3$, respectively, for the nail hardener.

Table 6 shows that the amounts of each product applied to the substrate materials were closely similar in the duplicate tests. (The test results shown have <u>not</u> been corrected for the small differences in product loadings.) Duplication of R_o results is reasonably good (within 25 percent RSD), except for the Elevated tests of the latex paint. The R_o values are very sensitive to the shape of the initial concentration increase and peak. For the latex paint the water vapor emitted from the product caused a loss of humidity control in the test chambers early in the test, and may have affected the initial emissions curve, causing poor duplication for that test. For the latex paint, the final emission rates are all 1.2 to 1.7 percent of the initial emission rates, and duplication of the final rates is good (15-20% RSD). Duplication of the final rates is not good for the nail hardener, however the final rates represent only 0.2 percent or less of the initial rates, and the duplication in final rates may simply be due to near depletion of HCHO emission from the small sample surface areas. The integrated HCHO emission results in Table 6 show better agreement than the R_o values, because they are less affected by the shape of the initial emission peak. All of the duplicate data for integrated HCHO emission agree within 15 percent (RSD values are all less than 10 percent). Note that the two products in Table 6 emitted about the same total amounts of HCHO, despite greatly different surface areas.

TABLE 6. SUMMARY OF DUPLICATE HCHO CHAMBER TESTS ON WET PRODUCTS

Product	Test Conditions	Surface Area (m^2)	Product(a) Loading (mg/cm^2)	Model Parameters(b)				Initial Rate R_o ($\mu g/m^2/hr$)	Final Rate ($\mu g/m^2/hr$)	Integrated(c) HCHO Emission (μg)
				a	b	c	d			
Lower Quality Latex Paint	Typical	1.49	9.75	92.7	6.21	76.2	0.490	518	8.1	649
		1.49	9.80	103	7.15	82.3	0.576	663	9.9	746
	Elevated	1.49	7.88	120	3.93	86.7	0.152	441	7.5	521
		1.49	9.07	113.8	7.88	76.0	0.109	854	10.1	597
Nail Hardener	Typical	0.007	15.6	350.3	3.25	338.9	0.787	178,000	124	837
		0.007	16.4	307.1	4.63	299.0	0.610	253,000	471	873
	Elevated	0.007	15.7	322.6	4.69	300.4	0.252	293,000	610	721
		0.007	17.9	369.8	4.93	357.6	0.248	354,000	260	716

(a) Average mass of product applied per square centimeter of substrate surface.
(b) Parameters a and c have units of $\mu g/m^3$; parameters b and d have units of hr^{-1}.
(c) Test duration 18 hours for latex paint, 22 hours for nail hardener.

5.1.7 Large/Small Chamber Comparisons

The largest body of data on HCHO emissions from products is that obtained by the wood products industry using standard large chamber procedures (e.g., Margosian, 1990, 1995). Those procedures are required by Federal regulations for certain products, and implemented by industry as voluntary standards for others. The present study used twin chambers of 1.43 m^3 volume, much smaller than those used by industry. The comparability of the present results to those obtained in large chambers was assessed by subjecting two UF wood products to the tests at Typical and Elevated conditions, and to a separate (and simultaneous) test in a large chamber. Battelle's 17.3 m^3 walk-in smog chamber was used as the large chamber for this purpose. The two products tested in this way were 5/8 inch particleboard underlayment and 3/4 inch stock hardwood plywood. For this purpose, additional sample pieces were obtained for these products at the same time as the samples for testing in the small chambers. The sample pieces used in both the large and small chambers were identical in size, so that the ratio of sealed edge area to exposed surface area was identical. The appropriate product loadings were achieved by using a larger number of sample pieces in the large chamber than in the small chamber. The quantity of material needed for the large chamber test prevented obtaining all samples from a single board, but all samples were obtained from adjacent boards in a product stack.

The procedure used was to conduct the large chamber test with the same product loading L as in the twin 1.43 m^3 chambers, and with the same air exchange rate (1.0 hr^{-1}) as in the Typical conditions. Achieving this large an air exchange rate in the large chamber necessitated using outside air (HCHO level <3 ppbv) to supplement the clean air supplied to the chamber. As a result, the large chamber temperature could not be maintained at 70°F, as for the Typical conditions. Instead, both the Typical and large chamber results were adjusted to conditions of 77°F and 50 percent RH using the correction factors in the ASTM large chamber procedure (ASTM, 1990a).

Table 7 shows the test conditions and results of the large/small chamber comparisons. For the 5/8 inch underlayment, the small chamber results were within 15 percent of the large chamber results. The 3/4 inch plywood exhibited a surprisingly low emission rate, but the rate determined in the small chamber was within 25 percent of that in the large chamber. These results are consistent with the agreement found in duplicate tests (section 5.1.6), and indicate that the emission rates obtained in the twin 1.43 m^3 chambers are representative of those that would be obtained in large chambers under the same conditions.

TABLE 7. RESULTS OF COMPARISONS OF PRODUCT EMISSIONS IN LARGE AND SMALL CHAMBERS$^{(a)}$

Product	Chamber	Temp. (°F)	RH (%)	HCHO$^{(c)}$ $\mu g/m^3$	Emission Rate $\mu g/m^2/hr$
5/8 inch underlayment	Large	78.2 (± 1.3)$^{(b)}$	55.3 (± 3.5)	98.0	213
	Small	69.6 (± 0.7)	51.3 (± 1.8)	83.6	182
3/4 inch plywood	Large	77.6 (± 0.7)	52.8 (± 1.7)	4.8	10.4
	Small	69.6 (± 0.9)	52.2 (± 3.2)	6.0	13.0

(a) Large chamber = 17.3 m^3; small chamber = 1.43 m^3; all tests conducted with product loading of 0.46 m^2/m^3.
(b) Mean (± std. dev.) and 1.0 air exchange per hour.
(c) Corrected to 77°F and 50 percent RH.

In a separate study, Battelle staff also used the 17.3 m^3 chamber to check the emission characteristics of particleboard underlayment supplied by industry for use in U.S. EPA's Residential Indoor Air Formaldehyde Testing Program (EPA, 1994). A sample of 5/8 inch Type 1-M-1 underlayment was tested in the chamber according to standard procedures (ASTM, 1990a), at a product loading of 0.43 m^2/m^3, and an N value of 0.5 hr^{-1}. Chamber conditions during the entire test averaged 79.1 (± 1.6) °F and 54.8 (± 2.3) percent RH. The HCHO level determined at the end of the test was adjusted to 77°F and 50 percent RH (ASTM, 1990a) using the actual chamber conditions during the DNPH sample collection, i.e., 77.3 (± 0.2) °F and 53.3 (± 0.6) percent RH. The adjusted concentrations from two simultaneous DNPH samples were 126 ppbv and 135 ppbv, in close agreement with the result of 144 ppbv obtained by industry for this material (Hare, et al., 1996). The close comparability of Battelle results with industry results in this test is consistent with the agreement in large and small chamber results shown in Table 7, and supports the representativeness of the product emission rates determined in the small chambers in this study. Consequently, the emission rates determined in this study can be compared with the much larger existing body of data on HCHO emissions from wood products.

5.2 External Data Quality Checks for HCHO and Other Carbonyls

As an additional check on the data quality, aliquots of DNPH samples, blanks, and standards were submitted to Air Toxics Ltd. (AT) (Folsom, California) for confirmatory analysis for the five target carbonyl compounds. AT reported the results in terms of the μg of each compound per 5 mL of DNPH solution. The AT analyses confirmed that HCHO was the primary compound present in the samples, with acetaldehyde also present in some samples, and the other target compounds rarely to never present. A total of 60 samples were sent to AT. Formaldehyde and acetaldehyde were detected by both labs in sufficient samples to allow a comparison of Battelle and AT results. For the other three target compounds, only AT results on Battelle's five-component standard are reported.

Figure 10 shows AT's results for HCHO plotted versus Battelle's results, which have been converted to μg/5 mL units for this comparison. The solid line is the 1:1 line, and the dashed line is the linear regression. The data fall close to the 1:1 line in nearly all cases, indicating confirmation of Battelle's HCHO results. The lone exception is a single sample in which AT reported nothing detected, whereas Battelle's results clearly show substantial HCHO content. With that outlier excluded, the linear regression has the form AT = 0.959 x Battelle + 0.09 μg/5 mL, for 51 data points, with $r^2 = 0.999$. Analysis of Battelle's standard solutions is also shown in Figure 10. Three separate analyses of the standard are represented by the open square at about (x, y) = (1.4, 1.4); the three different results are indistinguishable from one another in the figure.

The corresponding comparison for acetaldehyde is shown in Figure 11. The AT results were generally about 20-30 percent higher than the corresponding Battelle results. The linear regression line in Figure 11 has the form AT = 1.27 x Battelle + 0.008 μg/5 mL, for 28 data points, with $r^2 = 0.996$. Note that the AT analyses of the Battelle standard also fall on the regression line. Thus the slope of the line results from a disagreement between the Battelle standard and the AT standard. Given the stability of acetaldehyde in the five-component standard, and the excellent results shown above for HCHO in that standard, the validity of Battelle's acetaldehyde standard seems highly likely. In any case, the results in Figure 11 confirm both the absolute and relative levels of acetaldehyde emission in the chamber tests.

In two analyses of Battelle's five-component standard, AT reported 3.0 and 3.2 μg/5 mL of propionaldehyde, versus Battelle's value of 2.44 μg/5 mL; 3.1 and 3.4 μg/5 mL of MEK, versus Battelle's value of 2.86 μg/5 mL; and 6.6 and 7.1 μg/5 mL of MIBK, versus Battelle's value of 3.57 μg/5 mL. These results for propionaldehyde and MEK are similar to those shown in Figure 11 for acetaldehyde, i.e., a small difference between Battelle and AT, with AT results higher. The difference in results for the MIBK standard is much larger. We note that AT also reported a nearly constant level of about 0.5 μg/5 mL of MIBK in some samples. However, Battelle staff had previously established by HPLC analysis with different columns and conditions that an unknown interferant, but not MIBK, was present in these

