INDOOR AIR QUALITY & ITS IMPACT ON MAN

Environment and Quality of Life

Report No. 13

Determination of VOCs emitted from indoor materials and products

Interlaboratory comparison of small chamber measurements





Commission of the European Communities Directorate General for Science, Research and Development Joint Research Centre - Environment Institute

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INDOOR AIR QUALITY & ITS IMPACT ON MAN

(formerly COST Project 613)

Environment and Quality of Life

Report No. 13

Determination of VOCs emitted from indoor materials and products

Interlaboratory comparison of small chamber measurements

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reviewed by

The Steering Committee



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Abstract

An interlaboratory comparison using three materials has been organized to assess the agreement among laboratories undertaking tests to characterise the emission of volatile organic compounds from indoor materials and products using small test chambers. The twenty participating laboratories showed the following main results. Chambers of different materials (glass and stainless stell) and of widely different capacity (0.035 to 1475 ℓ .) appeared equally suitable. The repeatability of duplicate measurements (including sampling) within each laboratory was good. The test with a known n-dodecane source showed, for most laboratories, an unexpected and yet unexplained discrepancy. The interlaboratory agreement appeared reasonable (coefficient of variation 26-42%) when testing a PVC tile, but for a wax the scatter was very high.

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INTRODUCTION

During the last few years, increasing interest has been shown in the emission of volatile organic compounds (VOCs) from a variety of materials used indoors, in construction, furnishing and in different houshold activities. This interest is motivated by the wish to reduce the exposure of humans to toxic substances and, in general, to improve the quality of indoor air by the use of less polluting materials. The comparison of emission measurements carried out by different laboratories on such materials becomes particularly important in view of their utilization for material emission databases, which are now in preparation.

The U.S. Environmental Protection Agency has developed a guideline "Indoor Sources: using small environmental test chambers to characterize organic emissions from indoor materials and products", which was successively adopted as the ASTM Guide (1). This text has been revised and adapted by the European Concerted Action "Indoor Air Quality and its Impact on Man" and has been published as "Guideline for the characterization of VOC emitted from indoor materials and products using small test chambers" (2).

The scope of the experiment described here was twofold: firstly to obtain an experimental validation of the Guidelines mentioned above and secondly to assess the comparability of results obtained by different laboratories on the same material.

The Indoor Pollution Unit of the Environment Institute at the CEC Joint Research Centre (Ispra, Italy) assumed the task of co-ordinating the experiment and supplying the test materials. The national representatives in the European Concerted Action "Indoor Air Quality and Its Impact on Man" acted as information/invitation centres in their respective countries; the same function was carried out by the EPA/ AEERL Indoor Air Branch in the USA and in Canada.

A total of 22 laboratories (including two for which the analytical capability was supplied by others) expressed their intention to participate: two of them subsequently retired. The 20 laboratories participating in at least one of the tests and the scientists responsible are listed in Appendix A. Three test materials were distributed in September 1991, November 1991, and January 1992, respectively.

The output of the experiment, condensed in the draft of this report, was discussed in a meeting of the European participants: the minutes of the meeting are attached as Appendix C and several comments contained therein were included in the Conclusions (see below).

EXPERIMENTAL DESIGN

The comparison has been realized in three steps of increasing complexity. In the first step vials emitting a single compound, n-dodecane, at a known constant rate, which could be determined individually through the weight loss in a defined time interval, have been distributed. The scope was to check for losses (sinks) and other possible errors in the chambers and for accuracy of the analytical procedure. This was possible by comparing the emission rate determined from the weight of n-dodecane lost from the source during the experiment with that calculated from the measurements of concentration in the chamber after 24, 48 and 72 h and the air flowrate through the chamber.

In the second step each participant received two samples of PVC flooring material, for which the emission rate of four compounds (phenol, 1,2,4-trimethylbenzene, n-decane and n-undecane) and of TVOC (Total Volatile

Organic Compounds) was requested. In order to reduce the scatter of results due to the decline in emission rate with time for this material, in addition to wrapping the samples in aluminium sheets during storage, a precise period of two weeks was fixed for the test. This requirement was adhered to by most participants, a few of them delayed by one week because of a national holiday in the USA, one participant delayed three weeks and another one six weeks.

In the third step a water-based liquid floor wax was distributed requesting that sampling and measurement be carried out at ten different intervals in order to find out the concentration-time curve for four compounds (α -pinene, linalool, geraniol and α -cedrene) and TVOC. This curve is such that, after reaching a maximum, the concentration falls rapidly so that in 24 hours the test is concluded.

Additional details on the test materials and on the tests themselves are reported in the following sections and in Appendix B. No method has been prescribed for VOC sampling and analysis. In fact, according to the Guidelines, each investigator was free to use his/her usual procedure. Some details of the analytical methods used by the laboratories which provided them are reported in Appendix D.

The 24 chambers used for this experiment had capacities ranging between 35 cm³ (3) and 1.475 m³. Table 1 reports the single capacity values. The chamber wall material was stainless steel for 19 chambers and glass for 5. Few additional details on chambers are given in Appendix D.

RESULTS AND DISCUSSION

First test

The aim of this test was to check the whole procedure chamber-sampling-analysis by comparison of the emission rate of n-dodecane as determined by weight loss and by measuring its concentration in the chamber. The results are reported in Table 2 (individual concentration data) and in Table 3 (mean emission rates). The large differences in the emission (evaporation) rates which appear in the 2nd column in Table 3 are due to the varying air velocities and/or vial position in the chamber: a very clear illustration of this fact is given by the results obtained in the 225 litre chamber (laboratory n.3) with the fan on and off, respectively.

The participants in general complied with the experimental specifications, the majority of the chambers being operated at the temperature and RH specified or very close to them. The same was true for the air exchange rate, with the exception of laboratory 7 (0.25 h-1) and of laboratory 13, where the microchamber called FLEC (3) is employed (171 h-1).

A preliminary comment on the results of this test concerns the emission rate determined by concentration measurements at 24, 48, and 72 hours. As explained in Appendix B, the replication of the sampling and measurement at increasing times, was aimed at highlighting any reversible sink effect. The presence of such an effect would, with time, lead to increasing values of the concentration (and hence of the emission rate), due to the gradual saturation of the sink. This trend is evident in a few cases: e.g. laboratory 3 with fan on, laboratory 8 (both chambers) and laboratory 9. In other cases no clear trend is evident. Even the opposite trend (emission rate decreasing with time) occurs in one case (laboratory 5).

Comparing the emission rates obtained by weighing with those calculated from the air concentration (see Figure 1), it appears that the latter gives lower values in almost all cases, and much lower in some. The results were statistically evaluated by comparing ("t" test) the mean of the emission rates computed from

the measured chamber concentrations with the rate expected from the source weight loss for each individual laboratory. As could be anticipated just by a quick look at Figure 1, these differences, in general, are very significant (P < 0.01) - the few non-significant ones being related either to laboratories with near zero differences or to laboratories with considerably scattered concentration results.

Hypotheses to explain this discrepancy are as follows: irreversible or very slowly reversible sinks in the chamber, error in the flowrate determination, error in the analytical system, error in weight loss measurements and inadequate chamber mixing. In particular, an error in flow rate determinations occurs if the resistance of the flow measuring device is ignored, when this device is not permanently installed. If the resistance is not negligible, the measured flow rate will be lower than that occurring while no measurement is being carried out and hence the emission rate by concentration will be underestimated.

There are indications that sinks could explain at least part of the discrepancy in Figure 1. In fact, tests carried out at two laboratories by increasing chamber temperature up to 60 °C after removal of the source, showed higher n-dodecane concentrations in the air leaving the chamber than at 23 °C. Also when the inner face of the chamber door was washed with n-heptane in our laboratory measurable amounts of n-dodecane where found in the solvent. However the detected amounts were not sufficient to explain the difference between the expected and the measured concentrations. On the other hand, the discrepancy between expected and measured emission rates seem to be related to the ventilation rate and to the temperature of the chamber or the vapour pressure of the compound under investigation, as has been observed during the first test and in further experiments reported in Appendix E). These results support the sink hypothesis.

Second test

Grey 2 mm thick PVC flooring tiles were selected because they emitted a range of both polar and nonpolar compounds (see chromatogram in Figure 2).

In order to eliminate any bias due to different emission from edges and taking the chamber capacities into account, we decided to distribute this material cut into 10x10 cm samples: one of these samples yielded the desired loading ratio of 0.4 m² m⁻³ in the 50 l chambers, for smaller chambers a further cut being required. The homogeneity of this material was investigated at our laboratory by measuring the emission rate of twenty 10 x10 cm elements, selected at random by a uniformly random number generator from different PVC tiles. Actually 2 out of 25 elements were selected from each out of 30 tiles. The single elements were placed in a 5 l chamber under a flow of dry nitrogen (0.5 l min-1, i.e. 6 h-1 air exchange rate) at room temperature and a 1 l sample was collected after 1 hour. Table 4 reports the standard deviations and ranges observed for each of the target compounds, as well as for temperature, flow rate and weight, which are parameters that directly affect emission rate.

The participants in general complied with the experiment specifications, the majority of the chambers being operated at the temperature and RH specified or very close to them. The same was true for the air exchange rate, with the exception of laboratory 7 (0.25 h-1).

The participating laboratories have given the results of emission measurements in terms of emission rate ($\mu g \ h^{-1}$), as requested in the report forms (see Appendix B). These figures have been transformed into emission factor data ($\mu g \ h^{-1} \ m^{-2}$) by dividing by the appropriate sample area (208 cm² is the total area of a 10x10 cm element) introduced into the chamber to comply with the established loading

factor. In fact, three laboratories with the smallest chambers used the full 10x10 cm elements which resulted in a loading factor higher than prescribed: this had no apparent influence on the results, even in the case of the 4 \(\mathcal{L} \) chamber, where the loading factor was more than tenfold higher.

Individual results, classified per run, sampling hour and measurement into 8 data sets per compound, are reported in Tables 5 to 9 where dots indicate missing data.

These data are represented graphically in Figures 3-7, which give the average of the two measurements (or single measurements in a few instances where the two measurements were not available) requested at each run and sampling hour. All values of run 2 from laboratory 22 and all TVOC values from laboratory 15 are far higher than the other data. Removal of these data makes the 40 sets consistent with the hypothesis of data normality (Quantile/Quantile correlation test and Shapiro-Wilk test; P>0.05), two exceptions being the two TVOC sets of run 1 at 72 h, 1st and 2nd measurement. For these sets, the Dixon test identifies the two results from laboratory 9 (3995 and 3928 $\mu g.m^{-2}\ h^{-1}$) as outliers (P < 0.01). Removal of these data, however, only marginally improves the normality of the two sets. Moreover, the scope of the intercomparison is not that of arriving at a "spotless" consensus value but, rather, that of showing how, as a whole, the laboratories performed. Therefore, for the statistical analysis which follows, these two values were kept, the measure of removal being taken only against the gross outliers from laboratories 22 and 15 mentioned previously.

