AIVC 12,461

PERGAMON

Building and Environment 35 (2000) 53–57

BUILDING AND ENVIRONMENT

www.elsevier.com/locate/buildenv

Interlaboratory comparison experiment on the determination of formaldehyde emitted from mineral wool board using small test chambers

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Received 8 June 1998; received in revised form 12 August 1998; accepted 11 December 1998

Abstract

The paper presents results of interlaboratory comparison on the emission of formaldehyde from mineral wool board. Eleven laboratories took part in these studies. The results showed significant variances between laboratories. The discrepancy was related to the chamber conditions and sampling. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Building and furnishing material may emit many volatile organic compounds (VOC_s) into the indoor air [1]. Due to the toxicity of these compounds it is necessary to use less polluting material [2].

Formaldehyde is now a ubiquitous chemical that has been found at low levels at homes, in offices, and in the urban environment. Many sources that contribute to formaldehyde exposure in the indoor air include insulating materials, pressed wood products and soft furnishings fireproofed with formaldehyde based resins [3,4]. The emission of formaldehyde from these materials depends on ageing processes of time [5–8] and environmental conditions [9–11].

The indoor air standard for formaldehyde has been set up in many countries [12]. The Ministry of Health and Welfare in Poland recommended indoor air standards for 35 compounds including formaldehyde [13].

The comparison of emission measurements carried out by different laboratories becomes important in view of their utilisation for materials emission databases [14,15].

The aim of the interlaboratory study was twofold: firstly the comparison of formaldehyde determination in control water samples (first test) and secondly the comparison of formaldehyde emission rate determination from mineral wool board using a small test chamber (second test) according to the Polish Standard [16].

2. First test—the measurements of formaldehyde concentration in the control samples

2.1. Experimental design

Nine laboratories took part in series 1 and eleven in series 2 in the interlaboratory studies. The participating laboratories received four formaldehyde water samples (1,2,3,4 mg × cm^{-3}) for determination of this compound concentration in each sample.The concentrations of formaldehyde were so high due to the instability of diluted water solutions.

The sample analysis should be conducted during 7 days. Directly before analysis each sample had to be diluted 500 times or even more (5000 times) depending on the sensitivity of the analytical method used. The stability of the lowest formaldehyde concentration (1 mg × cm^{-3}) was checked in our laboratory includ-

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PII: S0360-1323(99)00003-7

Table 1
Results of the first test: concentration of formaldehyde in series 1 and 2. ($\bar{x}$—average; s—standard deviation)

	Formaldehyde concentration (μg × cm^{-3}) Series 1				Series 2			
	A	B	C	D	A	B	C	D
$\bar{x}$	1.94	3.74	5.83	7.71	1.96	3.89	5.50	7.38
s	0.21	0.57	0.47	0.68	0.16	0.17	0.37	0.41
$(s/\bar{x}) \times 100$	11.0	15.2	8.0	8.8	8.4	4.4	6.7	5.5
n	8	9	8	8	11	11	11	11
max	2.20	4.10	6.29	8.29	2.14	4.04	6.05	8.05
min	0.98	2.62	3.10	4.80	1.57	3.49	4.47	6.55

ing conditions of transport (12 h at room temperature) and storage (7 days at −20°C).

The participating laboratories used different colorimetric methods for formaldehyde determination:

- method with chromotropic acid—sulfuric, forming a purple monoacetionic chromogen [17]
- method with p-rosaniline, forming a violet complex of p-rosanilin-methyl-sulfonic acid [18]
- method with acetyloacetone, forming a yellow diacetyldihydrolutidine [19,20]

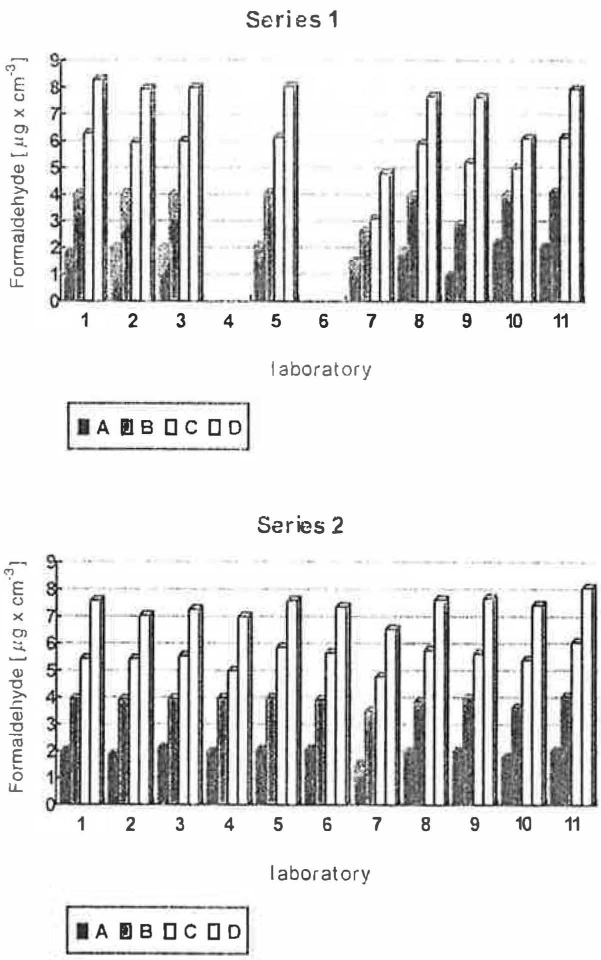

Fig. 1. Results of the first test: concentration of formaldehyde in series 1 and series 2.