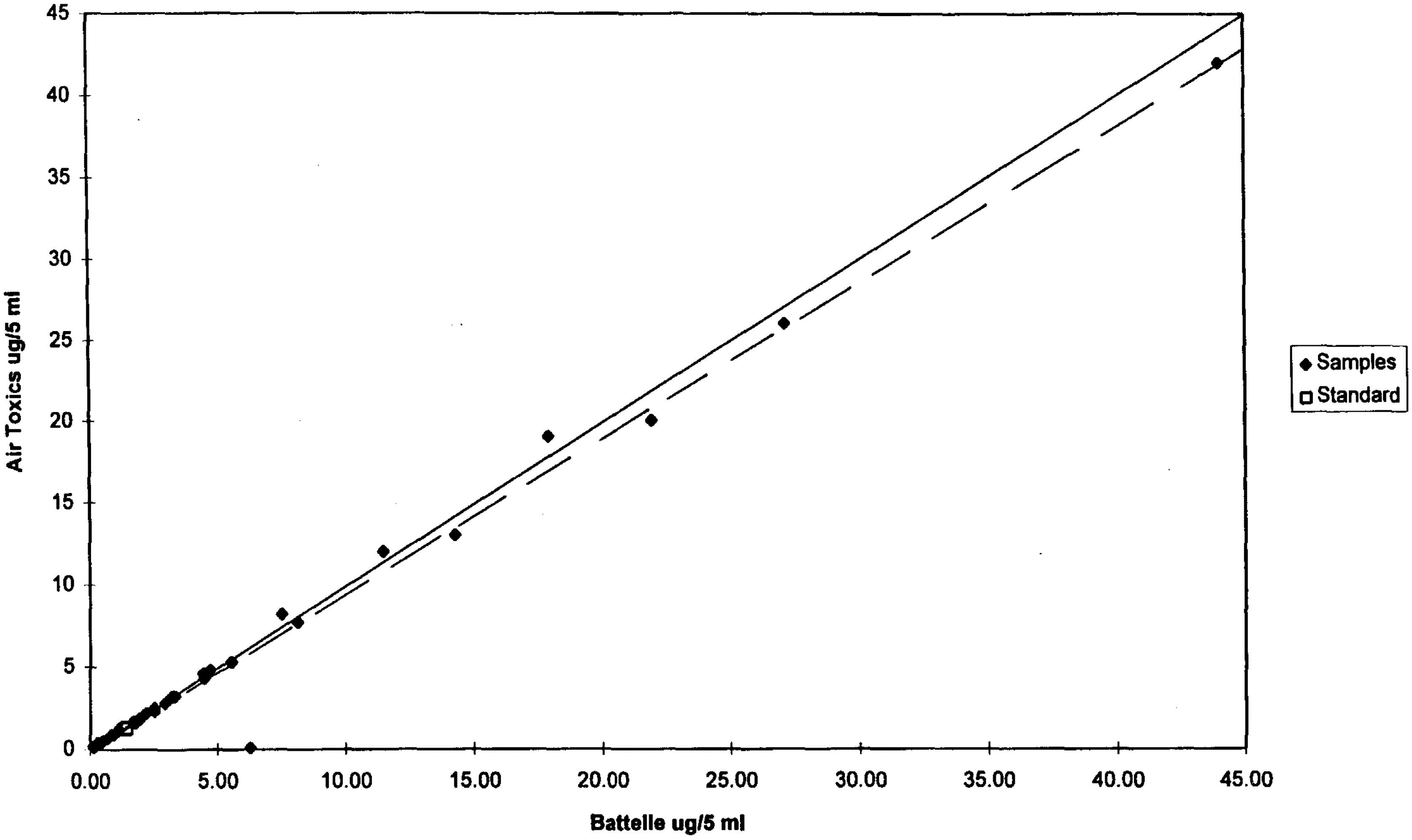

FIGURE 10. COMPARISON OF AIR TOXICS HCHO RESULTS TO BATTELLE RESULTS

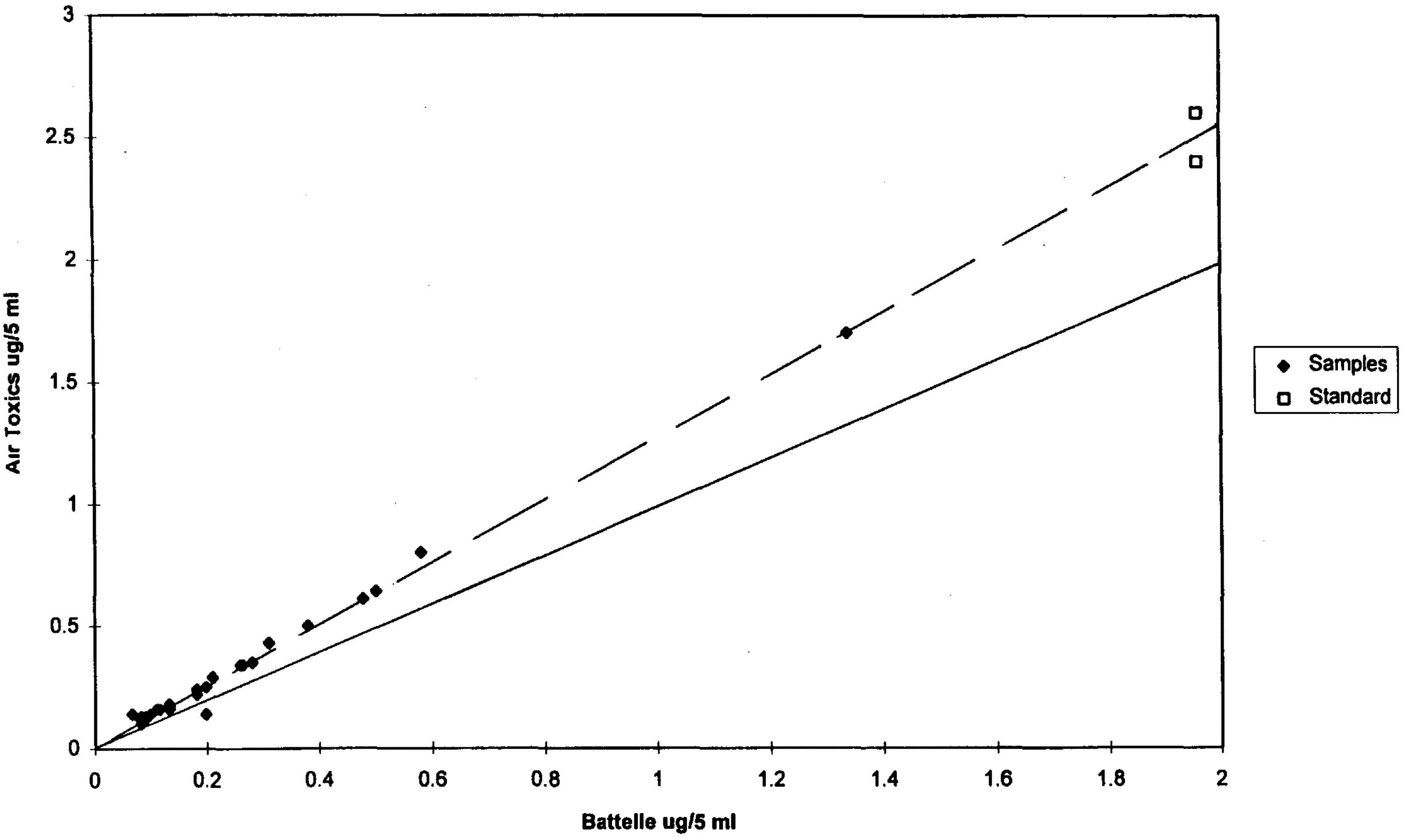

FIGURE 11. COMPARISON OF AIR TOXICS ACETALDEHYDE RESULTS TO BATTELLE RESULTS

samples. Since the routine analysis requested from AT could not have disclosed that interference, those AT results were disregarded.

5.3 Achievement of DQO's for HCHO Tests

As part of the Quality Assurance Project Plan (QAPP) written to accompany the test protocols for the HCHO chamber tests, a set of Data Quality Objectives (DQO's) was established. Those DQO's are listed in Table 1 of the QAPP, which is included as Appendix E of this report. The DQO's consist of target values for the precision accuracy, and data completeness of chamber conditions, sample surface area, and real-time and DNPH sampling, in both dry and wet product HCHO tests. Table 8 presents a summary of the actual results for every parameter for which a DQO was set (Appendix E). These actual results are based on the several tests and comparisons reported in Sections 5.1 and 5.2. Results which meet the corresponding DQO are shown in Table 8 in normal type; results which do not meet the corresponding DQO are in bold type, with comments in the table footnotes. The most conservative values were used for the actual results in Table 8. For example, DNPH method accuracy was assessed based on the regression slope in the comparison with AT results (Figure 10), although the comparison with real-time results (Figure 8) suggests better accuracy.

Table 8 shows that the target DQO's were met in nearly all cases. The few departures from the DQO's were minor, and Table 8 indicates good performance of the chamber tests.

5.4 Uncertainty Analysis for HCHO Tests

The degree to which the measured emission rates represent the true emission rates of the products tested depends on the uncertainties present in determining those emission rates. An estimate of the overall uncertainty in the measurement of HCHO emission rates can be obtained by appropriately summing the individual uncertainties, including both random errors (i.e., precision) and bias (i.e., accuracy), in various parameters of the tests. This estimate has been done for the test procedure overall, rather than for each individual test. In the case

TABLE 8. DATA QUALITY ACHIEVED IN HCHO TESTS

Parameter	Precision	Accuracy	Data Completeness	
			Dry Products	Wet Products
Temperature	0.40°C	0.42°C	95	95
Relative humidity	2.25 % RH	2.64 % RH	95	95
Air exchange rate	2%(a)	2%(a)	100	100
Sample area	1%	0.5-3%(b)	100	100
HCHO concentration				
Real-time monitor	9.1%(c)	5%(d)	98.4	100
DNPH sampling	4.3%	4.1%(e)	95.2	100

(a) Estimated from stability of mass flow controllers.

(b) Accuracy of all sample areas was within 1 percent except for artificial nails (used as a substrate for nail polish testing) and permanent press shirts.

(c) Precision based on all analyses of 1.33 x 10^{-5} M standard (section 5.1.3). Daily calibrations reduce the resulting uncertainty in individual test results.

(d) Estimated based on accuracy of DNPH method and agreement between real-time and DNPH methods.

(e) Accuracy assessed based on slope of comparison with external analyses (Figure 10); actual accuracy probably somewhat better, based on comparison with real-time data (Figure 8).

of dry products, the factors affecting the uncertainty directly are those found in the emission rate calculation, Equation 1:

$$E = \frac{CN}{L} = \frac{CQ}{A} \qquad (1)$$

where Q = air flow rate through the chamber. The uncertainties in these factors can be taken directly from Table 8. In addition, temperature and relative humidity exert an effect on the emission rate, at least for wood products (ASTM, 1990a), and thus errors in the control of these test parameters may affect the degree to which the test results represent the nominal test conditions. This uncertainty estimate included consideration of both types of factors.

Chamber temperature and relative humidity effects were assessed by treating the precision and accuracy tolerances of these parameters separately, and calculating the corresponding errors in emission rates using the correction algorithms in the ASTM (1990a) procedure. This approach implicitly assumes that HCHO emissions from all products respond to temperature and RH variations in the same way as do the bare UF wood products for which the corrections were developed. This approach thus may overestimate the impact of T and RH variations on other products.

From Table 8, the precision and accuracy tolerances on temperature were 0.40°C and 0.42°C (0.72 and 0.76°F), respectively. The variations in emission rates expected from temperature variations of these magnitudes are 6.0 and 6.1 percent, respectively (ASTM, 1990a). Similarly, the precision and accuracy tolerances on RH from Table 8 are 2.25 and 2.64 percent RH, respectively, which lead to corresponding variations in emission rates of 3.8 and 4.4 percent, respectively. The uncertainties in C, Q, and A can be drawn from Table 8. For C by DNPH determination precision and accuracy tolerances are 4.3 and 4.1 percent, respectively; for Q, precision and accuracy of 2 percent apply, based on the air flow rate measurements; and for A, precision and accuracy tolerances of 1 percent represent the great majority of the products tested. Combining these various uncertainties in a root-mean-square manner provides an estimate of the overall percent uncertainty in measuring emission rates for dry products, i.e.:

$$\begin{aligned} \% \, U = \; & (0.06^2 + 0.061^2 + 0.038^2 + 0.044^2 + 0.043^2 + 0.041^2 + 0.02^2 + \\ & 0.02^2 + 0.01^2 + 0.01^2)^{1/2} \\ = \; & 12.3\%. \end{aligned}$$

Comparison of this result to the 23.1 percent average RSD obtained in the duplicate tests on dry products (section 5.1.6) suggests that much of the variability in the duplicate test results probably came from sample-to-sample variability in the products tested, rather than from variability in performance of the measurements. That suggestion is consistent with the findings of more tightly controlled comparisons by Matthews et al. (1987) and DeBortoli and Colombo (1993).

The estimated overall uncertainties in measuring the emission rates of acetaldehyde and propionaldehyde are larger than that calculated above for HCHO, because the percent RSD values found for these compounds in duplicate samples were higher than that for HCHO (Section 5.1.4). Those values, used as the measure of analytical precision, are 9.1 percent for acetaldehyde and 16.6 percent for propionaldehyde. This relatively poorer precision is probably due to the much lower concentrations of these compounds, as compared to the HCHO levels observed. Substituting these precision values into the equation above, with the other factors unchanged, gives overall measurement uncertainties of 14.7 percent for acetaldehyde and 20.2 percent for propionaldehyde.

The uncertainties in the calculated HCHO emission rates of wet products are more difficult to estimate, because the errors inherent in the modelling approach are difficult to assess. In addition, the process of applying the wet products and introducing the treated substrates into the chamber is more complex than the procedure used for dry products. As a result, the overall uncertainty in wet product tests is likely to be higher than for dry products. This is especially true for products that emit large amounts of water, such as latex paints and fresh wallpaper. The results from the two duplicate tests on wet products (Section 5.1.6) indicate overall uncertainties of about 25 percent in determining initial emission rate (i.e., R_o) values. The uncertainty in determining total integrated emissions during the test appears to be somewhat less, i.e., within about 10 percent. An uncertainty of 15 to 20 percent in determining final emission rates is indicated by the duplicate results from the latex paint.

5.5 TDI Data Quality

The quality of the TDI measurement data is indicated by four different types of information: (1) the calibration results from the NBPA method, (2) evaluation and intercomparison of the TLD-1 and NBPA methods, (3) tests of transfer and recovery of TDI, and (4) chamber characterization tests. Results in those four areas are described below.

The NBPA analysis method employed standard solutions of 0.12 to 14 μg/ml of TD-80 in NBPA reagent. Calibration plots for both the 2,6- and 2,4- TDI isomers were linear over that calibration range, and showed zero intercepts. The 2,6-TDI calibration plot had the form Peak Area = $5.65 \times 10^5 \times$ (2,6-TDI, μg/ml), with an r^2 value of 0.994. The corresponding plot for 2,4-TDI showed Peak Area = $1.86 \times 10^6 \times$ (2,4-TDI, µg/ml), with $r^2 = 0.993$. The ratio of the two slopes was 3.3; comparison to the nominal 4:1 isomer ratio of the TD-80 indicates that the HPLC analysis was somewhat more sensitive for the 2,6-isomer than for the 2,4-isomer. A standard solution of 2.4 µg/ml was run most frequently in the analysis of samples, and the reproducibility of that standard indicates the precision of the analysis. For 2,6-TDI in the 2.4 µg/ml standard, an average peak area of 1,298,880 (± 181,269) was found, equating to a 14.0 percent relative standard deviation. For 2,4-TDI in that standard, the corresponding values were 4,263,170 (± 701,128), for a 16.4 percent RSD. Similar precision of 17.4 percent RSD was observed in the few samples in which TDI was spiked into half the sample, for confirmation of TDI retention times.