Table 10 gives summary statistics for the emission factors of each compound per run/sampling hour. In this Table, the means of the same run at different hours appear to be different and to decrease with time, whereas those of different runs at the same hour are rather similar and without a clear trend; the implication is that a steady emission rate has not yet been reached at 48 h, although the repeatability of the runs was quite good.

Paired replicate tests ("t", Wilcoxon signed rank and sign test), carried out on the averages of the two measurements per run and sampling hour supplied by each laboratory, show a significant difference between the means of the same run at diverse hours and a non-significant one between those of different runs at the same hour.

Considering the above findings and the type of experimental design used, the sources of variability of the data were quantified by the analysis of variance technique known as two-way, nested classification. The analysis, carried out on the measurements of different runs taken at the same hour, allows for the subdivision of the total variance of the data into three main components.

- S²_L (between laboratories) ascribed to laboratory differences;
- S²s (between samples, within laboratories) ascribed to sample heterogeneity and to possible variations that occurred within the laboratories from run to run;
- (between measurements, within samples) ascribed to variations that occurred in the duplicate measurements made at a given sampling hour (usually referred to as random error).

The analysis demanded two non-empty cells per laboratory, each containing at least one measurement. For this reason a minor number of laboratories could not be included therein (see Tables 5 to 9). For each compound, the analysis always showed significant variances "between samples" and "between laboratories" (P

< 0.01). The suggested estimates, expressed as standard deviations (square root of the corresponding variances), are reported in Table 11

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Despite some possible distortion due to data imperfection, the results look rather homogeneous at both times (compare the relative standard deviations), giving a reasonable measure of the small size of the random error compared to sample heterogeneity and interlaboratory bias. Variability due to sample heterogeneity is in good agreement with the results of the preliminary homogeneity test carried out in our laboratory (see above and Table 4). The interlaboratory bias is the most important source of variation of the data: to this aim, note that the standard deviation of a single measurement must be expressed as: $S = (S_1^2 + S_2^2 + S_M^2)^{\frac{1}{2}}$

Third test

The purpose of this step was to test the Guidelines and the agreement amongst laboratories in the case of a source that is rapidly exhausted and hence cannot provide a "constant" concentration. The assessment of the emission rate in this case requires several measurements and the use of a model to interpolate the concentration versus time curve. It was assumed that the emission decreases through a first order decay. It was requested that the initial emission factors and decay constants be estimated through equation 9 reported in Section 6c of the Guideline (2) and referred to as the decreasing emission rate model.

A liquid , water-based, floor wax was chosen for which the concentration-time curves of α -pinene, linalool, geraniol, α -cedrene and TVOC were requested. An example gas-chromatogram of the vapours from this material is shown in Figure 8.

The participants in general complied with the experimental specifications, the majority of the chambers being operated at the temperature and RH specified or rather close to them. The same was true for the air exchange rate, with the exception of laboratory 7 (0.25 h-1) and laboratory 13, which employed the unique type of micro-chamber called FLEC (171 h-1).

The participants were requested (see Appendix B) to use a chamber loading ratio L of $0.4~\text{m}^2~\text{m}^{-3}$ and spread $50~\text{cm}^3~\text{m}^{-2}$, to give an average wax layer thickness of 0.05~mm. Only a few laboratories reported using slightly different amounts (5%) from the specified value and just one used an amount which differed by 25%. Considering that these variations are small and that it was impossible to assign them either to wax thickness or to L alterations, it was regarded as reasonable to assume L = $0.4~\text{m}^2\text{m}^{-3}$ except as otherwise indicated. The peculiarity of laboratory $13~\text{(L}=506~\text{m}^2\text{m}^{-3}$, but wax amount as specified) and of laboratory $20~\text{(which only in run 1 adopted L} = <math>0.41~\text{m}^2\text{m}^{-3}$ using, however, $0.6~\text{cm}^3$ of wax instead of $1.065~\text{cm}^3$) is also worth mentioning.

The initial emission factors (EF)₀ (µg.m-² h-¹) and decay constants k (h-¹) estimated from the reported data using the above mentioned equation, range from very low to very high. From the concentration data provided by the participants, problems of at least three different kinds seem to have been encountered to varying degrees.

Analytical difficulties. Some laboratories, for instance, did get apparently poor separations, especially between linalool and geraniol. For example, one laboratory combined the data for linalool and geraniol. Other laboratories reported thermal decomposition of geraniol, which could not be observed in adhoc tests carried out in our laboratory (240-300°C, GC-FID-MS).

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<u>Chamber difficulties.</u> Examples of these difficulties are: (a) data lying well above the requested fitting curve due, presumably, to chamber sink effects or, (b) rather

scattered data due, presumably, to some loss of control of chamber parameters. It must be emphasized that all laboratories, to varying extent were faced with sink effects (often very severely). Generally, α -pinene and, to a lesser extent, linalool were the compounds least affected by such effects: Figures 9 and 10, taken from run 1 of laboratory 14a (the JRC Environment Institute), illustrates a non-severe sink case and a rather important one for α -pinene and geraniol, respectively. It must be noted that these figures do not show either the most favourable or the worst examples of such an effect.

Curve fitting difficulties. Non-linear regressions are sometimes difficult to carry out satisfactorily and apparently, for unknown reasons, some laboratories did not achieve their best parameter estimates. Causes might have been the data themselves (problems of model overparametrization, see later), poor parameter guesses and perhaps, in a very few instances, the application of a fitting model different to the one requested. Minor problems which do not strictly belong to the above category, but which affected the results were: (a) occasional selection on an unknown basis of the data to regress and, (b) regressions frequently carried out using simply the initial sampling time rather than, more correctly, the initial one plus half the sampling interval expressed in hours.

In an effort to compare "homogeneous" values, the results in Tables 12 to 16 are given after re-computation of all regressions on the basis of common rules, that is:

- no data selection.
- sampling time equal to the initial one plus half the sampling interval, in hours.

In addition most laboratories used zeros for data below the detection limit. Therefore, the data below detection limit reported by laboratories 1, 4, 20 and 22 were replaced by zeros. Furthermore, as nearly all the reported linalool chamber concentrations were much larger than the geraniol concentrations, the combined linalool/geraniol data mentioned above were classified as linalool.

Tables 12 to 16 report separate results for the two runs. Besides (EF) $_0$ and k for the decreasing emission rate model as described in the Guideline (2), the value of the initial amount of compound on the glass support M_0 ($\mu g \, m^{-2}$), is given. This parameter is the ratio between (EF) $_0$ and k and results from the fact that equation 6 of the Guideline (2):

$$(EF) = (EF)_0 \exp(-k t)$$

can be demonstrated as being equivalent to:

$$(EF) = k M_0 \exp(-k t)$$

i.e., the emission factor at a given time can be thought of as proportional to the exponentially decaying residual mass of compound per unit area of source, with k as the proportionality constant. Clearly, especially in the presence of sink effects, all these estimates may be incorrect to an extent which depends on how well the model fits the experimental data.

Previous experience (4) suggested that in general the empirical model gives more acceptable estimates of (EF)₀ for "difficult" data like, for example, those of Figure 10. For the sake of comparison, this parameter referred to as (EF)₀emp. in Tables 12 to 16 and estimated by equations 11 and 15 of the Guideline (2), is also reported. If sink effects do not perturb the data, a satisfactory agreement between the two different (EF)₀ estimates is usally obtained.

Table entries denoted as "over" mean that overparametrization of the fitting model occurred. In these instances the data looked in practice as though they were only due to a process of decay. In other words, lack of proper data in the rising part of the concentration curve resulted in the model being unable to perceive and locate the maximum, the fit then resulting in a variety of equivalent, but different and ambiguous estimates. Figures 11 to 25, which visualize the above values in log form, clearly show the large range of results (for comparison, those from the PVC tile exercise would have filled two log decades only).

Considering the scatter of the data, it was regarded as adequate just to provide non-parametric summary statistics of the results. These included all results and are reported per compound in Tables 17 to 21.

CONCLUSIONS

The experiment has highlighted several interesting aspects of the state-of-the-art in determining VO€ emission from materials by small test chambers. On the basis of the data analysis carried out, the principal aspects are the following.

At the level of variability encountered, the wide range of chamber capacity (0.035 to 1475 ℓ) does not introduce any systematic difference in the results. This conclusion is supported by the fact that no significant correlation is found between results and chamber volume (P>0.05) for n-dodecane (percent difference between expected and observed emission rate) and PVC tile (emission factors). However, larger chambers show a tendency to give less scattered results than smaller chambers for PVC tile and this may be explained by the heterogeneity of the material, more important for the smaller sample sizes.

Also the chamber wall materials, glass and stainless steel, appear to be equally suitable for this experiment: no difference was observed in a co-variance analysis of results (see above) on chamber volume, carried out for the two chamber groups.

With a few exceptions, the repeatability of duplicate measurements within each laboratory is good in the first and second test; the PVC tile results, for instance, show a relative standard deviation between measurements in the range of 5.2 to 13% (See Table 11). The repeatability is worse between runs, where also different samples are used however. The scatter between runs is particularly large in the third test: this may reflect the difference in spreading the wax on the support and different air velocities.

The first test shows an unexpected and not yet explained difference, occurring in most laboratories, between the emission rate determined by concentration and that determined by weight loss measurement; the reason(s) for this difference, (which was very large for few laboratories) needs to be investigated further.

The agreement amongst laboratories in the second test, in the light of the type of determination, may be considered acceptable (relative standard deviations ascribed to interlaboratory differences range between 25.7 and 41.7%, see Table 11). If further work has to be done to reduce such differences, this should follow an understanding of the bias observed in the first test.

In the case of the wax test, the large range of estimates for the initial emission factors and decay constants reveals that a number of problems should be solved before aiming at a "consensus" in chamber tests of this kind. This finding shows the need for caution when looking at reported results of emission parameters

from such chamber experiments. At least the model used for fitting purposes and a plot showing how much the fit adheres to the data points should be reported.

Finally the question remains as to how accurate a measure of the real emission rate was provided by the three tests, particularly that involving the wax. Though there is no direct answer, there are few indications which may be helpful. One is reported in Figure 26, which represents a ranking of the laboratories, for the compounds determined in the 1st and 2nd test, established, using the percent difference between observed and expected emission rates and the mean emission factor, respectively. The Figure shows a certain tendency to rank high or low-more evident for some laboratories. This could imply that, like in the 1st test, the "consensus" emission rate of the 2nd test is lower that the real one. A second indication of accuracy, limited to linalool i.e. the main compound emitted from the 2nd test material, was obtained at our laboratory through direct GC analysis of the wax: the content of linalool resulted 10 740 \pm 703 μg m-2 (4 determinations), which is very close to the 75th percentile of M_0 in Table 18.

ACKNOWLEDGEMENTS

The authors gratefully aknowledge the collaboration of all the scientists participating in the experiment and listed in Appendix A; moreover, they are indebted to the European participants for their contribution in the discussion of the results. Finally, the collaboration of Helmut Knöppel in the critical discussion of this report and of Derrick Crump for the revision of the English are also gratefully acknowledged.