2.2. Results and discussion

Dixon test identifies the results from two laboratories as outliers in the series 1. Table 1 and Fig. 1 represent the results of two series of formaldehyde analysis. The comparison of these results shows that series 2 gives better accuracy than series 1, relative coefficient of variation's range between 4.4–8.4% and 8.0–15.2%, respectively. The results of series 2 suggest that participating laboratories have sufficient experience in the formaldehyde analysis.

3. Second test—measurement of formaldehyde emission from mineral wool board

3.1. Experimental design

Eleven laboratories participating in the first test took part in the inter-laboratory comparison on the emission of formaldehyde. The material selected for the experiment was a mineral wool board (180/150) glued with phenol-formaldehyde resin. Two identical samples of material were delivered directly from the plant to each laboratory. The material was cut in pieces of 12.5 × 25.0 × 5.0 cm in size (0.1 m^2 area). Considering a loading ratio of 1 m^2 × 1 m^{-3}, taking the area of all six walls in consideration, each sample consists of a number of pieces proportional to the chamber value. The material, if wrapped in polyethylene, appears to maintain its emission properties for some time.

The test was carried out 14 days (run 1) and 16 days (run 2) after the production of this material. It was necessary to avoid any variation that might have occurred due to time difference in the test. Samples were stored at room temperature until the beginning of the experiment.

Table 2
Chambers and experimental conditions

Laboratory	Chambers				Conditions		
	Volume [l]	Wall material[a]	Size l × w × h (cm)	Fan[b]	Temp. (°C)	RH (%)	Air change rate (h^{-1})
1	600	SS	60 × 100 × 100	FNR	22.5	50	1
2	600	SS	100 × 100 × 60	FR	23.0	45	1
3	293	SS	10 × 59.7 × 49.1	FR	23.0	40	1
4	500	glass	–	FNR	17.0	73	1
5	300	Al	100 × 60 × 50	FNR	20.0	45	1
6	200	SS	–	FNR	23.0	–	1
7	200	SS	50 × 50 × 80	FNR	21.5	43	1
8	200	glass	–	FR	23.0	45	1
9	600	Al	–	FR	21.5	26	1
10	600	Al	–	FNR	24.5	47	1
11	200	glass + Al	–	FR	23.0	44	1

[a] SS = stainless steel; Al = aluminium.
[b] FR = fan running; FNR = fan not running.

The prescribed chamber conditions were: temperature 23°C, relative humidity 45%, air exchange $1 \times h^{-1}$, loading factor $1\ m^2 \times m^{-3}$, the air sampling 24 h and 28 h at the beginning of experiment [16]. Probably, however, they do not reach the formaldehyde steady state in the chamber. Sampling and analyses were carried out in duplicate.

The participants did not always comply with experiment specifications, the majority of the chambers being operated at temperatures of 20.0–24.5°C and RH 40–50% (Table 2).

The preliminary homogeneity test of mineral wool board was carried out in our laboratory by measuring the emission rate of 36 pieces (6 pieces in 0.6 m^3 chamber volume) selected at random. The measuring was conducted 8 days after production date. These data are presented in Table 3.

3.2. Results and discussion

The results obtained from each participating laboratory, classified per run, sampling hours and measurement into 8 data are reported in Table 4. These data are represented graphically in Fig. 2, which gives the average of two measurements (or single measurement in a few instances where the two measurements are not available). All values of run 1 and 24 h of run 2 from laboratory 4 were far higher than the other data. These values were excluded from the average calculation. Table 5 shows a summary of statistics for the emission rate of formaldehyde per run and sampling hour. The averages of the two runs appear to be different, whereas those of different hours in the same run are rather similar.

Two-way nested classification analysis of run 1 and run 2 (Table 6) shows that differences between samples are rather insignificant but between laboratories are very high. Variability due to the sample heterogeneity is in good agreement with the results of the preliminary test carried out in our laboratory (Table 3). The precision of formaldehyde determination is sufficient as the first-test (Table 1) showed. The most important source of variation (second-test) is interlaboratory bias due to heterogeneity of chamber conditions and probably sampling air.