To examine the comparability of the TLD-1 and NBPA methods used in the TDI screening, the two methods were evaluated using a source of vapor-phase TDI. That source was a permeation tube of 2,4-TDI, with a nominal permeation rate of 250 ng/minute. The tube was maintained in a commercial calibrator equipped to dilute the permeation tube output with either dry or humidified (<50 percent RH) high purity air. As a test of the two methods, and a check on the output of the tube, the two sampling methods were closely coupled to the outlet of the permeation calibrator on several occasions. In this arrangement there was minimal length of tubing upstream of the TLD-1 or the NBPA impingers, and consequently minimal loss of TDI can be expected. The results of these tests are shown in Figure 12, which shows the measured TDI concentration plotted versus the nominal concentrations based on the 250 ng/min rate. Results are shown from both the TLD-1 and NBPA methods, including zero air results at the origin, and the linear regression to the data is shown. The regression line has the form Measured ppbv = 0.58 (Nominal ppbv) + 0.21 ppbv, with $r^2 = 0.938$.

Figure 12 indicates first of all that the actual TDI output of the permeation tube was approximately 145 ng/min, rather than 250. More importantly, the two methods agree reasonably well in that finding. In the three cases in which TDI was sampled simultaneously with the two methods, the agreement was within 11 percent, 17 percent, and 37 percent, at nominal TDI concentrations of 5.5, 9.2, and 4.3 ppbv (actual values of 3.2, 5.3, and 2.5

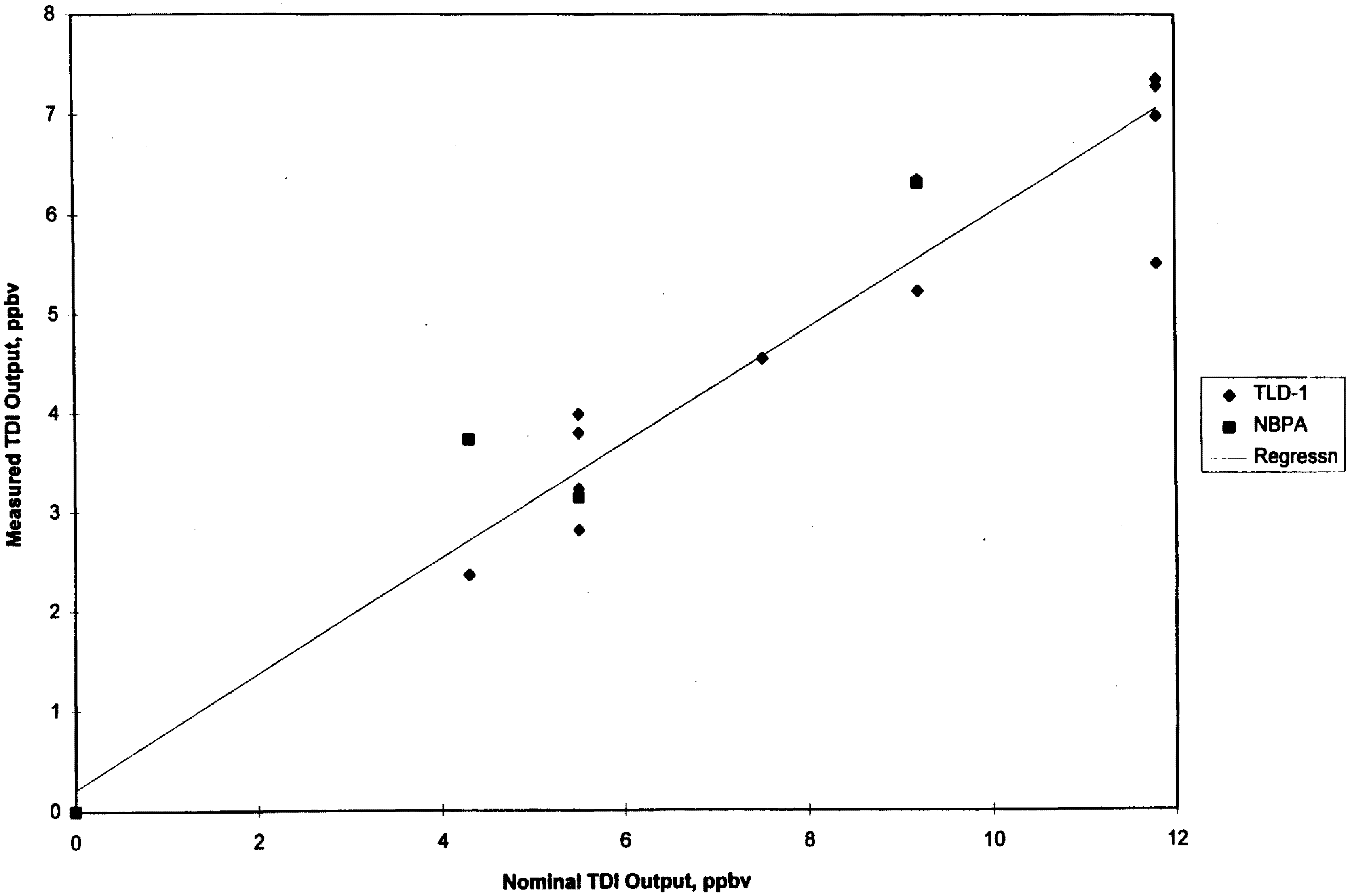

FIGURE 12. COMPARISON OF MEASURED TDI LEVELS BY TLD-1 AND NBPA TO NOMINAL OUTPUT OF PERMEATION TUBE

ppbv), respectively. This sensitivity and degree of agreement confirmed the suitability of both methods for use in the screening tests. Furthermore, the absence of any TDI indicated by both methods when sampling zero air through the calibrator indicated that memory effects in transfer of TDI through Teflon tubing were small.

Because of TDI's reactivity and tendency to adsorb onto surfaces, the potential exists for TDI to be lost in the process of sampling. Thus it was necessary to determine how well TDI could be transferred through sampling tubing to the NBPA impinger or to the TLD-1 monitor. The effectiveness of transfer of TDI was evaluated by inserting lengths of clean Teflon tubing between the calibrator and the TLD-1 monitor. It had been observed during the tests summarized in Figure 12 that the TLD-1 responded rapidly upon altering the output TDI concentration from the calibrator, or upon switching between zero air and ppbv levels of TDI. Tests confirmed that this behavior also occurred when TDI was transported significant distances through tubing. Figure 13 shows the response of the TLD-1 to 2,4-TDI in humidified air, after passage through about 4 feet of 1/4" O.D. Teflon tubing. The data in Figure 13 show about 50 minutes of operation of the TLD-1, during which the calibrator output was successively switched from zero air, to 3.2 ppbv TDI, to zero air again, to 3.2 ppbv TDI briefly, to 6.8 ppbv TDI, and finally back to zero air. Figure 13 shows that the TLD-1 responded to the step changes in concentration within about two minutes, and stabilized thereafter at the appropriate reading. The results of this and other tests indicated that equilibration of transfer lines with ppbv levels of TDI was not a serious limitation. More complete transfer and shorter stabilization times were obtained with humidified dilution air (as in Figure 13) than with dry air. This behavior is not unexpected, since both theoretical (Coutant and McClenny, 1991; Coutant, 1993) and experimental (reviewed by Kelly and Holdren, 1995) studies have shown that the presence of water reduces the adsorption of vapor-phase species, apparently by occupying active surface sites. As a result humidified air was used as makeup air to replace that withdrawn by sampling in all TDI tests.

The final step in assuring the quality of the TDI data was to characterize the TDI screening chamber. Humidified air containing known low levels of TDI from the permeation

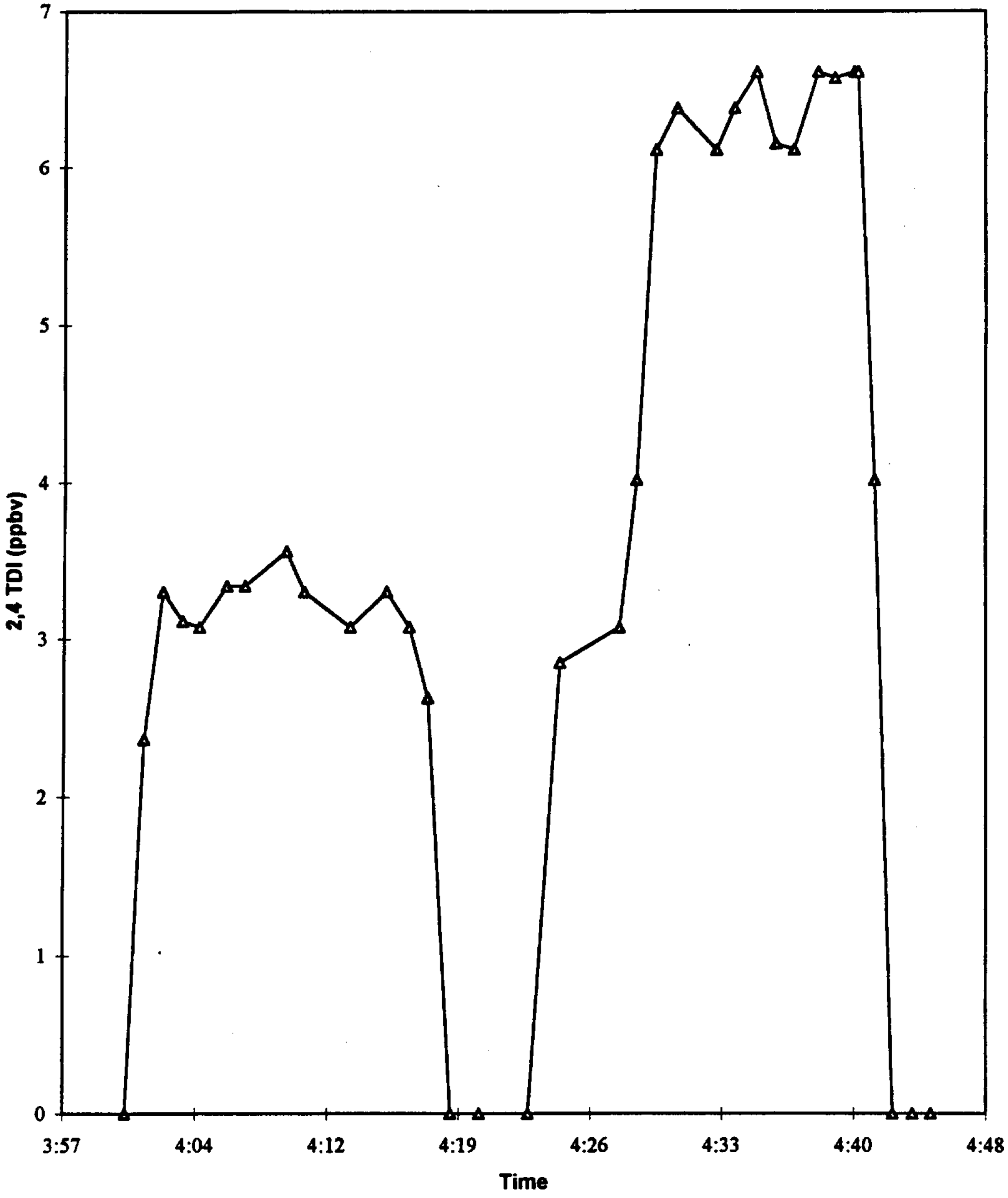

FIGURE 13. RESPONSE OF TLD-1 MONITOR TO VARYING LEVELS OF 2,4-TDI FROM THE PERMEATION SOURCE

source was passed through various chambers, and the TDI content was monitored at the chamber outlet by the TLD-1 monitor. No TDI remained in the vapor phase after passage through a 0.44 m^3 steel and glass chamber, maintained at 50°C, or through a 300 L Tedlar gas sampling bag enclosed in the same chamber. "Mapping" of TDI levels within these chambers, by placing the TLD-1 monitor within the chambers, confirmed that TDI was present in the vapor phase only near the gas flow inlet to the chamber. Apparently loss of TDI to the chamber surfaces rapidly removed TDI from the vapor phase. As an alternative, an all-glass chamber was constructed by fitting inlet and outlet ports to a 9 L glass desiccator. That 9 L chamber was then placed within the heated 0.44 m^3 chamber. Drawing TDI into the 9 L chamber with the TLD-1 monitor, at actual concentrations of 4.3 to 6.8 ppbv, showed TDI recoveries at 50°C of 66 to 97 percent in the chamber outflow, with an average recovery of 79.6 percent. From these results we estimate an average exponential loss rate for TDI in the glass chamber of about 0.7 hr^{-1} (i.e., a half-life of about 1 hour). These findings are consistent with those of a previous effort at TDI screening, in which about 50 percent recovery of TDI was observed through a 3 L glass chamber, using about 7 ppbv TDI at 50°C in dry air (Hodgson, 1996). Comparison of the present results with those of Hodgson (1996) confirms our observation that the presence of humidity offers some advantage in the stability of TDI. As a result of this characterization effort, the 9 L glass chamber was adopted for use in all TDI tests.