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Table 1. Capacity of the chambers used in the experiment

Laboratory n. ⁽¹⁾	capacity (litres)	wall material (3)
13	0.035	SS
5 .	4	glass
18	18.7	plated steel
10a	21	glass
11	27	ss
6	30.7	glass
16a	51.8	ss
20	ن 52	ss
19	52.8	ss
15 and 22	53	ss
16b	.86.6	ss
12	180	ss
3	225	ss
7	234	ss
14a	280	ss
14b	450	glass
8a	950	ss
8b	980	ss
10b	989	glass
1 and 4	1000	ss
9	1007	SS
2	1475 ⁽²⁾	ss

⁽¹⁾ The notation a and b refer to different chambers in the same laboratory

⁽²⁾ Chamber with 1000 l capacity and external circulation volume of 475 l

⁽³⁾ ss = stainless steel

Table 2. Results of the 1st test: C12 known source Measured concentrations

	Concentrations (μg m ⁻³)								
Laboratory ⁽¹⁾	24 h	ours	48 h	ours	72 h	ours			
	1st sampling	2nd sampling	1st sampling	2nd sampling	1st sampling	2nd sampling			
1	43.5	46.1	47.2	46.3	48.2	46.4			
2'	28.0	21.0	24.6	22.2					
2"					50	50			
3'	324.0	278.2	334.0	352.3	349.6	366.1			
3''	167.5	171.4	164.8	174.6	168.6	161.7			
4	55		59		58	55			
5'	12700	12000	10200	9000	7700	7700			
5''	4400	4800				_ _			
6	2521	2688	2572	2581		No. 400 AM			
7	524	578	591						
8a	10	9.0	24	25	24	26			
8b	10	12			28	25			
9	38.1		41.8		49.7				
10a	1270	1230	1350	1310	1050	1080			
10b	33.0	34.9	29.8	32.4	29.6	33.0			
11	670	720	680	710					
12	167	173	163	161					
13	6500	6470	5630	5740					
14a	421	432	399	397	425	437			
14b	156		158	164	165	159			
15	675.7	702.5	834.1	754.9	659.4	640.4			
16a	748	762	823	801	845	819			
16b	461	499	523	480	493	518			
18	1927	2011	1908	1953					
19			731	534	703	711			
20	650	600	775	725	725	690			
22	699	690	649	678					

⁽¹⁾ see notes in Table 3

Table 3. Results of the 1st test: C12 known source Comparison of emission rates

Laboratory ⁽¹⁾	Emission rate by weight (µg.h ⁻¹)	Em concen	ission rate tration (µ	by g.h ⁻¹) ⁽²⁾	Notes
•	(μg /	24 hours	48 hours	72 hours	
1	55.1	44.8	46.7	47.3	fan on
2'	55.5	36.1	34.5		fan off
2''	81.6	: -		50	ext. circulation excluded, fan on
3'	98.3	68.2	77.8	81.1	fan on
3"	39.4	38.9	38.9	37.9	fan off
4	114	58	62	60	fan on
5'	107	49.4	38.4	30.8	fan on
5''	119	119	<u> </u>		6.45 h ⁻¹ , fan on
6	67.3	79.0	77.1		fan on
7	54.7	32.2	34.6		0.25 h ⁻¹ , no fan
8a	39.2	10	25	26	fan off
8b	42.3	12		26.5	fan on
9	64	37.2	40.8	48.5	fan on
10a	51.7	24.9	26.5	21.2	no fan
10b	67.6	36.7	33.6	33.8	no fan
11	36.0	18.9	18.8		fan on
12	124	31	29		fan on
13	46.2	38.2	33.5		FLEC
14a	133	115	107	116	fan on
14b	89.9	70.2	72.5	72.9	fan on
15	53.0	39.5	45.5	37.2	no fan
16a	44.6	39.1	42.1	43.0	no fan
16b	42.6	41.5	43.4	43.7	no fan
18	36.5	36.9	36.1		no fan
19	44.5		33.4	37.3	no fan
20	45.6	32.0	38.4	36.3	no fan
22	36.3	36.9	35.2		no fan

⁽¹⁾ The notation ' and " refers to different conditions in the same chamber

⁽²⁾ Mean of duplicate determinations

Table 4. Homogeneity of the PVC test material (as derived from 20 elements 10 x 10 cm, see text)

	Element weight	Chamber		Emission rate (arbitrary units)			
	(g)	temperature airflow (°C) (h-1)	phenol	1,2,4-tmb	n-decane	n-undecane	
mean	31.14	23.5	5.72	17.9	4.42	9.88	9.45
std. dev.	0.83	0.68	0.090	2.09 🕳	0.97	3.23	2.04
% std. dev.	2.7	2.9	1.6	11.7	21.9	32.7	21.6
min.	29.95	22.5	5.64	14.1	3.02	5.50	6.14
max.	33.27	24.5	6.00	21.9	6.15	15.36	13.10

Table 5. Emission factors of phenol from PVC tile [μ g.h⁻¹ m⁻²]

Laharatani	Run n. 1		Rur	Run n. 1		Run n. 2		Run n. 2	
Laboratory	48 h	48 h	72 h	72 h	48 h	48 h	72 h	72 h	
1	903	966	708	783		•	•	•	
2	994	1061	769	851	1003	1014	813	763	
3	683	683	558	567	731	712	587	577	
4	673	678	555	538	668	663	565	673	
5	126	•	122	•	144	•	189	176	
6	915	805	813	821	884	790	805	762	
7	598	636	601	561	•	•	•	•	
8a	1005	•	916	•	913	870	740	738	
8b	954	•	839	•	803	784	702	719	
9	852	947	1394	1359	923	974	817	780	
10b	•	•	•	9 154	•	•	•	•	
11	•	•	•	•	•	•	•	•	
12	433	541	385	385	409	325	264	288	
14a	1274	1250	954	897	1242	1242	1090	1098	
14b	1213	1202	919	924	1042	999	1047	913	
15	395	432	400	393	375	415	396	360	
18	1005	1005	760	740	981	981	966	1000	
19	889	856	572	567	548	519	452	442	
20	800	649	797	444	530	512	468	383	
22	928	957	•	•	•	3168	2740	2659	

Table 6. Emission factors of 1,2,4-trimethylbenzene from PVC tile [$\mu g.h^{-1}.m^{-2}$]

1 - 1	Run	n. 1	Run	Run n. 1		n. 2	Run n. 2	
Laboratory	48 h	48 h	72 h	72 h	48 h	48 h	72 h	72 h
1	60.4	59.5	47.8	52.8	•	•	•	•
2	97.8	104	92.9	91.3	88.1	99.4	76.9	62.5
3	60.6	66.3	51.9	60.6	62.5	44.2	46.2	44.2
4	76.9	76.9	69.7	69.7	86.5	84.1	79.3	91.3
5	35.4	35.4	26.0	28.5	89.4	115	61.1	63.5
6	111	106	79.7	93.0	102	115	84.4	89.9
7	66.3	68.1	54.9	54.6	•	•	•	•
8a	81.7	•	72.1	•	79.3	69.7	62.5	62.5
8b	72.1	٠	62.5	•	60.1	60.1	57.7	57.7
9	69.0	73.8	99.8	96.2	82.2	77.6	76	68.3
10b	79.3	69.7	57.7	55.3	64.9	64.9	62.5	72.1
11	51.9	57.2	42.8	49.5		•	•	•
12	43.3	40.9	32.4	34.9	45.7	38.5	32.4	27.6
14a	80.1	80.1	66.5	66.5	80.1	80.9	65.7	64.9
14b	91.9	94.0	72.1	72.6	81.7	78.5	66.8	66.2
15	21.1	27.5	30.7	32.3	18.8	19.3	29.8	19.1
18	70.2	70.7	55.8	56.3	90.9	90.9	88.5	89.9
19	81.7	76.9	62.5	62.5	57.7	48.1	45.7	40.4
20	43.8	56.5	47.3	46.7	25.8	46.0	.36.3	64.2
22	66.8	67.8	•	•	199	233	201	202

Laboratory	Run	n. 1	Rur	n. 1	Run n. 2		Run n. 2	
Labolatory	48 h	48 h	72 h	72 h	48 h	48 h	72 h	72 h
1	173	173	135	152	•	•	•	•
2	186	192	155	162	192	191	160	144
3	173	192	144	173	163	125	125	115
4	161	168	135	132	171	166	147	173
5	61.5	62.5	39.8	46.2	259	288	182	183
6	278	274	212	258	290	264	224	251
7	143	147	132	134	•	•	•	•
8a	180	•	166	•	178	159	147	144
8b	144	•	130	•	142	137	137	137
9	215	222	298	293	229	222	208	187
10b	200	202	159	151	185	178	161	159
11	130	124	98.6	160	•	•	•	•
12	120	120	95.0	88.9	120	102	75.7	73.3
14a	203	200	167	166	208	211	170	167
14b	252	256	196	198	215	209	175	175
15	27.9	35.6	42.3	42.9	35.3	22.5	25.0	11.3
18	118	121	97.1	97.6	216	216	213	213
19	192	188	139	144	139	115	106	101
20	29.0	40.2	38.3	32.7	27.4	27.6	18.7	24.0
22	148	155	•	•	625	529	461	461

Table 8. Emission factors of n-undecane from PVC tile [$\mu g.h^{-1}.m^{-2}$]

l alsavatawa	Run	Run n. 1		Run n. 1		n. 2	Run n. 2	
Laboratory	48 h	48 h	72 h	72 h	48 h	48 h	72 h	72 h
1	162	161	129	143	•	•	•	•
2	178	175	154	155	178	163	154	141
3	163	173	135	154	163	115	125	115
4	154	154	127	123	142	135	120	142
5	55.8	57.7	43.8	46.9	153	172	117	118
6	236	261	192	223	234	249	193	220
7	145	149	135	138	•	•	•	•
8a	188	•	161		185	163	151	139
8b	144	•	132	•	135	132	127	132
9	•	•	•	•	•	•	•	•
10b	192	180	142	139	173	180	142	154
11	140	128	97.6	104	•	•	•	•
12	113	120	103	103	108	103	81.7	78.1
14a	193	194	158	155	191	192	155	153
14b	228	227	173	174	201	193	159	160
15	35.6	47.0	49.5	51.4	42.0	20.0	29.4	11.9
18	150	153	126	126	209	210	206	206

Table 9. Emission factors of TVOC from PVC tile [$\mu g.h^{-1}.m^{-2}$]