4. Conclusion

The interlaboratory results showed significant variances between laboratories, only in small part caused by formaldehyde analysis or sample heterogeneity. The discrepancy was related to the chamber condition and sampling. These results support the necessity of using

Table 3
Homogeneity of the mineral wool board. ($\bar{x}$ average; s standard deviation)

	Temperature (°C)	RH (%)	Emission factor ($\mu g \times m^{-2} \times h^{-1}$)
$\bar{x}$	21.5	41.0	61
s	0.77	4.6	5.3
$(s/\bar{x}) \times 100$	3.6	11.2	8.7
min	20.5	35.0	53
max	22.0	47.0	68

Table 4
Emission factors of formaldehyde from mineral wool board (μg × m^{-2} × h^{-1})

Laboratory	Run 1				Run 2			
	24 h	24 h	28 h	28 h	24 h	24 h	28 h	28 h
1	172	174	153	155	174	180	198	201
2	44	44	50	50	42	42	45	45
3	81	81	77	77	77	77	63	63
4	408	395	340	315	312	315	210	225
5	109	114	128	127	112	141	132	138
6	55	55	57	57	48	48	51	51
7	39	36	54	22	34	61	55	44
8	60	–	52	–	51	–	49	–
9	38	37	37	38	50	55	44	52
10	46	50	50	52	45	70	58	63
11	48	–	50	–	55	–	57	–

Table 5
Summary statistics of emission factors of formaldehyde for mineral wool board per run and sampling time

Run (h)	*N*	Mean (μg × m^{-2} × h^{-1})	S.D. (μg × m^{-2} × h^{-1})	Variance
1 (24)	10	69.7	42.8	1832
1 (28)	10	69.5	39.7	1576
2 (24)	10	73.6	44.0	1936
2 (28)	10	75.9	51.0	2601

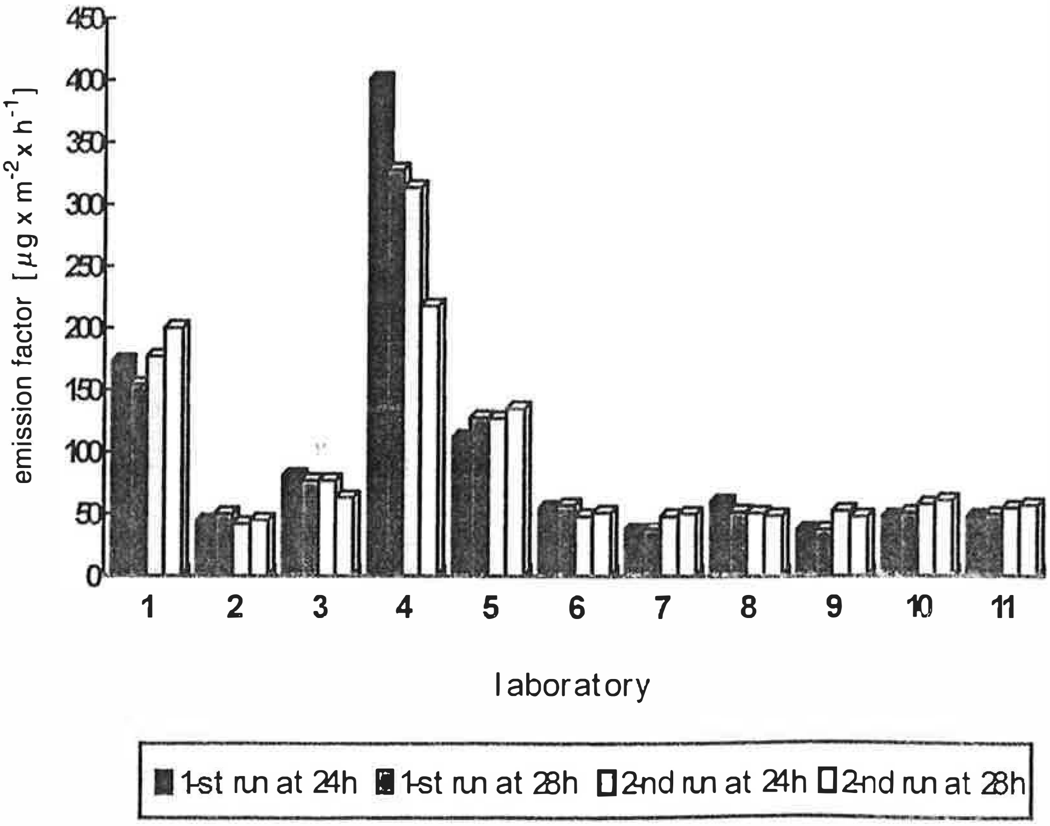

Fig. 2. Mineral wool board emission factors of formaldehyde.

Table 6
Two-way nested classification analysis of runs 1 and 2 for mineral wool board. (S_L^2—variance between laboratories; S_S^2—variance between samples, within laboratories; S_M^2—variance between measurements, within samples: $V_{L,S,M}$—degrees of freedom: $F_{L,S}$—Snedecor's factor; $P_{L,S}$—probability)

	Hour	S_L^2	V_L	F_L	p_L	S_S^2	V_S	F_S	p_S	S_M^2	V_M
Formaldehyde	24	432.126	8	625.012	0.0000	2.507	1	3.626	0.0730	0.691	18
	28	253.958	8	427.419	0.0000	2.834	1	4.769	0.0425	0.594	18

identical experimental conditions and including air speed measurements in chambers.

Acknowledgements

The authors acknowledge the contribution of participating laboratories, and Prof. Leszek Zaborski M.D. who helped in the statistical evaluation of the studies.

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