The sensitivity of the TDI screening tests in the 9 L glass chamber was presented in Section 4.4.3. It is also worthwhile to consider the overall uncertainty of the final TDI test results obtained with the concrete water stop product (Appendix G). That uncertainty includes both bias and precision terms, i.e., the accuracy of determining the TDI concentration curve with the TLD-1 monitor, and the reproducibility of the entire test procedure. The accuracy of the TLD-1 data may be estimated by comparisons with the NBPA method. As noted above, the two methods agreed within about 15 percent at constant TDI levels above 3 ppbv, produced by the TDI permeation source. On the other hand, the two methods agreed only within about a factor of two, in sampling during the actual final TDI tests on the water stop product (see Section 6.5). However, the issue is complicated by the fact that TDI levels changed very rapidly during those tests, making the latter comparison of real-time and integrated results questionable. In terms of precision, duplicate final TDI tests (Section 6.5) resulted in a 15 percent RSD for initial emission rate determinations, and a 6 percent RSD for determinations of the total amount of TDI emitted. Combining the 15 percent values for accuracy and precision in a root-mean-square fashion provides an estimate of 21 percent for the uncertainty in determining initial TDI emission rates in the final tests. However, this result must be considered a lower limit to the actual overall uncertainty, due to the scarcity of confirming data.

Note that loss of TDI to the chamber walls in the final tests was negligible, because of the short residence time of air in the test chamber. As a result, uncertainty in the 0.7 hr^{-1} exponential loss rate for TDI is unimportant in estimating the overall uncertainty in test results. Even a large uncertainty in that loss rate cannot lead to hypothetical TDI losses that significantly affect the test results.

A final effort in TDI determination in this study is worth noting. Rinsing of the glass chamber walls with the NBPA reagent was investigated as a possible means of recovering any TDI adsorbed on the chamber walls. This approach was tested by exposing the chamber to known TDI levels for extended periods of time, while monitoring TDI in the chamber outflow, before rinsing the chamber with 10 ml of reagent. No peaks attributable to TDI were found in the resulting HPLC analyses, but numerous unknown peaks were seen, possibly resulting from surface contaminants, or from decomposition of TDI and/or the NBPA reagent. As a result, this approach was not pursued.

6.0 RESULTS

In this section the chamber test results are presented, with emphasis on the emission rates of HCHO and other compounds. The HCHO emission data from dry products are presented first, followed by data on emissions of the other target compounds from those products. HCHO emission rates from wet products are then presented, along with comments on the presence of other target compounds from those products. Finally, TDI emission results are presented.

6.1 HCHO Emission Rates from Dry Products

Table 9 summarizes the HCHO emission rate results determined by means of Equation 1 for dry products. The products and corresponding results in Table 9 are grouped into broad product categories (e.g., bare UF wood products, coated UF wood products, etc.). Within each of the categories individual products are listed in decreasing order of their HCHO emission rate in the Typical conditions. The categories in turn are approximately in decreasing order of average emission rates. All products in Table 9 are numbered sequentially. This is to facilitate comparisons with other data, and does not represent either the order of testing or any ranking in terms of emission strength. Each numbered product in Table 9 is a distinct sample; for several products more than one sample was obtained from different sources at different times in the study (e.g., 5/8" industrial particleboard, products 5, 11, and 15).

Shown in Table 9 are the product identification, the product loading in the chamber (m^2/m^3), the HCHO emission rates in both Typical and Elevated conditions, in $\mu g/m^2/hr$, and an indication of duplicate test results for eight products. The duplicate data were shown in Figure 9 and discussed in section 5.1.6. Minimum detectable emission rates (e.g., <2.7) are shown in Table 9 for products with no significant emissions; those values are based on the product loading, the chamber conditions, and the required 1 ppbv HCHO minimum change (see Section 4.3.1). For product 35, permanent press shirts, results are also shown both before and after washing. Note that the emission rates for shirts (products 35 and 36) in

TABLE 9. FORMALDEHYDE EMISSION RATES FROM DRY PRODUCTS ($\mu g/m^2/hr$)

No.	Product Group and Identity		Prod. Loading m2/m3	Test Conditions Typical	Test Conditions Elevated
	Bare Urea-Formaldehyde (UF) Wood Products				
1	1/4" UF particleboard		0.46	1580	1170
2	5/8" Particleboard underlayment		0.46	508	393
3	Bare MDF cabinet doors		see footnote	364	535
4	3/4" Medium density fiberboard (MDF)		0.26	258	254
5	5/8" Industrial particleboard (I.P.)		0.46	237	311
6	5/8" MDF	dup 1	0.26	210	318
		dup 2	0.26	335	385
7	1/4" Prefinished hardwood plywood wall panelling		0.46	181	140
8	5/8" Mobile home decking		0.46	174	241
9	1/2" Hardwood veneer plywood		0.46	170	154
10	3/4" Industrial particleboard	dup 1	0.46	170	181
		dup 2	0.46	120	130
11	5/8" Industrial particleboard	dup 1	0.46	158	164
		dup 2	0.46	130	172
12	3/4" Industrial particleboard		0.46	147	153
13	5/8" Particleboard underlayment		0.46	119	134
14	3/4" Industrial particleboard		0.46	117	177
15	5/8" Industrial particleboard		0.46	104	110
16	1/2" Stock hardwood plywood		0.46	103	147
17	1/4" Stock hardwood plywood		0.46	101	71
18	3/4" Stock hardwood plywood	dup 1	0.46	77	66
		dup 2	0.46	65	69
19	3/4" Stock hardwood plywood		0.46	8.6	6.8
	Coated UF Wood Products				
20	MDF cabinet doors w. white acid-cured finish		see footnote	460	1300
21	5/8" I.P. black textured non-recoatable paper laminate		0.46	55	120
22	5/8" I.P.recoated white ice paper waterborne topcoat		0.46	48	83
23	5/8" Mobile home decking w. waterproof coating		0.46	35	52
24	3/4" I.P. melamine laminate (imported)	dup 1	0.46	29	44
		dup 2	0.46	16	86
25	5/8" I.P. w. red cherry paper laminate		0.46	26	29
26	3/4" I.P. melamine laminate (imported)		0.46	21	18
27	5/8" I.P. w. rigid vinyl bonanza oak laminate		0.46	16	31
28	5/8" I.P. vinyl coated		0.46	8.6	2.9
29	Interior door w. particleboard core		0.46	7.0	15
30	5/8" I.P. vinyl coated	dup 1	0.46	6.7	1.7
		dup 2	0.46	<2.7	1.3
31	3/4" I.P. melamine laminate (domestic)	dup 1	0.46	5.7	2.2
		dup 2	0.46	3.4	3.2
32	5/8" I.P. w. electron-beam-cured acrylic coating		0.46	<2.7	5.7
33	3/4" I.P. melamine laminate (domestic)		0.46	<2.7	4.6

TABLE 9. (Continued)

			Prod. Loading	Test Conditions	
No.	**Product Group and Identity**		**m2/m3**	**Typical**	**Elevated**
	Permanent Press Fabrics				
34	Permanent press draperies		3.25	215	173
35	Permanent press shirts (unwashed)		7.05	107	77
	" " " (washed once)		7.05	42	33
36	Permanent press shirts		7.05	45	55
37	Permanent press sheets		3.24	42	53
	Decorative Laminates				
38	20 mil cabinet liner decorative laminate		1.83	51	59
39	50 mil rigid general purpose laminate		1.83	14	15
40	50 mil general purpose laminate	dup 1	1.83	4.0	6.0
		dup 2	1.83	4.2	6.1
	Fiberglass Products				
41	Fiberglass R-19 roll insulation		0.87	32	31
42	Fiberglass ceiling tiles		1.04	23	18
43	Fiberglass ceiling tiles		1.02	16	11
	Bare Phenol-Formaldehyde (PF) Wood Products				
44	1/4" Perforated PF hardboard		0.46	9.2	9.5
45	3/4" Softwood plywood		0.46	8.0	6.9
46	3/4" Oriented strandboard		0.46	6.8	16
47	3/4" Softwood plywood		0.46	4.1	13
	Paper Products				
48	Paper grocery bags		2.73	< 0.5	0.7
49	Paper towels		2.08	<0.6	<0.2

All test results are steady state emission rates after 20 to 24 hours in the test chamber.

Prod. Loading: Exposed surface area of product divided by 1.43 cubic meter chamber volume. In testing of products 3 and 20, loading rates were 0.58 m2/m3 in Typical conditions, and 0.52 m2/m3 in Elevated conditions, due to sizes of cabinet doors received.

Typical: Results obtained in the chamber held at 70 F, 50 % RH, and 1.0 air change per hour.

Elevated: Results obtained in the chamber held at 80 F, 50 % RH, and 0.3 air change per hour.

dup1,2: Results indicate emission rates determined in duplicate chamber tests.

$\mu g/m^2/hr$ can be converted to emission rates per shirt (in μg/shirt/hr) by multiplying by 2.52 m^2/shirt, which is the total measured surface area (both sides) for the shirts tested.

Table 9 shows that bare UF wood products exhibited the highest HCHO emission rates as a group, although the range of emission rates found for this category was large. The great majority of test results for bare UF products were above 100 $\mu g/m^2/hr$. The categories of coated UF wood products and permanent press fabrics exhibited lower emission rates, with the commercially-applied acid-cured finish on MDF cabinet doors a notable exception. This coated UF product produced the highest emission rate under Elevated conditions, and the third highest under Typical conditions. The categories of decorative laminates, fiberglass products, and PF wood products produced low HCHO emissions. HCHO emissions from paper goods were essentially zero.

The uncertainties in the results shown in Table 9 were discussed in Section 5.4, i.e., an overall measurement uncertainty of 12.3 percent was calculated. This uncertainty implies that values in Table 9 that differ by less than about 40 percent from one another (i.e., less than 3 times the uncertainty estimate) may not be significantly different in a statistical sense. On this basis, many of the products within each category are quite similar to one another in emission rate. On the other hand, the highest- and lowest- emitting products within a category may exhibit very different rates. However, the differences between products in different categories are often much larger than the 40 percent uncertainty criterion estimated above, confirming that substantial differences exist in the HCHO emission rates of different types of products.

Further discussion of these emission results, and specific product-to-product comparisons, are presented in Section 7.

6.2 Emission Rates of Acetaldehyde, Propionaldehyde, MEK, and MIBK from Dry Products

The emission rates determined by means of Equation 1 for acetaldehyde and propionaldehyde from dry products are shown in Table 10. None of the tested products

TABLE 10. ACETALDEHYDE AND PROPIONALDEHYDE EMISSION RATES FROM DRY PRODUCTS ($\mu g/m^2/hr$)

No.	Product Group and Identity	Acetaldehyde Typical	Acetaldehyde Elevated	Propionaldehyde Typical	Propionaldehyde Elevated
	Bare Urea-Formaldehyde (UF) Wood Products				
1	1/4" UF particleboard	< 2.0	0.6	< 2.6	< 0.8
2	5/8" Particleboard underlayment	2.9	3.3	< 2.6	1.7
3	Bare MDF cabinet doors	3.7	13.7	< 2.1	1.9
4	3/4" MDF	< 3.5	< 1.1	< 4.6	< 1.4
5	5/8" Industrial particleboard (I.P.)	16.4	32.2	3.8	8.2
6	5/8" MDF	6.3	9.1	< 4.6	2.8
		< 3.5	5.4	< 4.6	1.8
7	1/4" Prefinished hardwood plywood wall panelling	< 2.0	< 0.6	< 2.6	< 0.8
8	5/8" Mobile home decking	2.0	6.1	< 2.6	1.7
9	1/2" Hardwood veneer plywood	< 2.0	1.4	< 2.6	2.0
10	3/4" Industrial particleboard	5.9	14.7	< 2.6	3.3
		4.7	9.5	< 2.6	2.4
11	5/8" Industrial particleboard	3.1	7.3	< 2.6	2.1
		2.3	3.7	< 2.6	< 0.8
12	3/4" Industrial particleboard	6.0	8.9	< 2.6	3.4
13	5/8" Particleboard underlayment	4.7	6.8	< 2.6	1.9
14	3/4" Industrial particleboard	< 2.0	1.7	< 2.6	< 0.8
15	5/8" Industrial particleboard	14.7	23.2	< 2.6	3.3
16	1/2" Stock hardwood plywood	< 2.0	< 0.6	< 2.6	< 0.8
17	1/4" Stock hardwood plywood	< 2.0	0.9	< 2.6	< 0.8
18	3/4" Stock hardwood plywood	< 2.0	< 0.6	< 2.6	< 0.8
		< 2.0	< 0.6	< 2.6	< 0.8
19	3/4" Stock hardwood plywood	3.9	5.4	< 2.6	< 0.8
	Coated UF Wood Products				
20	MDF cabinet doors w. white acid-cured finish	4.1	7.2	< 2.1	3.5
21	5/8" I.P. black textured non-recoatable paper laminate	5.4	13.4	< 2.6	3.7
22	5/8" I.P.recoated white ice paper waterborne topcoat	5.6	11.3	< 2.6	3.3
23	5/8" Mobile home decking w. waterproof coating	3.3	5.4	< 2.6	1.4
24	3/4" I.P. melamine laminate (imported)	< 2.0	5.1	< 2.6	< 0.8
		< 2.0	8.5	< 2.6	1.1
25	5/8" I.P. w. red cherry paper laminate	15.2	20.8	< 2.6	3.6
26	3/4" I.P. melamine laminate (imported)	15.6	NM	< 2.6	NM
27	5/8" I.P. w. rigid vinyl bonanza oak laminate	8.9	27.2	< 2.6	5.1
28	5/8" I.P. vinyl coated	< 2.0	2.7	< 2.6	< 0.8
29	Interior door w. particleboard core	11.4	12.2	< 2.6	1.7
30	5/8" I.P. vinyl coated	3.8	2.7	< 2.6	< 0.8
		< 2.0	2.5	< 2.6	< 0.8
31	3/4" I.P. melamine laminate (domestic)	< 2.0	1.2	< 2.6	< 0.8
		< 2.0	< 0.6	< 2.6	< 0.8
32	5/8" I.P. w. electron-beam-cured acrylic coating	6.8	2.6	< 2.6	< 0.8
33	3/4" I.P. melamine laminate (domestic)	2.2	1.6	< 2.6	< 0.8