Labaratam	Rur	n n. 1	Rur	n n. 1	Run n. 2		Rui	n n. 2
Laboratory	48 h	48 h	72 h	72 h	48 h	48 h	72 h	72 h
1	2025	1957	1404	1730	•	•	•	•
2	3316	3444	3075	2984	3216	3466	2678	2745
3	•	•	•		•	•	•	•
4	2149	2151	1656	1627	2111	1995	1697	2012
5	1654	•	1635	1423	2365	2673	1423	
6	•	•	•	•	•	•	•	•
7	1221	1250	1144	1135	•	•	•	•
8a	1675	•	1495	1481	1615	1466	1231	1226
8b	1897	1286	1281	1317	1380	1603	1204	1216
9	2202	1772	3995	3928	4255	2856	2589	2356
10b	1418	1202	1058	913.5	1154	1226	1130	961.5
11	1413	1404	1208	1365	•	•	•	•
12	1022	1106	925	913	1190	998	781	793
14a	2588	2668	2179	2011	2444	2540	2035	2043
14b	3088	2901	2185	2153	2329	2324	1923	1902
15	7067	7740	7500	7885	6490	6106	7019	4952
18	1269	1514	1072	1163	2192	2207	2139	2144
19	1947	1798	1317	1231	1178	995	851	784
20	966	1213	1074	963	902	926	676	879
22	1837	1899	•	•	7596	7067	6202	6250

Table 10. Summary statistics of emission factors for PVC tile per run and sampling time

Compound	Run (hour)	N	Mean [μg.h ⁻¹ .m ⁻²]	Std. Dev. [μg.h ⁻¹ .m ⁻²]
	1 (48)	33	828	263.5
Phenol	1 (72)	31	706	270.1
	2 (48)	29	759	276.9
	2 (72)	30	652	266.3
	1 (48)	38	68.2	21.06
1,2,4-Trimethylbenzene	1 (72)	36	59.7	19.61
	2 (48)	32	70.2	25.15
	2 (72)	32	61.1	19.23
	1 (48)	38	158	65.1
n-Decane	1 (72)	36	139	65.2
	2 (48)	32	169	71.6
	2 (72)	32	142	61.4
	1 (48)	36	150	59.3
n-Undecane	1 (72)	34	124	47.9
	2 (48)	30	148	60.5
	2 (72)	30	126	54.8
	1 (48)	32	1852	670.2
TVOC	1 (72)	32	1658	808.9
	2 (48)	26	1985	867.5
	2 (72)	25	1577	662.0

Table 11. Two-way nested classification analysis of runs 1 and 2 for PVC tile - figures in brackets are percent standard deviations relative to the mean

Compound	Hour	N	Mean [μg.h ⁻¹ .m ⁻²]	Տ_L [µg.h ⁻¹ .m ⁻²]	S _s [μg.h ⁻¹ .m ⁻²]	Տ_M [µg.h ⁻¹ .m ⁻²]
Phenol	48	56	791	269.3 (34.0)	87.6 (11.1)	41.4 (5.2)
	72	57	681	242.8 (35.7)	130.4 (19.2)	58.2 (8.6)
1,2,4-Trimethylbenzene	48	62	70.0	19.25 (27.5)	13.81 (19.7)	6.35 (9.1)
	72	62	61.3	15.75 (25.7)	11.52 (18.8)	5.45 (8.9)
n-Decane	48	62	165	57.2 (34.7)	44.5 (27.0)	9.4 (5.7)
	72	62	141	53.6 (38.0)	39.0 (27.7)	9.8 (6.9)
n-Undecane	48	58	148	58.7 (39.6)	25.0 (16.9)	10.2 (6.9)
	72	58	125	48.7 (39.0)	22.6 (18.1)	8.0 (6.4)
TVOC	48	50	1957	668.7 (34.2)	399.4 (20.4)	254.1 (13.0)
	72	51	1656	690.5 (41.7)	385.0 (23.2)	86.2 (5.2)

Table 12. Emission parameters of a-pinene from wax

		Ru	n 1			Ru	ın 2	
Laboratory	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.ۺ ⁻²]	(EF) emp. [µg.ĥ ⁻¹ .m ⁻²]	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̂ ⁻²]	(EF), emp. [µg.h ⁻¹ .m ⁻²]
1	2642	8.472	311.8	2544	7040	22.64	310.9	7529
2	14920	108.9	137	4755	2708	13.36	202.7	2992
4	1263	5.858	215.5	1442	•	. •	•	•
5	2678	12.17	220.1	3004	4888	14.68	333	4641
6	5515	23.69	232.9	3929	6196	21.75	284.9	5046
7	629.8	6.991	90.08	634.9	•	•	•	•
8a	over	over	over	over	2215	7.954	278.4	2948
9	1179	9.606	122.7	1514 -	•	•	•	•
10b	3150	33.71	93.44	1662	1479	10.92	135.4	1591
12	71630	14.37	4984	69530	121000	24.02	5040	134200
13	1925	16.08	119.8		•	•	•	•
14a	2251	13.69	164.4	2498	1116	9.158	121.8	1183
14b	3013	12.91	233.3	2962	2681	16.69	160.6	2440
15	over	over	over	over	over	over	over	over
19	862.7	4.225	204.2	1720	933.3	3.564	261.9	1458
20	104.9	6.995	14.99	143.9	100.5	0.5553	181	161.7
22	4940	15.25	323.9	8436	2922	8.824	331.1	over

		Ru	ın 1		Run 2			
Laboratory	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̊ ⁻²]	(EF) emp. [µg.h ⁻¹ .m ⁻²]	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̊ ⁻²]	(EF), emp. [µg.h ⁻¹ .m ⁻²]
1	57000	7.317	7791	over	197200	24.45	8064	247400
2	95430	11.92	8006	76410	34570	8.659	3993	41280
4	18110	4.421	4096	19800	•	•	•	•
5	over	over	over	62820	over	over .	over	91720
6	64550	11.42	5652	83910	69410	11.31	6137	88080
7	12720	1.889	6733	13070	•	•	•	
8a	43190	4.530	9535	43340	14850	1.767	8405	19690
9	41710	9.278	4495	35180	•	•	•	•
10b	21610	2.778	7779	21350 **	22260	2.934	7587	26740
12	282900	4.541	62310	452000	381300	5.333	71500	527800
13	8755	0.8361	10470	805.7	•	•	•	•
14a	96960	13.02	7449	115200	84800	12.67	6695	95990
14b	101700	11.33	8972	108100	89780	13.13	6838	97460
15	3583	2.039	1757	3954	3824	2.645	1445	5620
19	19720	2.920	6751	31150	21230	2.409	8814	31010
20	1228	0.4559	2694	over	1177	0.3684	3194	16930
22	15180	1.370	11080	17530	9091	1.417	6417	11580

Table 14. Emission parameters of geraniol from wax

		Ru	n 1	<u> ئەرىپىيىسى دەرەنىكى دەرەمەرە دەرەپىيىسى بورەپىلىپىيى</u>		Ru	n 2	
Laboratory	(EF) [μg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̊ ⁻²]	(EF) emp. [µg.h ⁻¹ .m ⁻²]	(EF) _ô [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̊ ⁻²]	(EF) emp. [µg.h ⁻¹ .m ⁻²]
1	9932	8.865	1120	over	22930	21.14	1085	32610
2	89820	30.50	2945	76510	82660	21.40	3863	73530
6	3205	2.030	1579	5180	6950	6.745	1030	8628
7	2152	1.254	1717	2634	•	•	•	
8a	1310	1.479	885.4	1320	227.3	0.6710	338.8	298.7
9	1382	2.997	461.1	1425	•	· •	•	•
10b	over	over	over	over	1329	4.012	331.2	1412
12	2724	0.02377	114600	58480	1430	0.02540	56290	18310
13	2315	0.8807	2628	over	. •	•	•	•
14a	1005	4.693	214.1	1353	1223	1.934	632.0	1967
14b	973.3	1.372	709.3	1472	1061	1.723	615.7	1798
15	254	0.4112	617.7	244.3	176.1	0.1669	1055	153.1
20	6794	1.867	3639	7685	4275	0.5947	7189	5159

Table 15. Emission parameters of a-cedrene from wax

		Ru	n 1			Ru	n 2	
Laboratory	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.㎡ ⁻²]	(EF) emp. [µg.h ⁻¹ .m ⁻²]	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̈ ⁻²]	(EF) emp. [μg.h ⁻¹ .m ⁻²]
1	968.9	3.196	303.1	1621	1335	4.569	292.1	1720
2	3692	7.554	488.7	3364	2199	6.664	330.0	2247
6	1925	13.15	146.4	1584	2090	11.87	176.1	1773
7	225.8	0.6069	372.1	328.7	•	•	•	•
8a	1017	5.045	201.6	1244	269.2	1.051	256.3	320.7
9	924.1	6.432	143.7	834.9	•	•	•	•
10b	712.0	0.7518	947.1	690	528.9	1.395	379.1	682.7
12	582.2	0.9071	641.8	1614	641.7	2.330	275.4	635.4
13	241.2	0.4811	501.3	7.973	•	•	•	•
14a	1892	4.707	401.9	2520	1944	4.416	440.2	2285
14b	1958	4.482	436.8	2210	1943	4.969	391	2246
15	87.24	0.6490	134.4	107.9	248.2	2.229	111.4	over
19	460.2	2.047	224.8	756.7	383.6	1.322	290.2	558.9
20	704.8	2.672	263.8	4218	277.9	0.4790	580.2	3368
22	617.7	1.183	522.1	681.3	738.6	6.044	122.2	722.1

Table 16. Emission parameters of TVOC from wax

		Ru	ın 1			Ru	ın 2	
Laboratory	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̊ ⁻²]	(EF) emp. [µg.h ⁻¹ .m ⁻²]	(EF) [µg.h ⁻¹ .m ⁻²]	K [h ⁻¹]	Μ [μg.m̂ ⁻²]	(EF) emp. [µg.ĥ ⁻¹ .m ⁻²]
1	69050	4.734	14590	95820	253000	20.80	12160	339100
2	200000	14.70	13610	174900	174400	11.08	15730	266400
6	50870	4.512	11280	59020	•		•	•
7	23400	1.393	16800	32360	•	•	•	•
8a	74410	5.574	13350	80220	28420	1.868	15210	42550
9	13410	0.5029	26670	24370	•		•	•
10b	20210	1.669	12110	43640	26830	3.157	8500	34720
12	163400	2.369	68960	417800	101200	2.709	37340	112400
13	14690	0.7030	20900	over	•	•	•	•
14a	136400	7.956	17140	184400	124800	7.339	17010	167000
14b	135600	7.354	18440	161900	119500	7.541	15840	152100
15	104600	1.417	73790	149000	178400	4.020	44390	over
19	56290	3.322	16940	95050	56450	2.669	21150	93650
20	19180	4.058	4728	30010	11840	1.244	9516	25320
22	34870	1.579	22080	46100	28550	2.312	12350	37610

Table 17. Distribution of a-pinene results from the wax test

(a) Run 1

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ m ⁻²]	104.9	1179	2642	4940	71630
K [h ⁻¹]	4.225	6.995	12.91	16.08	108.9
M _o [μg m ⁻²]	14.99	119.8	204.2	233.3	4984
(EF) _o emp. [µg.h ⁻¹ m ⁻²]	143.9	1514	2521	3929	69530