TABLE 10. (Continued)

No.	Product Group and Identity	Acetaldehyde Typical	Acetaldehyde Elevated	Propionaldehyde Typical	Propionaldehyde Elevated
	Permanent Press Fabrics				
34	Permanent press draperies	< 0.3	< 0.1	< 0.4	< 0.1
35	Permanent press shirts (unwashed)	< 0.2	< 0.1	< 0.2	< 0.1
	" " " (washed once)	< 0.2	< 0.1	< 0.2	< 0.1
36	Permanent press shirts	< 0.2	< 0.1	< 0.2	< 0.1
37	Permanent press sheets	< 0.3	< 0.1	< 0.4	< 0.1
	Decorative Laminates				
38	20 mil cabinet liner decorative laminate	< 0.5	< 0.2	< 0.7	< 0.2
39	50 mil rigid general purpose laminate	< 0.5	< 0.2	2.7	0.7
40	50 mil general purpose laminate	< 0.5	< 0.2	1.3	0.3
		< 0.5	< 0.2	11.7	3.4
	Fiberglass Products				
41	Fiberglass R-19 roll insulation	< 1.0	< 0.3	< 1.4	< 0.4
42	Fiberglass ceiling tiles	1.0	1.3	< 1.2	< 0.4
43	Fiberglass ceiling tiles	< 0.9	0.3	< 1.2	< 0.4
	Bare Phenol-Formaldehyde (PF) Wood Products				
44	1/4" Perforated PF hardboard	< 2.0	1.5	< 2.6	< 0.8
45	3/4" Softwood plywood	6.5	8.0	< 2.6	0.9
46	3/4" Oriented strandboard	15.2	21.4	11.1	17.8
47	3/4" Softwood plywood	6.9	56.4	< 2.6	1.1
	Paper Products				
48	Paper grocery bags	< 0.3	< 0.1	< 0.4	< 0.1
49	Paper towels	< 0.4	< 0.1	3.8	1.3

All test results are steady state emission rates after 20 to 24 hours in the test chamber.

Typical: Results obtained in the chamber held at 70 F, 50 % RH, and 1.0 air change per hour.

Elevated: Results obtained in the chamber held at 80 F, 50 % RH, and 0.3 air change per hour.

NM: Not measured or data not available.

produced detectable emissions of MEK or MIBK, nor were those two compounds ever detected in chamber background air (i.e., concentrations always less than 0.1 ppbv).

Table 10 is organized in the same manner as Table 9, in that results are listed by product categories. The products listed in Table 10 are numbered as in Table 9, to allow direct comparison with the HCHO emission results. The product loadings for all tests were shown in Table 9. Of the 49 products listed in Table 10, 38 were found to emit acetaldehyde or propionaldehyde in at least one test. As in Table 9, the minimum detectable emission rates are shown for products with no detectable emissions; those rates are calculated from the product loading (Table 9), the chamber conditions, and an assumed 0.5 ppbv minimum change of the target compounds (see Section 4.3.1).

Table 10 shows that acetaldehyde and propionaldehyde emission rates were much lower than those of HCHO. The maximum acetaldehyde emission rate found was only 56.4 $\mu g/m^2/hr$, and that of propionaldehyde only 17.8 $\mu g/m^2/hr$. Bare UF products, coated UF products, and PF products were the principle categories in which emission of these compounds was observed. Both of the maximum rates noted above were produced by PF products. Comparison of Tables 9 and 10 indicates that for some coated UF products and some PF products the mass emission rates of acetaldehyde and propionaldehyde may equal or exceed those of HCHO. However, the uncertainties in the measured rates prevent a definite conclusion. Bare UF products emitted very small amounts of acetaldehyde and propionaldehyde, relative to their HCHO emissions.

6.3 HCHO Emission Results from Wet Products

Table 11 presents the HCHO emission rate results determined from the chamber tests using the modelling approach described in section 4.4.2. Plots of the actual HCHO emission curves are presented in Appendix F. Shown in Table 11 are the substrate loading in the chamber, the product loading on the substrate surface, the maximum HCHO concentration measured in the test, the initial emission rate of the product after application, the final steady state emission rate, and the total mass of HCHO released during the test. For each product,

TABLE 11. FORMALDEHYDE EMISSION RESULTS FROM WET PRODUCTS

Product	Test Condition(a)	Substrate Loading (m^2/m^3)(b)	Product Loading (mg/cm^2)(c)	C_{max} ($\mu g/m^3$)	Initial HCHO Emission R_0 ($\mu g/m^2/hr$)	Final HCHO Emission ($\mu g/m^2/hr$)	Integrated HCHO Emission (μg)(d)
Paints:							
Lower quality latex paint	T	1.04	9.75	75	518	8.1	649
	E	1.04	7.88	105	441	7.5	521
(duplicate)	T	1.04	9.80	80	663	9.9	746
	E	1.04	9.07	108	854	10.1	597
Higher quality latex paint	T	1.04	9.6	79	326	9.8	901
	E	1.04	10.5	163	494	5.3	611
Wallpaper:							
Paper-based wallpaper	T	1.04	NA(e)	165	691	27	1,689
	E	1.04	NA	192	–(f)	–	–
Cosmetics:							
Fingernail hardener	T	0.0049	15.6	180	178,000	124	837
	E	0.0049	15.7	255	293,000	610	721
(duplicate)	T	0.0049	16.4	195	253,000	471	873
	E	0.0049	17.9	295	354,000	260	716
Nail polish	T	0.0084	10.3	14.5	20,700	–	53.7
	E	0.0084	11.4	24.5	62,600	–	52.8
Fingernail hardener ("Formaldehyde free")	T	0.0049	11.3		No detectable emissions		
	E	0.0049	14.4		No detectable emissions		
Commercially Applied Floor Finish:							
Base coat	T	0.0047	20 mils(g)	950	1,050,000	10,800	7,780
	E	0.0047	20 mils	1,950	1,247,000	17,100	9,100
Top coat	T	0.0047	25 mils	900	421,000	4,660	5,950
	E	0.0047	25 mils	1,800	799,000	13,600	7,500

(a) T = Typical conditions, E = Elevated conditions.
(b) Surface area of substrate divided by 1.43 m^3 chamber volume.
(c) Mass of product applied per cm^2 of substrate surface.
(d) Duration of continuous HCHO measurement in all tests was 22 hours, except: lower quality latex paint = 18 hours; paper-based wallpaper = 15.5 hours; nail polish = 10.5 hours. Total HCHO emissions for all products were calculated only for the duration of the continuous measurements.
(e) NA = not applicable.
(f) Emissions in this test could not be properly modelled due to loss of control of chamber humidity.
(g) Mass loading of product was not obtained; thickness of freshly applied coating is shown, in mils (1 mil = 0.001 in.).

results are listed for both the Typical and Elevated conditions. Duplicate test results are also shown for two products. Those duplicates were discussed in section 5.1.6. Note that no correction has been made for differences in product loadings (mg/cm^2) in the two chambers or in duplicate tests. The C_{max}, R_o, and total HCHO emission results in Table 11 are for the test conditions as listed.

The products listed in Table 11 cover a wide range of substrate loading, initial and final emission rates, and integrated HCHO emission. The commercially-applied floor finish exhibited by far the highest HCHO emissions, in terms of both initial and final rate and integrated HCHO emission. Emissions from the base coat were substantially greater than emissions from the top coat, for very similar product loadings. Despite a very small surface area for application (0.0067 m^2), the floor finish products caused the highest C_{max} values of any wet product, and released between about 6 and 9 milligrams of HCHO into the test chambers. For comparison, the nail hardener exhibited the second highest R_o values, with a similar application surface area, but released only about one tenth as much HCHO as the floor finish products. Nail polish produced a still lower R_o value, and much lower total HCHO emissions. The effect of a large surface area for product application is shown by the results in Table 11 for paints and wallpaper. Although these products exhibited relatively low emission rate values, the total amount of HCHO released was substantial because of the realistically high surface area used in testing these products. Emissions from the higher quality latex paint were approximately the same as from the lower quality paint. For all products in Table 11, the final HCHO emission rates were a very small fraction (i.e., <1.7 percent) of the initial rates.

The importance of the floor finish as a source of HCHO is hidden to some extent by the small surface area used in testing (Table 11). This small surface area was required in order to keep chamber HCHO levels within the linear range of the continuous monitor. In actual use, the floor finish products are applied to large areas of flooring. If the floor finish were applied at realistic loading rates in the chambers, i.e., comparable to those used for paints and wallpaper, it is clear from Table 11 that very large HCHO releases would occur. Fortunately, these floor finish products are not used by the general public, but are to be applied only by qualified contractors. Thus residential HCHO exposure is likely to be reduced somewhat by the time lag between commercial application and exposure of the resident. However, even the final steady-state emission rates from the floor finish were relatively high, i.e., up to a factor of ten higher than the HCHO emission rate from the highest-emitting dry products (Table 9).

The concentrations of the other target carbonyl compounds, determined by DNPH sampling at the end of the chamber tests, were always low. No MEK or MIBK was detected in any test of wet products (i.e., <0.1 ppbv). No significant amounts of acetaldehyde or propionaldehyde (i.e., <0.1 ppbv) were detected in testing of the commercially-applied floor finish or the nail hardeners. Traces of acetaldehyde (1.1 ppbv) and propionaldehyde (0.3 ppbv) were detected in the Elevated conditions in the test of wallpaper, but not in the Typical conditions. Latex paints also showed trace emissions of both compounds. Under Typical and Elevated conditions in the paint tests, acetaldehyde levels were 0.1 to 0.8 ppbv, and 1.2 to 2.1 ppbv, respectively. Propionaldehyde was found at 0.3 ppbv in Elevated conditions only. These results suggest that for most of the wet products tested, acetaldehyde and propionaldehyde emissions are minimal. However, continuous or repetitive measurements of these compounds starting immediately after product application would be needed to confirm this suggestion. No HCHO or acetaldehyde was detected in the DNPH samples from testing the nail polish, but propionaldehyde was detected at 5 ppbv (12 $\mu g/m^3$) in both chambers. That level is a substantial fraction of the peak HCHO levels observed for that product (Table 11), and suggests that further testing for propionaldehyde emissions may be needed.

6.4 TDI Results from Screening Tests

Screening tests were conducted on groups of similar products, or on single products, according to the protocol in Appendix D. Table 12 summarizes the results of the TDI screening tests. Listed in the table are a brief description of the products tested, the positive/negative outcome of the screening tests, and an approximate upper limit to the TDI emission rate, as calculated in Section 4.4.3, for those products with no detectable emissions. Most of the screening tests were conducted with groups of similar products, as indicated in

TABLE 12. SUMMARY OF TDI SCREENING TESTS

Products Tested	Screening Result	TDI Emission Rate[(a)] (μg/m²/hr)
Carpet Padding (5 samples, 3/8" to 1/2")	N	<0.018
Carpet Padding (4 samples, 7/16" to 1/2")	N	<0.018
Mattress and Sheet Foam (6 samples)	N	<0.018
Furniture Cushion Foam (4 samples)	N	<0.018
Spray PU Varnishes (4 samples)	N	<0.22
Brush-On PU Varnishes (4 samples)	N	<0.22
Brush-On PU Varnishes (4 samples)	N	<0.22
General Purpose Water Sealers (3 samples)	N	<0.22
Concrete-Only Sealers (2 samples)	N	<0.22
Mastic Construction Adhesive	N	<0.22
High Performance PU Caulk	N	<0.22
Commercially Applied Water Stop Product	P	Large

N = negative result in screening; P = positive result.
(a) Adjusted to room temperature. See Section 4.4.3 for calculation.

Table 12. Samples were segregated into types within each product category, prior to screening in groups. For example, water sealants intended for use on a variety of surfaces were tested separately from those intended only for use on concrete.