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ m ⁻²]	100.5	1298	2695	5542	121000
K [h ⁻¹]	0.5553	8.389	12.14	19.22	24.02
Μ _ο [μg m ⁻²]	121.8	170.8	270.2	321.0	5040
(EF) _o emp. [µg h ⁻¹ m ⁻²]	161.7	1458	2948	5046	134200

Table 18. Distribution of linalool results from the wax test

(a) Run 1

Parameter	Minimum	25th Percentile	Median	· 75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	1228	13950	31660	79990	282900
K [h ⁻¹]	0.4559	1.964	4.476	10.30	13.02
Μ _ο [μg.m ⁻²]	1757	5074	7614	9254	62310
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	805.7	17530	35180	83910	452000

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _ο [μg.h ⁻¹ .m ⁻²]	1177	11970	28420	87290	381300
K [h ⁻¹]	0.3684	2.088	4.134	11.99	24.45
M _o [µg.m ⁻²]	1445	5065	6767	8235	71500
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	5620	19690	41280	95990	527800

Table 19. Distribution of geraniol results from the wax test

(a) Run 1

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	254.0	1158	2234	5000	89820
K [h ⁻¹]	0.02377	1.067	1.673	3.845	30.50
M _o [µg.m ⁻²]	214.1	663.5	1350	2787	114600
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	244.3	1353	2053	7685	76510

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	176.1	1061	1380	6950	82660
K [h ⁻¹]	0.02540	0.5947	1.829	6.745	21.40
M _o [µg.m ⁻²]	331.2	615.7	1043	3863	56290
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	153.1	1412	3563	18310	73530

Table 20. Distribution of a-cedrene results from the wax test

(a) Run 1

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	87.24	460.2	712.0	1892	3692
K [h ⁻¹]	0.4811	0.7518	2.672	5.045	13.15
M _ο [μg.m ⁻²]	134.4	201.6	372.1	501.3	947.1
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	7.973	681.3	1244	2210	4218

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _ο [μg.h ⁻¹ .m ⁻²]	248.2	330.8	690.2	1944	2199
K [h ⁻¹]	0.4790	1.359	3.373	5.507	11.87
M _ο [μg.m ⁻²]	111.4	216.2	291.2	385.1	580.2
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	320.7	635.4	1720	2247	3368

Table 21. Distribution of TVOC results from the wax test
(a) Run 1

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	13410	20210	56290	135600	200000
K [h ⁻¹]	0.5029	1.417	3.322	5.574	14.70
Μ _ο [μg.m ⁻²]	4728	13350	16940	22080	73790
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	24370	43640	87640	161900	417800

Parameter	Minimum	25th Percentile	Median	75th Percentile	Maximum
(EF) _o [µg.h ⁻¹ .m ⁻²]	11840	28420	101200	174400	253000
K [h ⁻¹]	1.244	2.312	3.157	7.541	20.80
Μ _ο [μg.m ⁻²]	8500	12160	15730	21150	44390
(EF) _o emp. [µg.h ⁻¹ .m ⁻²]	25320	37610	103000	167000	339100

Figure 1. C12 known source emission rates

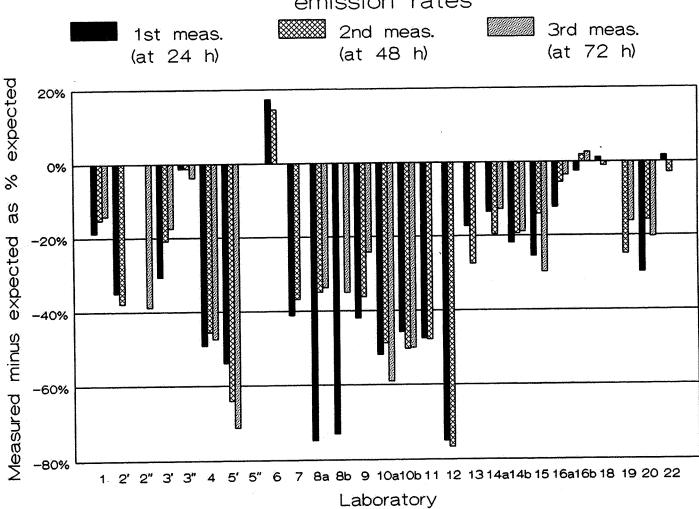


Figure 2. Gas-chromatogram of VOCs from PVC tile: 1) phenol; 2) 1,2,4-trimethylbenzene; 3) n-decane; 4) n-undecane

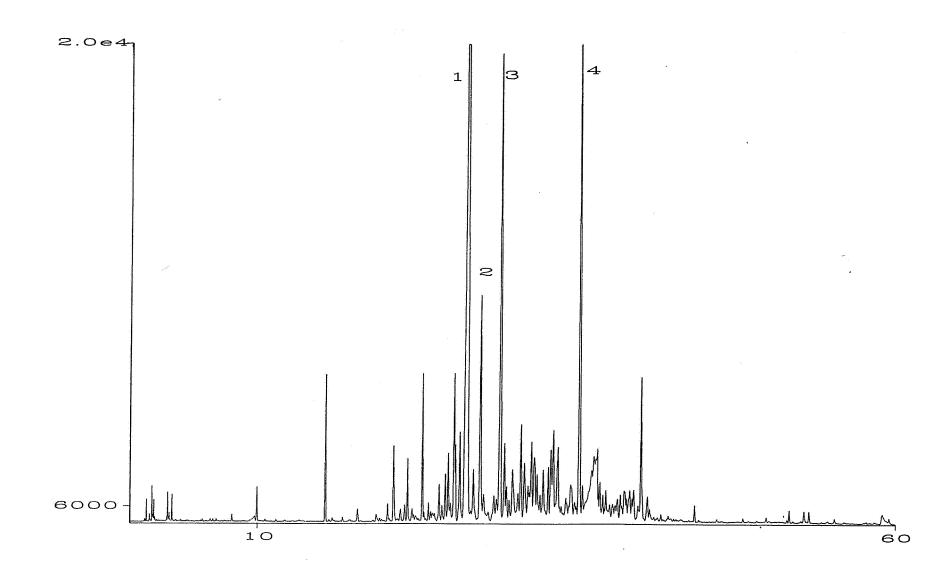


Figure 3. PVC tile emission factors phenol

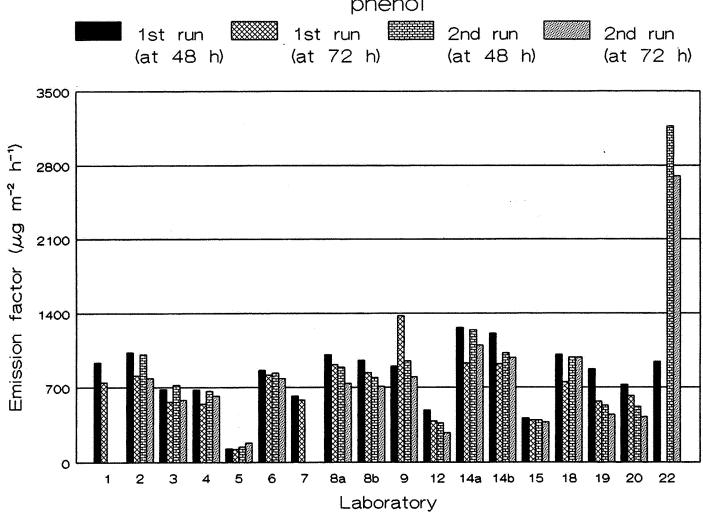


Figure 4. PVC tile emission factors 1,2,4-trimethylbenzene

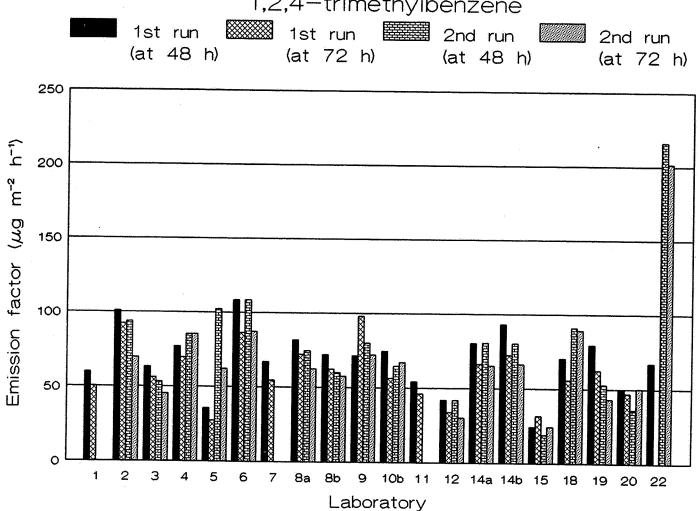


Figure 5. PVC tile emission factors n-decane

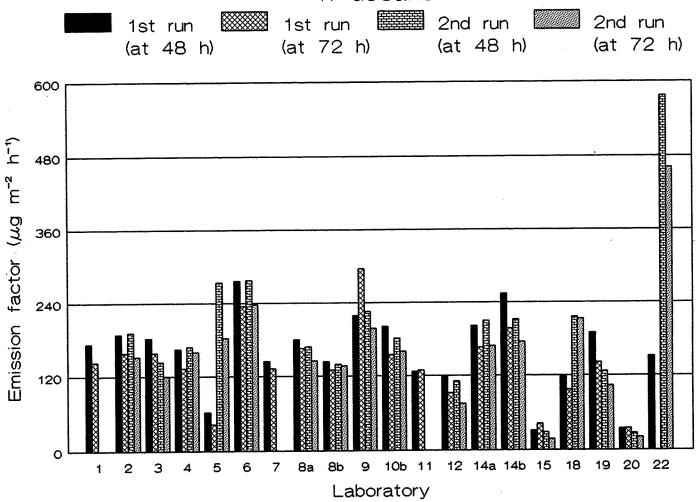


Figure 6. PVC tile emission factors n-undecane

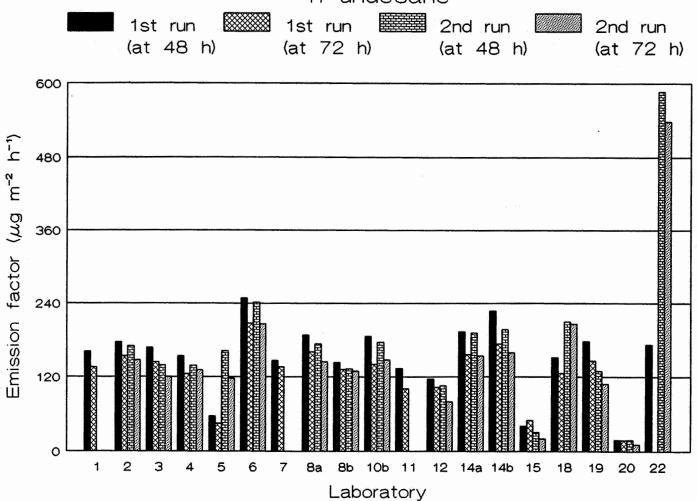


Figure 7. PVC tile emission factors TVOC

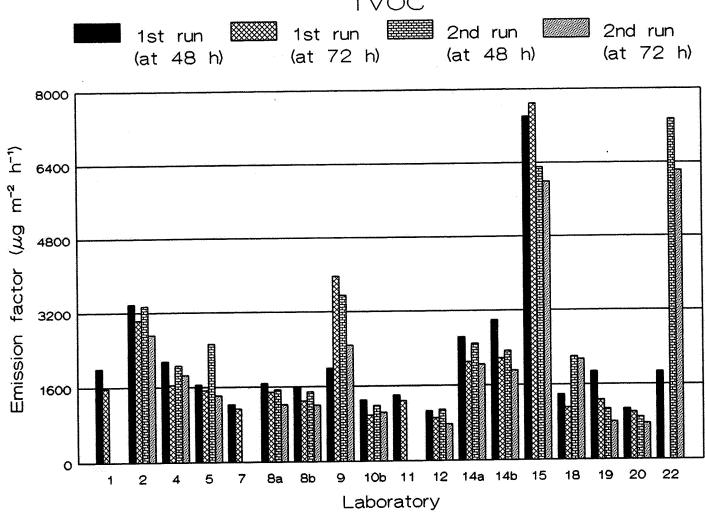


Figure 8. Gas-chromatogram of VOCs from floor wax: 1) α -pinene; 2) linalool; 3) geraniol; 4) α -cedrene