As Table 12 shows, the screening results were negative in all of the first 11 tests, meaning that no indication of TDI was observed with either the TLD-1 or the NBPA method. In contrast, in the twelfth test, the water stop product for concrete produced a large and immediate response on the TLD-1 monitor, rapidly saturating the color formation in the paper tape. An NBPA sample taken shortly thereafter indicated TDI levels sufficient to consume the

NBPA reagent present, i.e., exceeding about 2 ppmv. That level is consistent with the estimated vapor pressure of roughly 7.5 ppmv TDI over 4 percent by weight TDI (III, 1980). On the basis of this large positive response, the water stop product was subjected to final testing.

Because the TLD-1 was also sensitive to other isocyanates, the absence of any response in all but one of the screening tests indicates that in those tests any emissions of such compounds were negligible. An upper limit room temperature emission rate of less than 0.76 $\mu g/m^2/hr$ can be estimated for other isocyanate compounds, based on the assumption that the TLD-1 is equally sensitive to TDI and other isocyanates.

6.5 TDI Results from Final Tests

The emission curves and model fits for the final tests on the concrete water stop product are shown in Appendix G. The calculated results from those tests are shown in Table 13, which lists the test temperature, the initial TDI emission rate, the total quantity of TDI emitted during the test, and the percentage of the emitted TDI that was the 2,6-isomer. This product reacted rapidly with moisture in the air, so that TDI emission effectively ceased within one hour or less. Table 13 shows that good reproducibility was obtained in the duplicate tests at 70°F. A 15 percent RSD was obtained for the initial emission rates, and a 6 percent RSD for the total TDI emissions. As was found for the wet HCHO products, the reproducibility of total emitted mass was better than that for initial emission rates. Table 13 also shows that the initial TDI emission rate at 80°F was only about 25 percent higher than the average initial rate of 288,000 $\mu g/m^2/hr$ at 70°F. Given the overall uncertainty in TDI test results of at least 21 percent, estimated in Section 5.5, it cannot be concluded that the initial TDI emission rate at 80°F is truly different from that at 70°F. However, the total amount of TDI emitted at 80°F was about 5 times as high as that at 70°F. The total amounts of TDI emitted at 70°F and at 80°F (Table 13) were approximately 1 percent and 5 percent, respectively, of the TDI present in the samples tested.

TABLE 13. RESULTS OF FINAL TESTING FOR TDI EMISSION FROM COMMERCIALLY-APPLIED CONCRETE SEALER

Test Temperature	Initial Emission Rate Ro, μg/m²/hr	Total TDI Emitted (μg)	Percent 2,6-TDI
70°F	319,000	35[a]	75.2
70°F	257,000	38[a]	97.8
80°F	360,000	179[b]	79.2

(a) Total duration of product emission approximately 0.5 hour.
(b) Total duration of product emission approximately 1 hour.

As noted in the footnotes to Table 13, TDI emissions peaked and then dropped to undetectable levels within one-half hour at 70°F, and within one hour at 80°F. Because of this rapid variation of TDI emission from the product it was impossible to sample with NBPA during a period of truly stable TDI concentrations. Nevertheless, the NBPA results for total TDI may be compared with the average TLD-1 response during the periods of NBPA sampling. In the first test at 70°F, a total TDI concentration of 0.33 ppbv was indicated by NBPA, compared to an average from the TLD-1 of less than the 2 ppbv detection limit. In the second test at that temperature, NBPA sampling was started earlier in the test. The NBPA result was 3.14 ppbv, and the TLD-1 average was 5.1 ppbv. In the test at 80°F, the NBPA result was 25.4 ppbv, and the TLD-1 average was 59 ppbv. The cause of the low NBPA result in that latter test is unknown, but the results are suggestive of a leak in the sample air line to the NBPA impingers. In general, however, the NBPA results serve to confirm the approximate TDI levels indicated by the TLD-1 monitor.

The NBPA samples in the final tests showed that the emitted TDI was largely present as the 2,6-isomer, whereas the product formulation contained largely the 2,4-isomer. As shown in Table 13, the NBPA results indicated that 75-98 percent of the TDI released to air was the 2,6-isomer. This observation is consistent with the reported lower reactivity of the 2,6-isomer, and its resulting tendency to be over-represented in TDI emissions from reacted polyurethane products (Rando, et al., 1984).

7.0 DISCUSSION

In this section some interesting aspects of the emission data are reviewed, and further discussion of product-to-product differences is presented.

7.1 Summary Aldehyde Emission Results

The detailed HCHO emission data presented in Table 9 in Section 6.1 are summarized in Figure 14, which shows a box plot of the HCHO emission rates under Typical conditions by product category. The upper and lower ends of the box show the 75th and 25th percentile, respectively, of the emission data for the indicated category. The line within the box indicates the median, and the vertical bars indicate the 90th and 10th percentiles of the data. For those categories with enough data points, individual data points outside the 10th-90th percentile range are also shown. The emission rate scale in Figure 14 is logarithmic, to adequately show the range of the data. Note that all the emission data are per unit area of product (i.e., micrograms per m^2 per hour). Thus the emission rates alone do not fully describe the potential for emissions in a home; the product area present in the home is also important.

Figure 14 shows that uncoated UF wood products exhibited a wide range of HCHO emission rates, and the highest overall emission rates of any dry product category. Coated UF products showed a HCHO emission range about one order of magnitude lower than the uncoated UF products. This result is consistent with other observations that HCHO emission from vinyl-, paper-, or decorative-laminate-coated UF wood products is lower than from bare UF products (e.g., Groah et al., 1984; Koontz and Hoag, 1995). The lone exception among the coated UF products was the fresh commercially-applied acid-cured coating on cabinet doors, which emitted HCHO at a rate comparable to the highest of the bare UF products. New permanent press fabrics emitted at rates intermediate between the bare and coated UF products. Decorative laminates, fiberglass products, and bare PF wood products all showed emission rates roughly one order of magnitude lower than the bare UF products, and

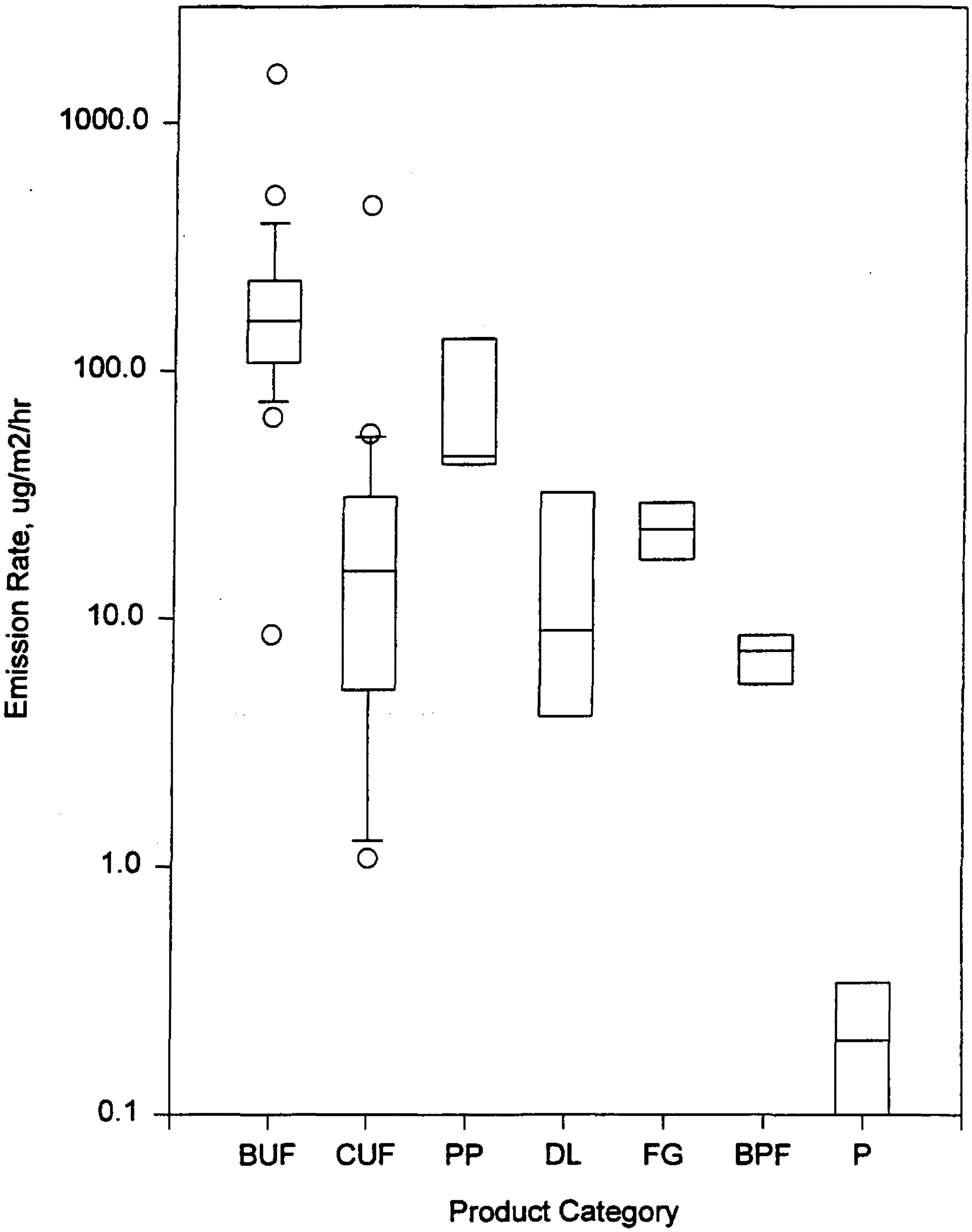

FIGURE 14. BOX PLOT OF HCHO EMISSION DATA FROM DRY PRODUCTS. BUF = BARE UF PRODUCTS; CUF = COATED UF PRODUCTS; PP = PERMANENT PRESS FABRICS; DL = DECORATIVE LAMINATES; FG =FIBERGLASS PRODUCTS; BPF = BARE PF PRODUCTS; P = PAPER GOODS

comparable to those of the coated UF products. Paper goods exhibited negligible HCHO emissions, about two orders of magnitude lower than those of any other product category.

Comparison of the summary data in Figure 14 to the uncertainties in HCHO emission rates discussed earlier indicates clear differences between some product categories. For example, UF emission rates on average were higher than those of other categories by a factor of 5 to over 500. On the other hand, some categories show a range and median that is not significantly different from those of other categories. The overall ranking which emerges from the summary data is bare UF products >PP fabrics >coated UF products, decorative laminates, fiberglass, and bare PF products >paper goods, where product categories separated by commas are not significantly different in their range of product emissions.

The present results may be compared to numerous previous studies addressing HCHO emission rates from the same product categories summarized in Figure 14. In this comparison, earlier data cited in Appendix A in units of $\mu g/m^2/day$ have been converted to $\mu g/m^2/hr$ for consistency with the present results.

Previously reported HCHO emission rates for UF particleboard range mostly from about 100 to 2,000 $\mu g/m^2/hr$ (Pickrell et al., 1982, 1983; Tichenor and Mason, 1988; Levin, 1989; Groah et al., 1993). A recent small chamber study by Koontz and Hoag (1995) indicates bare particleboard emission rates of 240 to 1,900 $\mu g/m^2/hr$, after 24 hours in the test chamber. However, the current ANSI standard for domestic particleboard production (ANSI, 1993) sets a large chamber HCHO level of 300 ppbv (370 $\mu g/m^3$) for most types, and 200 ppbv (250 $\mu g/m^3$) for flooring products. These levels correspond to HCHO emission rates of about 440 and 290 $\mu g/m^2/hr$, respectively, based on $N = 0.5\ hr^{-1}$ and $L = 0.43\ m^2/m^3$ (ASTM, 1990). According to industry sources, the great majority of current particleboard production meets these standards (Margosian, 1990, 1994), and nearly all the particleboard results in Table 9 fall below those emission rates. Comparison with the previous studies cited above also indicates that the HCHO emission rates of currently available particleboard products are generally lower than those reported in earlier studies. An exception is the 1/4" UF particleboard (product number 1 in Table 9). This product was the highest-emitting of all dry products tested. However, as noted earlier, this product is an inexpensive alternative to

PF hardboard. It is made without the extremes of heat and pressure used in manufacture of industrial grade particleboard, and is not comparable to such products. Its relatively high emission rate is perhaps not surprising given its means of production, and emission standards for particleboard (ANSI, 1993) do not apply to this product.

Previously reported HCHO emission rates for MDF range from about 700 to 2,300 $\mu g/m^2/hr$ (e.g., Grot et al., 1985). The current ANSI standard for MDF (ANSI, 1994) calls for a large-chamber HCHO level of no more than 300 ppbv (370 $\mu g/m^3$) at $N = 0.5\ hr^{-1}$ and $L = 0.26\ m^2/m^3$. This standard equates to an emission rate of about 700 $\mu g/m^2/hr$, i.e., lower than the lower end of previously reported emission rates. All of the bare MDF products tested in this study showed HCHO emission rates well below that value (Table 9). Recent small-chamber tests by Koontz and Hoag (1995) also show results that equate to 264 and 440 $\mu g/m^2/hr$ of HCHO emission from two samples of MDF. Those results are close to the MDF data in this study (Table 9).

The present results indicate that particleboard and MDF products available in California generally meet the applicable industry standards for HCHO emission (ANSI, 1993, 1994). Note, however, that the appearance or common name of a product is not a good indication of its emission rate. For example, the 1/4" UF particleboard was sold as a "hardboard" product, a name that generally implies relatively low HCHO emissions. Consumers can best assure themselves of relatively low HCHO emissions from bare UF wood products by looking for a stamp on the product that indicates compliance with ANSI A208 standards (ANSI, 1993, 1994).

Most previously reported HCHO emission rates for hardwood plywood and panelling fall in the range of about 60 to 1,500 $\mu g/m^2/hr$ (Pickrell, 1982, 1983; Levin, 1989; Groah et al., 1993). The results of Koontz and Hoag (1995) equate to emission rates of about 870 and 1,700 $\mu g/m^2/hr$, for two samples of hardwood veneer-covered particleboard with UF adhesive. All results for such products in this study were below 200 $\mu g/m^2/hr$ (Table 9). This comparison also suggests that HCHO emission rates of currently available UF products are generally lower than those from products produced several years ago.

Previous HCHO emission data for other product categories are less numerous than for UF wood products. For coated UF wood products, some information is available. Groah et al. (1984) reported chamber HCHO concentrations for vinyl-coated hardwood plywood that equate to emission rates of about 25-35 $\mu g/m^2/hr$. These are similar to results shown in Table 9 for vinyl-covered particleboard. Koontz and Hoag (1995) show small-chamber results that equate to HCHO emission rates of 22 to 300 $\mu g/m^2/hr$ for a variety of paper-, laminate-, and vinyl-covered particleboard samples. Vinyl-covered products exhibited particularly low emission rates of 34 to 50 $\mu g/m^2/hr$, similar to results noted above. Koontz and Hoag (1995) also report emission rates of 340 and 590 $\mu g/m^2/hr$ from two samples of paper-coated MDF.

In this study new permanent press fabrics recently removed from their packaging showed HCHO emission rates of about 40 to 200 $\mu g/m^2/hr$. These results are comparable to those of Pickrell et al. (1982, 1983) who reported emission rates from less than 1 to several hundred $\mu g/m^2/day$ from a variety of fabrics, using small static chambers for testing. The variability of emissions from the fabrics tested by Pickrell et al. (1982, 1983) was considerable. Pickrell et al. (1982, 1983) reported that new previously unwashed clothes had emission rates of 15 to 750 $\mu g/m^2/hr$. The results for all permanent press fabrics in this study fall in the low end of that range.

Formaldehyde emission from decorative laminates has not been evaluated to a large extent previously. Chamber tests at Battelle prior to this study showed a HCHO emission of about 5 $\mu g/m^2/hr$ from general purpose laminate, under conditions simulating in-home use. That result is similar to the rates found in this study for 50-mil laminates. However, an emission rate of about 50 $\mu g/m^2/hr$ was found in this study for 20-mil cabinet liner laminate.

Fiberglass products tested in this study had emission rates of about 10 to 30 $\mu g/m^2/hr$. These results are similar to those from earlier studies. Pickrell et al. (1982, 1983) tested six types of insulation products in small static chambers, and found HCHO emissions of 2 to 26 $\mu g/m^2/hr$. A single test in a larger ventilated chamber showed a HCHO rate of 125 $\mu g/m^2/hr$. Matthews and Westley (1987) measured HCHO emission from fiberglass roll insulation and found rates of 26 to 53 $\mu g/m^2/hr$ from new products, dropping to 10 to 25 $\mu g/m^2/hr$ after one to three months. Higher HCHO emission rates (45 to 174 $\mu g/m^2/hr$) have also been reported from fiberglass products by Leigh (1996). However those tests were conducted using a mini-chamber method shown to overestimate emission rates by about a factor of ten relative to a small chamber method.

Previous tests of PF wood products have shown HCHO emissions much lower than those from UF products (Pickrell et al., 1982, 1983; Matthews et al., 1985; Emery, 1986), and some have reported HCHO emissions as non-detectable (Pickrell et al., 1982, 1983; Emery, 1986). Quantitative emission rates from PF products have been reported as less than 83 $\mu g/m^2/hr$ (Emery, 1986), less than about 2 $\mu g/m^2/hr$ (Pickrell, et al. 1982, 1983), and as 10-30 $\mu g/m^2/hr$ (Matthews et al., 1985). Those results are consistent with the HCHO rates of 4 to 16 $\mu g/m^2/hr$ found for PF products in this study.

Paper products currently produced for residential use are expected to contain less HCHO than those produced several years ago, because of greater reliance on neutral-cure polyamide resins, rather than UF resins, for wet strength. This expectation appears to be borne out by the study results. Paper products tested in this study released negligible amounts of HCHO (i.e., < 1 $\mu g/m^2/hr$), whereas Pickrell et al. (1982, 1983) reported rates of 11 to 28 $\mu g/m^2/hr$. However, in this study paper towels and grocery bags were tested, while Pickrell et al. (1982, 1983) tested paper cups and plates. Such products were not tested in this study because of information that UF resins are no longer used in their manufacture.

Only limited quantitative comparisons can be made with previous HCHO emission data for wet products. Very high HCHO emissions have been reported from a Swedish floor finish, which may be similar to the product tested in this study (Table 11) (Van Netten, et al., 1988; Godish, 1995). Van Netten, et al. (1988) reported that HCHO emissions continued for several years after application of that product. Peak HCHO emission rates of 195 to 550 $\mu g/m^2/hr$ have been reported for three paper-based wallpaper samples (De Bortoli, et al., 1993b); those values are reasonably close to the initial value determined for a single product in this study (Table 11). Also, acid-cured floor and cabinet finishes have been shown to emit substantial amounts of HCHO (Godish and Guindon, 1990), though emission rates cannot be calculated from the data provided. These limited results are consistent with the results shown in Tables 9 and 11.

A summary comparison of the results of this study to previously published HCHO emission rates is shown in Table 14. For each product type for which a reasonable comparison can be made, the range of previous data cited above is listed, along with the range of data from this study. The emission rates corresponding to the ANSI particleboard and MDF standards are also shown. The primary feature illustrated by Table 14 is that for most categories the present emission rates are lower than most previous data, possibly indicating the effect of improved product formulation and production steps in making current products.

TABLE 14. SUMMARY COMPARISON OF HCHO EMISSION RATES FROM THIS STUDY TO THOSE FROM PREVIOUS STUDIES

	Range of HCHO Emission ($\mu g/m^2/hr$)	
Product Type	This Study	Previous Data[a]
All UF particleboard	104-1,580[b]	100-2,000
Industrial particleboard	104-311	440 (ANSI Standard)
Particleboard and underlayment	119-508	290 (ANSI Standard)
MDF	210-535	264-2,300 700 (ANSI Standard)
Hardwood plywood/panelling	7-181	60-1,700
Coated UF Products	3-120	22-300
Permanent Press Fabrics	40-200	15-750
Fiberglass Products	10-30	2-125
PF Wood Products	4-16	2-83
Wallpaper	690	195-550

(a) See text for citation of previous studies.

(b) Highest emissions were due to sample of 1/4" UF particleboard (product No. 1, Table 9) that was not manufactured under ANSI voluntary standards.

7.2 Specific Product-to-Product Comparisons

Although for many product types more than one sample was obtained for HCHO testing, in general direct product-to-product comparisons cannot be made. For example, separate samples of the same type and thickness of wood product may not be from the same lot, or even the same manufacturer. However, for some products, samples were obtained that do allow direct comparisons of emission rates. These products fall into four groups: (1) industrial particleboard, bare and with paper or vinyl coatings; (2) particleboard mobile home decking, with and without a waterproof coating; (3) MDF cabinet doors, with and without a manufacturer-applied acid-cured finish; and (4) permanent press shirts, tested before and after washing. The first three of these sample sets were obtained through the cooperation of manufacturers, who intercepted materials from their production processes for testing. The fourth set of samples was obtained by washing a set of new shirts once in a domestic washing machine after initial chamber tests, and then retesting the laundered shirts. The results from these four product sets are shown in Table 15, which lists the products, numbered as in Tables 9 and 10. The emission rates of HCHO, acetaldehyde, and propionaldehyde in both Typical and Elevated conditions are shown in Table 15, and can also be found in Tables 9 and 10.

The results in Table 15 show that for both the particleboard and the mobile home decking, the effect of a surface coating was to substantially reduce the HCHO emission rate. Paper coatings on the particleboard reduced HCHO emissions by 60 to 90 percent. The vinyl coating on particleboard reduced HCHO emission by 90 to 93 percent. These results on specific products are similar to those from previous studies (Groah et al., 1984; Koontz and Hoag, 1995). The waterproof coating on mobile home decking reduced HCHO emissions by about 80 percent. All these emission reductions clearly exceed the calculated 40 percent uncertainty range in HCHO emissions (Section 6.1), and thus the emission reductions observed are highly credible. Emissions of acetaldehyde and propionaldehyde from particleboard were also reduced by the paper and vinyl coatings, but the significance of the reduction is not as strong, in light of the larger uncertainties for those species. Emissions of these compounds from the decking were very low and apparently not affected by the waterproofing.

TABLE 15. DIRECT PRODUCT-TO-PRODUCT COMPARISONS

	Emission Rates ($\mu g/m^2/hr$)					
	HCHO		Acetaldehyde		Propionaldehyde	
Product No./Name	T(a)	E	T	E	T	E
UF Particleboard						
5. Bare	237	311	16.4	32.2	3.8	8.2
21. w. Black Non-Recoatable Paper Laminate	55	120	5.4	13.4	<2.6	3.7
22. w. Recoated Paper, Waterborne Top Coat	48	83	5.6	11.3	<2.6	3.3
25. w. Red Cherry Paper Laminate	26	29	15.2	20.8	<2.6	3.6
27. w. Rigid Vinyl Laminate	16	31	8.9	27.2	<2.6	5.1
Mobile Home Decking						
8. Bare	174	241	2.0	6.1	<2.6	1.7
23. w. Waterproof Coating	35	52	3.3	5.4	<2.6	1.4
MDF Cabinet Doors						
3. Bare	364	535	3.7	13.7	<2.1	1.9
20. w. Acid-Cured Finish	460	1,300	4.1	7.2	<2.1	3.5
Permanent Press Shirts						
35. Unwashed	107	77	<0.2	<0.1	<0.2	<0.1
Washed	42	33	<0.2	<0.1	<0.2	<0.1

(a) T = Typical conditions; E = Elevated conditions.

The data for MDF cabinet doors in Table 15 show that the HCHO emissions were increased by the presence of the acid-cured finish, even though the bare MDF doors were already a strong HCHO emitter. The increase in HCHO emission was modest (about 27 percent) at Typical conditions, and within the uncertainty range of the emission determination, but a much larger increase (about a factor of 2.4) at Elevated conditions clearly exceeds the measurement uncertainty. It must be noted that the acid-cured finish was recently applied to the test samples; the impact of a well-aged finish on MDF emissions might be different. The acid-cured coating had no clear effect on the minimal emissions of acetaldehyde and propionaldehyde from the cabinet doors.

Table 15 also shows that a single washing reduced HCHO emissions from permanent press shirts by about 60 percent. This effect is due to removal of HCHO from the fabric's coating by the water used in washing. Presumably repeated washings could further lower the HCHO emission rate.

7.3 Comparison of Emission Rates Under Typical and Elevated Conditions

An interesting feature of the HCHO emission rate data is the comparison of rates under Typical and Elevated test conditions. The relative emission rates in Elevated and Typical conditions are of interest because they indicate the sensitivity of HCHO emission rates to variations in real-world conditions. Efforts to model indoor emission rates and human exposures require knowledge of that sensitivity. The two sets of test conditions used in this study were chosen to represent a reasonable range of indoor conditions in California homes. The Elevated conditions differ from the Typical conditions in use of both a higher temperature (80°F vs. 70°F) and a lower air exchange rate (0.3 hr^{-1} vs. 1.0 hr^{-1}). As a result, the measured concentrations of HCHO were higher in the Elevated conditions than in the Typical conditions. However, as shown in Table 9, the HCHO emission rates from dry products in the two test conditions were generally similar. Figure 15 illustrates this fact, by a plot of HCHO emission rates in Elevated conditions versus those determined simultaneously in Typical conditions for the dry products. Plotting the entire data set in this way minimizes the impact of uncertainties in individual values, and allows the overall pattern of results from the data to be seen. The data plotted in Figure 15 are the same as those shown in Table 9; the solid line in Figure 15 is the 1:1 line.