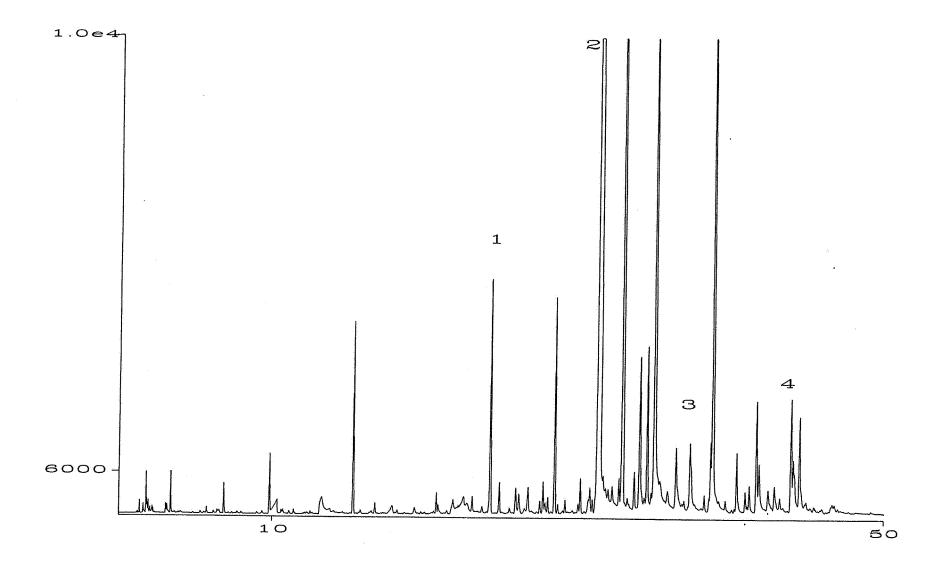


Figure 9. Example of wax curve fits α -pinene

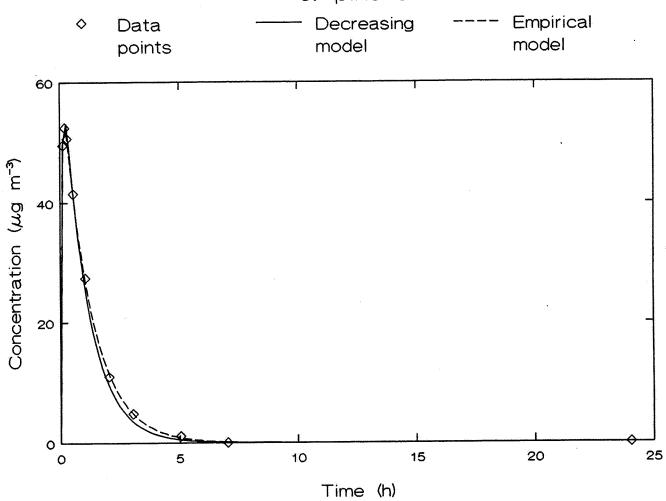


Figure 10. Example of wax curve fits geraniol

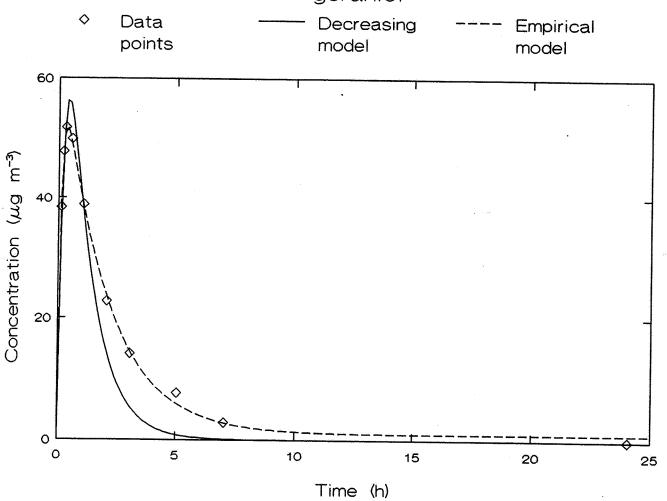


Figure 11. Wax initial emission factors

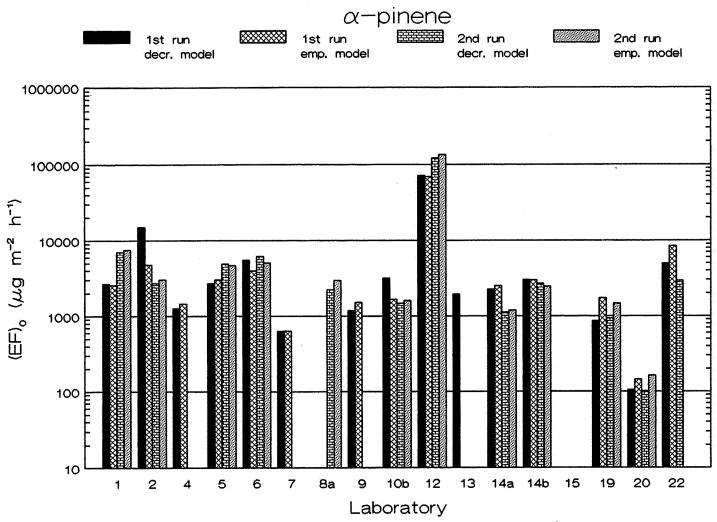


Figure 12. Wax initial emission factors linalool

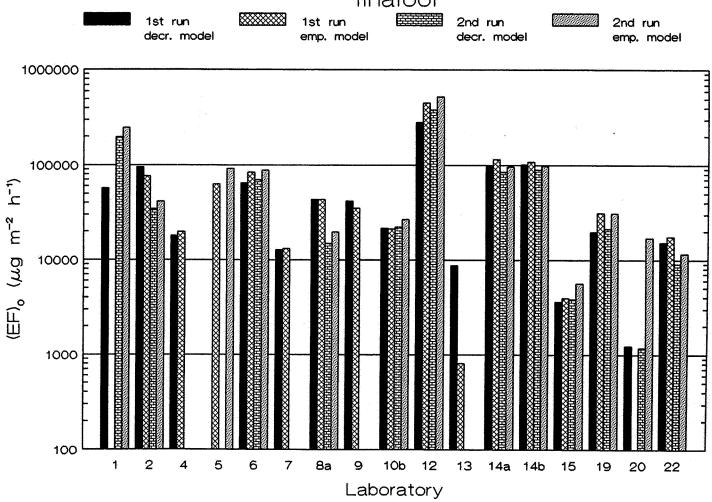


Figure 13. Wax initial emission factors geraniol

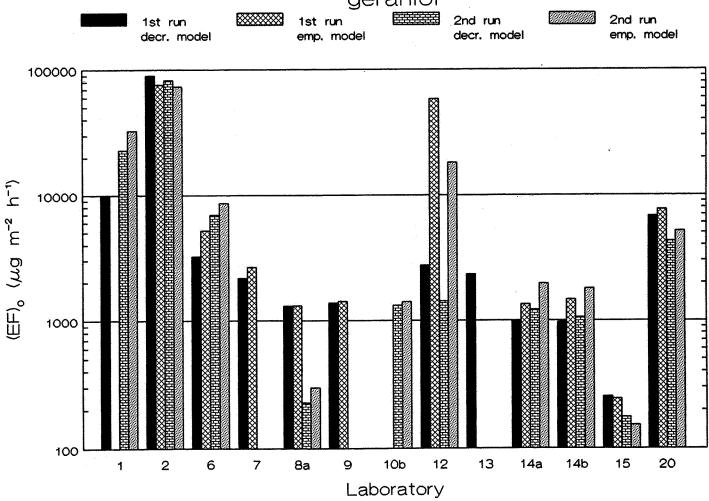


Figure 14. Wax initial emission factors α -cedrene

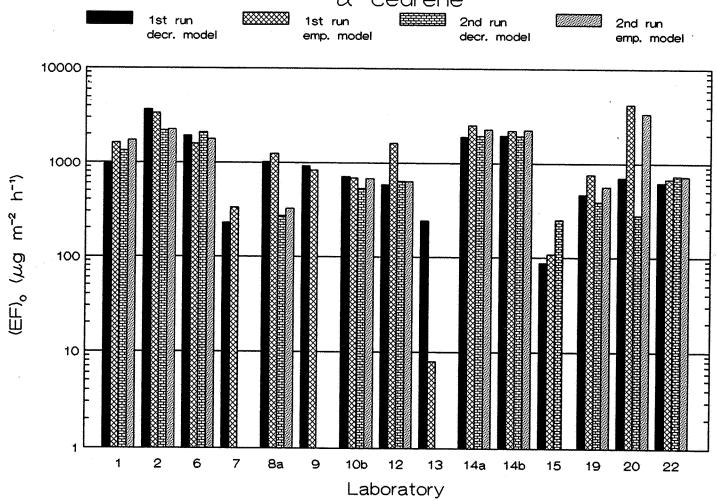


Figure 15. Wax initial emission factors

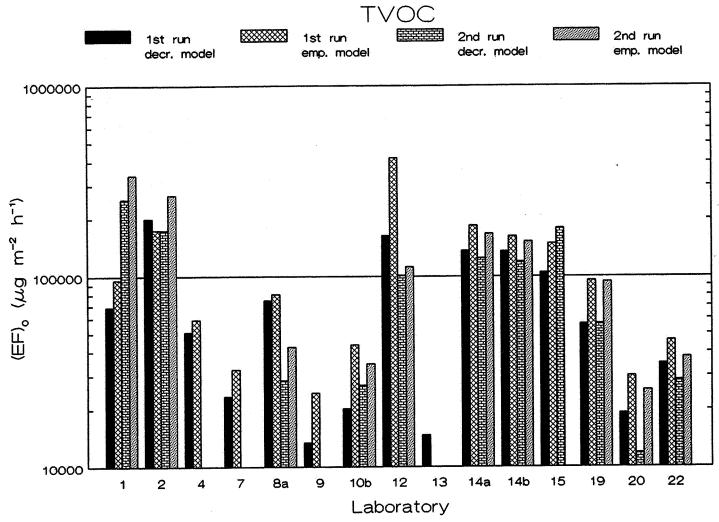


Figure 16. Wax decay constants
α-pinene
2nd run

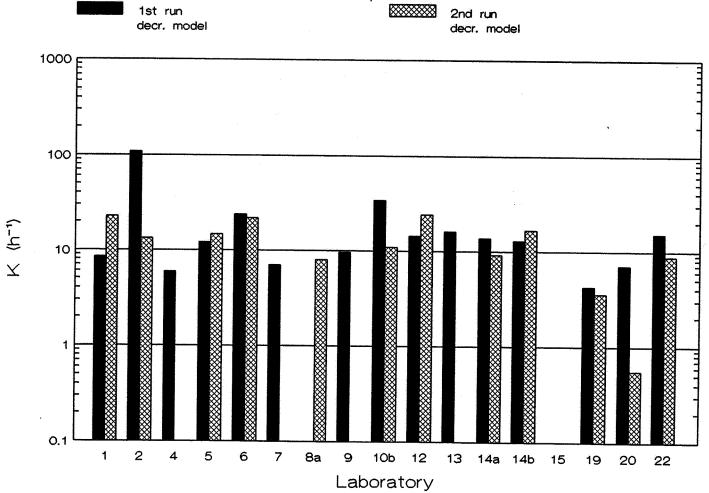


Figure 17. Wax decay constants linalool

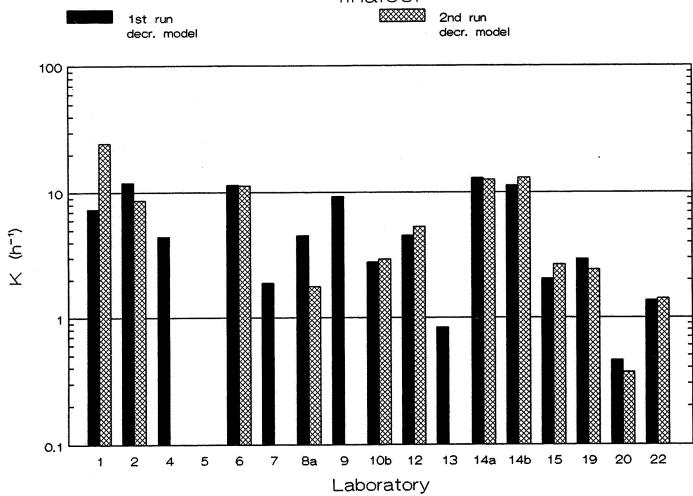


Figure 18. Wax decay constants geraniol

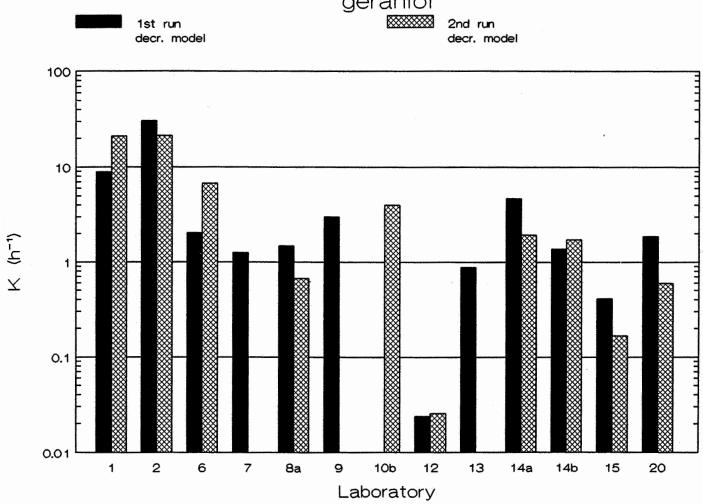


Figure 19. Wax decay constants α -cedrene

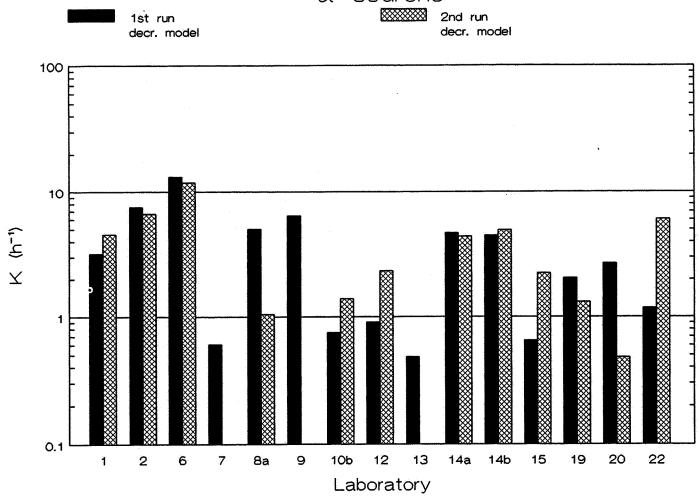


Figure 20. Wax decay constants TVOC

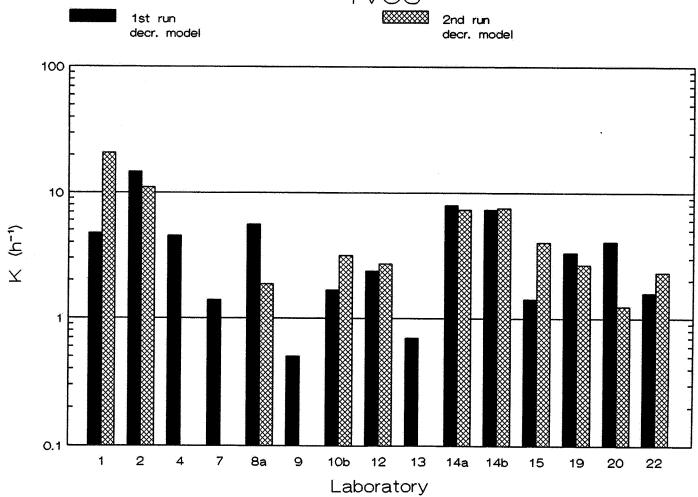


Figure 21. Wax initial masses α -pinene

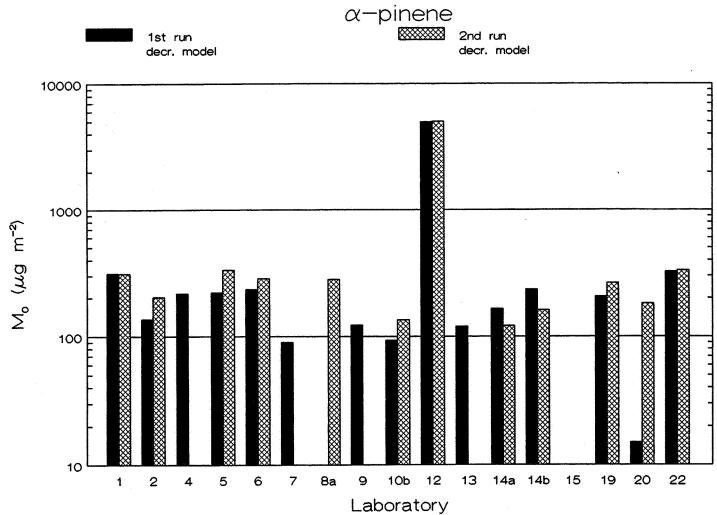


Figure 22. Wax initial masses linalool

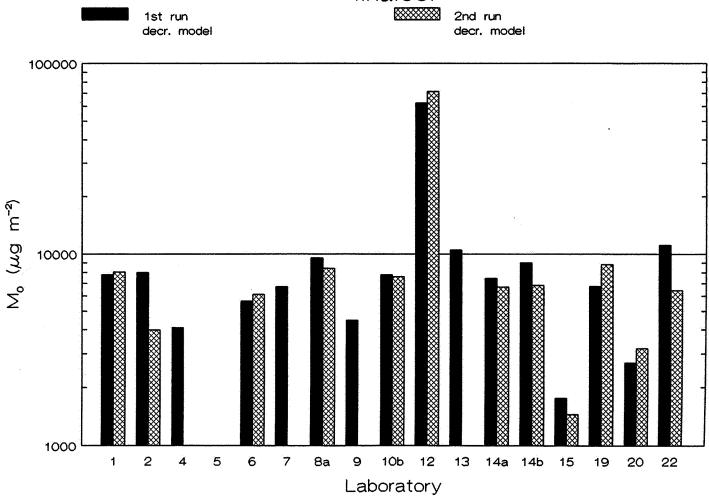


Figure 23. Wax initial masses geraniol

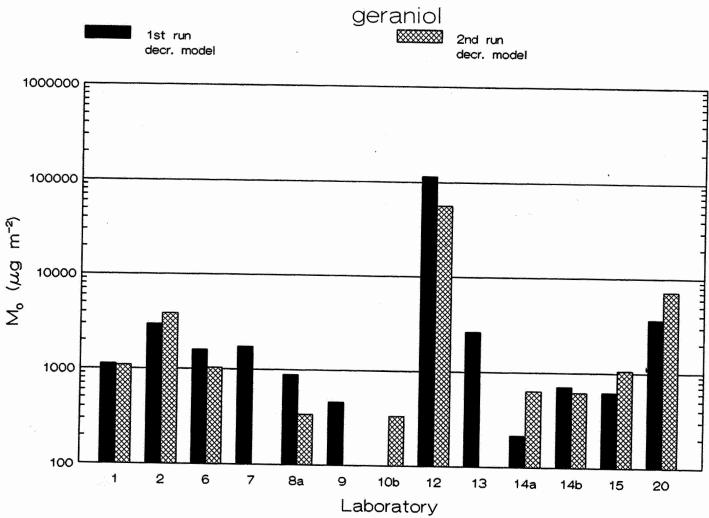


Figure 24. Wax initial masses α -cedrene

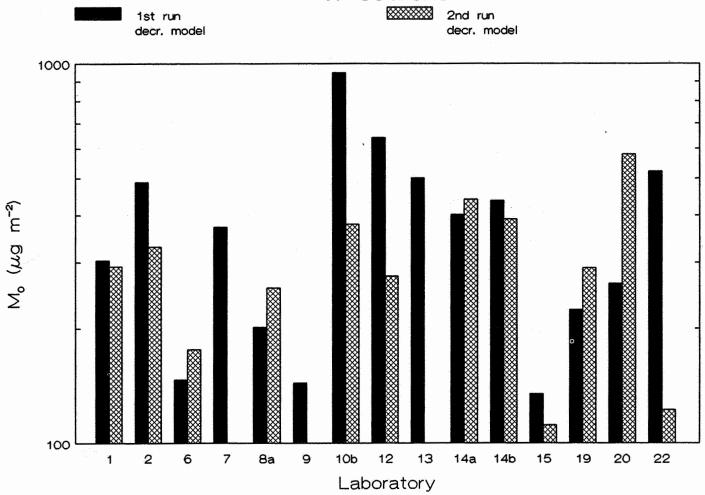
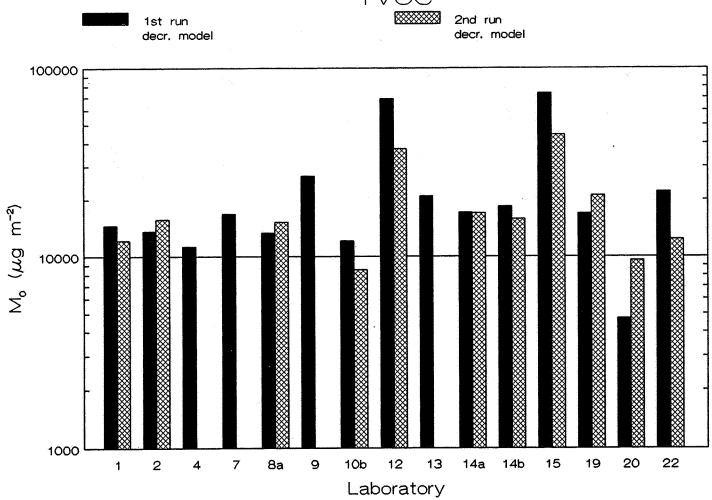
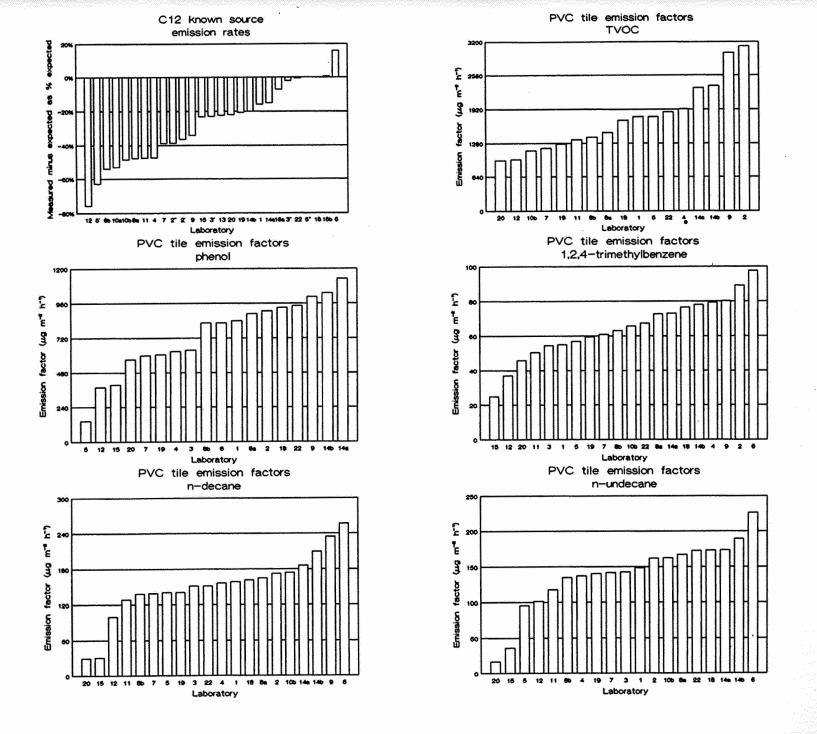


Figure 25. Wax initial masses
TVOC
2nd run





obtained q Figure C12 ģ 26. known the Ranking participating source <u>o</u> and mean laboratories PVC results

APPENDIX A

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APPENDIX B

Directions for the 1st test C12 known source

We are reminded that the purpose of this experiment is to validate the procedures described in the previously distributed European Guideline (COST-613) and in the ASTM D5116-90 Guideline: these procedures should therefore be followed wherever applicable. Additional specifications are contained in the following:

Chamber conditions: 23°C, 45% RH, 1.0 h-1 air change rate

0.5 ml of the pure compound supplied in the sealed vial are transferred by means of a syringe into the empty 2 ml vial. The vial is weighed to the nearest tenth of a milligram and while still open, is introduced into the chamber - the weight must be recorded. The weight loss rate of this source depends on the air velocity on the mouth of the vial (50 - 200 μ g/h have been observed). After a period of 24 and 48 hours respectively from the introduction, VOC sampling must be carried out in duplicate each time. Should the concentration after 48 hours be remarkably higher than after 24 hours (which indicates the presence of a sink), a further sampling should be carried out after 72 hours. If the measured C12 concentration indicates a small weight loss rate, it is advisable to keep the vial in the chamber a couple of days more in order to achieve good weighing. In any case, the vial must remain in the chamber under the same conditions of temperature, air change rate and air velocity until it is weighed again.

The concentration values, as well as the two vial weights and the emission rate values, shall be reported using the attached data reporting form. The emission rate is obtained by the following equation:

$$E = N.V.c = Q.c$$

where E represents the emission rate ($\mu g.h^{-1}$), N is the air exchange rate (h^{-1}), c symobolizes the concentration ($\mu g.m^{-3}$), Q represents the flowrate through the chamber (m^3h^{-1}) and V is the chamber volume (m^3).

Interlaboratory Chamber Experiment results of test n.1: C12 known source

laboratory
chamber volume (m³)
chamber wall material
is the chamber equipped with a fan?
if yes, value of air velocity at vial position is desirable (m.s-1)
measured air exchange rate (h-1)
measured temperature (°C)
measured relative humidity (%)
date material arrived from Ispra
date and hour of first weighing of the vial
date and hour of first VOC sampling
date and hour of second VOC sampling
date and hour of second weighing of the vial
weight of the vial at first weighing (g)
weight of the vial at second weighing (g)
emission rate from weight loss of vial ($\mu g \ h^{-1}$)
concentration in the chamber after 24 hours (µg m ⁻³), 1st sampling
concentration in the chamber after 24 hours (µg m ⁻³), 2nd sampling
derived emission rate (µg h ⁻¹) *
concentration in the chamber after 48 hours (µg m ⁻³), 1st sampling
concentration in the chamber after 48 hours (µg m ⁻³), 2nd sampling
derived emission rate (µg h-1) *
concentration in the chamber after 72 hours (µg m ⁻³), 1st sampling**
concentration in the chamber after 72 hours (µg m ⁻³), 2nd sampling**
derived emission rate (µg h-1) *

^{*} use the equation reported in the attached description
** only in the case of a remarkable difference between the 24 h and 48 h concentrations (see directions)

Directions for the 2nd test PVC tile

We are reminded that the purpose of this experiment is to validate the procedures described in the previously distributed European Guideline (COST-613) and in the ASTM D5116-90 Guideline: these procedures should therefore be followed wherever applicable. Additional specifications are contained in the following:

Chamber conditions: 23°C, 45% RH, 1.0 h-1 air change rate

Each laboratory receives two identical samples, to be analysed independently. The material is supplied in squares of 10x10 cm in size, these are obtained by cutting 50x50 cm PVC tiles. Based on a loading ratio of 0.4 m²/m³, taking the area of the front and back of the squares into consideration, each sample consists of a number of squares proportional to the chamber volume. As only one square is suitable for a 50 litre chamber, those with chambers smaller than 50 litres will either have to cut the square (thus complying with the proposed loading ratio but having a different edge contribution), or analyse the full square - with a different loading ratio...or do both. More material is supplied to colleagues who have the smallest chambers in order to make use of this opportunity.

The material, if wrapped in an aluminium sheet, appears to maintain its emission properties for some time. However, to avoid any variation which might occur due to a time difference in the test, we strongly advise that the test be carried out in the 4th week of November (25-29 November) and in the first week of December (2-6 December). Until then, please store the samples in a refrigerator.