For most dry products, the data in Figure 15 are scattered along the 1:1 line. Of the 57 data points in Figure 15, 43 indicate Elevated emission rates between 0.5 and 1.5 times the corresponding rate in Typical conditions. There was a tendency for Elevated emission rates to

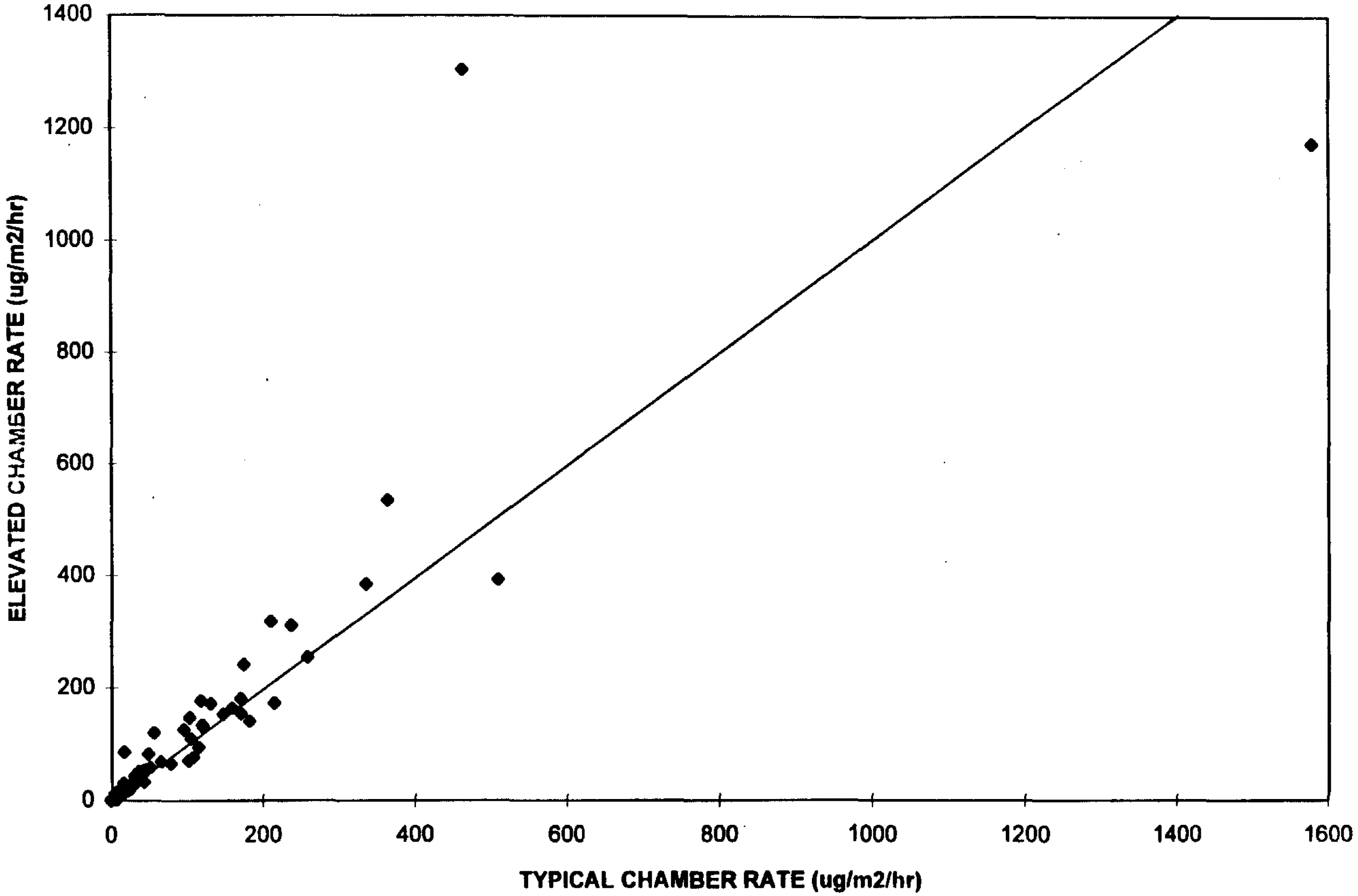

FIGURE 15. COMPARISON OF HCHO EMISSION RATES IN TYPICAL AND ELEVATED CONDITIONS

be slightly higher than Typical emission rates. For example, the average Elevated/Typical emission rate ratio from all 57 data points was 1.36, and the median value was 1.08. However, the overall result shown in Figure 15 is that HCHO emission rates in the two sets of test conditions were generally not much different.

The two highest data points in Figure 15 are of interest. A sample of 1/4" UF particleboard, which was the highest emitting dry product in Typical conditions (product No. 1 in Table 9), showed emission rates of 1,580 $\mu g/m^2/hr$ in Typical conditions and 1,170 $\mu g/m^2/hr$ in Elevated conditions. On the other hand, the MDF cabinet doors with acid-cured coating (product No. 20 in Table 9) showed emission rates of 460 $\mu g/m^2/hr$ in Typical conditions, and 1,300 $\mu g/m^2/hr$ in Elevated conditions. This latter Elevated/Typical ratio of over 2.8 is considerably higher than the corresponding ratio of less than a factor of 1.5, found for the bare MDF cabinet doors (product No. 3 in Table 9), suggesting that HCHO emission from the acid-cured coating is more sensitive to changes in test temperature than is emission from the MDF itself.

A review of the dry product emission rates shows that some product categories exhibited more consistent behavior than others, with respect to Elevated vs. Typical emission rates. The bare UF wood products consistently showed Elevated rates quite close to those in Typical conditions. For bare UF products, the average (± std. dev.) of all Elevated/Typical emission rate ratios was 1.09 (± 0.25). Thus those products in general show little variation in HCHO emissions over the range of test conditions. Permanent press fabrics, decorative laminates, and fiberglass products also showed similar behavior. In contrast, coated UF wood products and PF wood products showed greater variability from one product to another in terms of relative emission rates in Elevated and Typical conditions. The relatively low emission rates found for many of these products may be a factor in the variability of E/T emission rate ratios. In the case of the coated UF products, the nature of the coating itself may also affect the sensitivity of the emission rate to changes in test conditions.

Table 11 in Section 6.3 shows the response of HCHO emission from wet products to differences in the test conditions. In general the wet products exhibited higher R_o values in the Elevated conditions, indicating more rapid evolution of emissions at the higher temperature in that chamber. However, the total mass of HCHO emitted was often lower in the Elevated conditions than in the Typical conditions. This observation may indicate that more rapid curing or drying of the applied products restricted later emissions of HCHO. This behavior was not universal, however, as both the base and top coats of the commercially-applied floor finish showed higher R_o values and higher total HCHO emissions in Elevated conditions than in Typical conditions.

Two main opposing factors control the relative emission rates of HCHO in the Elevated and Typical conditions. The higher temperature in the Elevated conditions favors higher emission rates. However, the lower air exchange rate in the Elevated conditions results in higher absolute HCHO concentrations, which can restrict the rate of diffusion of HCHO from the product. The results in Figure 15 show that these two factors are roughly in balance for most of the products tested, that is, the restriction of emission caused by reduced air exchange approximately cancels the increase in emissions caused by a higher temperature. The scatter shown in Figure 15 reflects the uncertainties in the emission rate determination, and the sample-to-sample differences in the relative balance of these two factors. In addition, the response of each sample to absolute humidity may play a role. Although both chambers were maintained at 50 percent RH, the absolute humidity in the Elevated conditions was about 40 percent greater than in the Typical conditions.

The comparisons shown above are consistent with previous evaluations of product emissions under varying test conditions, though changes in both air exchange rate and test temperature have not been evaluated previously. For example, Nelms et al. (1986) tested particleboard under constant temperature and RH conditions, but with varying product loadings and air exchange rates. In that study reducing N/L lowered HCHO emission rates, all other parameters being constant. At N and L values similar to those in this study a reduction of N/L by a factor of 3, comparable to the difference in N/L between the two test conditions in this study, reduced HCHO emission rates by about 40 percent (Nelms et al., 1986). For comparison, the increase in HCHO emission expected between 70 and 80°F (ASTM, 1990) is about a factor of 1.8. Thus approximate compensation of these two factors is not unexpected. Black and Bayer (1986) also tested hardwood plywood and particleboard underlayment at different N/L ratios, at N and L values similar to those in this study. At various constant L values in a small chamber, reducing N by a factor of 2 reduced HCHO emission rates from particleboard underlayment by 22 to 52 percent. For hardwood plywood, the corresponding reductions in HCHO emission were 16 to 29 percent. The present results are also consistent in part with the observations of Pickrell et al. (1984), who found that HCHO emission rates from particleboard and plywood were reduced at lower air exchange rates. However, Pickrell et al. (1984) reported no effect of temperature on HCHO emission rates from particleboard and plywood, over the range of 25-35°C. The absence of a temperature dependence is surprising, but may be due to the very high product loadings (8.6 and 11 m^2/m^3) and high chamber HCHO concentrations (11,400 to 24,300 $\mu g/m^3$, or 9.2 to 19.6 ppmv) in the tests by Pickrell et al. (1984).

Wet products have also been tested for sensitivity to N/L effects, albeit for total VOC emissions, not HCHO emissions. Tichenor and Guo (1991) found that R_o values for total VOC's from three products were decreased sharply by lower N values at constant L. However, over a seven-day test period the total emissions per m^2 of product surface were relatively constant, despite changes in N and L (Tichenor and Guo, 1991). The latter results are consistent with those for total HCHO emissions in Table 11. However, the former results contrast with the generally higher R_o values found in this study in the Elevated conditions (Table 11). This observation suggests that the higher temperature in the Elevated conditions in this study outweighed the restriction of HCHO emission caused by the lower N value, resulting in generally higher R_o values.

7.4 Discussion of TDI Test Results

The primary result of the TDI screening in this study was the absence of detectable TDI emissions, despite the exaggerated screening conditions and the use of both real-time and integrated methods of TDI measurement. The TDI screening tests were sensitive enough to detect TDI emissions corresponding to lifetime indoor cancer risks of about 1×10^{-6} (Section 4.4.3). Thus the negative screening results suggest that the cancer risk from TDI emission from residential materials is probably negligible. Furthermore, the loss of TDI to surfaces observed in the chamber characterization effort in this study suggests that any TDI emitted in residences will not remain in the air for long. Instead, TDI will rapidly be adsorbed on the numerous surfaces in a home. This effect makes it even less likely that significant exposure to TDI will result from inhalation of TDI emissions occurring indoors. However, this effect also suggests dermal or ingestion exposure to TDI or its decomposition products, present on surfaces or in house dust, as possible alternative exposure pathways. In any case, the absence of detectable TDI emissions in the screening tests indicates that release of TDI to air from common residential products is negligible.

The absence of TDI emissions from the products tested probably results from both the reactivity of TDI and the use of other isocyanate formulations in PU products. The reactivity of TDI probably results in minimal residual levels of free TDI in fully reacted PU products, such as the polyurethane foams. On the other hand, especially for the wet PU products, the toxicity and volatility of TDI has motivated a shift to other less toxic and/or less volatile components. Many products now are made with other isocyanates such as methylene diphenyl diisocyanate (MDI) or with a prepolymer or dimer of an isocyanate. The exact nature of the isocyanate reactant was not established for all products tested, but the products tested do encompass the variety of PU products commonly available to California residents.

The TLD-1 monitor used in the TDI testing was not specific for TDI. The absence of response from the monitor in the screening tests thus also indicates no detectable emission of other isocyanates that might have been present in the products tested. Therefore, assuming equal sensitivity for all isocyanates, the negative screening results also indicate at most minimal emissions for any other isocyanates that may be present in the tested products.

The only product found to emit TDI was the commercially-applied concrete water stop product. Although of little consequence for residential use, that product does serve as a useful benchmark of TDI emissions. The final tests of that product (Section 6.5) showed an initial room-temperature TDI emission rate of about 288,000 $\mu g/m^2/hr$. Based on the composition of the product (up to 4 percent TDI by weight) and assuming that TDI emissions scale linearly with TDI weight fraction, a different product containing (e.g.) 40 ppm by weight TDI would have an initial emission rate of roughly 288 $\mu g/m^2/hr$. This scaling is of course only an estimate, and is reasonable only for comparison to other wet products similar to the water stop product. It is not feasible to make comparable estimates of the total amount of TDI that other products might emit, since that emission will be limited by the speed of reaction of the product in question. It is noteworthy that despite the rapid initial emission rate of the water stop product, the total TDI emitted in the final tests at 70°F amounted to only about one percent of the TDI present in the tested sample. At 80°F the TDI emissions were about 5 percent of the total TDI in the sample.

The final tests of the water stop product showed that most of the TDI emitted was the 2,6-isomer, rather than the 2,4-isomer which is predominant in the product formulation. Although preferential emission of the 2,6-isomer has been observed in PU foam manufacturing facilities, and attributed to its lower reactivity relative to the 2,4-isomer (Rando et al, 1984), the present results are the first to show that effect with a wet product. The toxicity of the 2,4- and 2,6-isomers may differ, so that accounting for the identity of the emitted TDI isomers may be important in TDI exposure assessments.

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