As both the front and back of the squares must be free to release the vapours, they should be placed on a convenient support (grid), in the same zone of the chamber as the C12 source.

The concentrations of phenol, 1,2,4-trimethylbenzene, n-decane, n-undecane and TVOC must be determined. They will not reach a steady state in the chamber but after reaching a maximum value, they will decline; however after 40 hours, the decline appears to be slow or very slow. Therefore VOC sampling is prescribed after 48 and 72 hours from introduction into the chamber. Sampling and analysis have to be carried out in duplicate.

The emission rate shall be derived from the concentration data using the same equation already used for C12.

Interlaboratory Chamber Experiment Results of test n.2 : PVC Tile Run n.

laboratory	
chamber volume (m³) chamber wall material measured air exchange rate (h-1)	
measured temperature (°C) measured relative humidity (%)	
date material arrived from Ispra	
date and hour material was placed in the chamber	
date and hour of first VOC sampling (48h)	
date and hour of second VOC sampling (72h)	

	Concentration (µg m ⁻³)		Emission Rate (μg h ⁻¹)	
	48h	72h	48h	72h
Phenol				
1st sampling 2nd sampling				
1,2,4-trimethylbenzene				
1st sampling 2nd sampling				
n-decane 1st sampling 2nd sampling				
n-undecane				
1st sampling 2nd sampling				
Total VOC ≥ C6*				
1st sampling 2nd sampling				_

^{*} toluene response factor

Directions for the 3rd test liquid floor wax

We are reminded that the purpose of this experiment is to validate the procedures described in the previously distributed European Guideline (COST-613) and in the ASTM D5116-90 Guideline: these procedures should therefore be followed wherever applicable. Additional specifications are contained in the following:

Chamber conditions: 23°C, 45% RH, 1.0 h⁻¹ air change rate.

Each laboratory receives enough wax to carry out two runs with a loading factor of 0.4 m²/m³ and a wax density of 50 cm³/m², taking the chamber volume(s) into account. This means that, e.g. for a chamber of 1 m³, a volume of 20 cm³ of wax must be spread on a support of 0.4 m². As vials with a maximum capacity of 5 cm³ are used, four of them contain the wax necessary for one run in the 1 m³ chambers. No (known) difference exists between vials as all have been filled within a few minutes from a single wax bottle.

It is recommended that glass be used as the support material. The wax can be transferred onto the glass surface through a disposable syringe and then spread by means of a putty knife or the like. It is obvious that the support area and the wax volume must be defined as accurately as possible. Shaking the vials before sampling the wax is highly recommended. The length of time between when the spreading of the wax starts and when the chamber door is closed (also very important) should be 5 minutes, a time-span long enough for the wax to also spread onto the largest supports. If, for any reason, this condition cannot be met, the effective time must be reported.

Taking time as zero (t_0) at the moment when the chamber door is closed, ten air samples must be collected at the following times (hours): 0.083 (5 minutes), 0.167 (10 minutes), 0.25, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0, 24. The time of sampling refers to the beginning of the sample collection; the duration of sampling should be roughly 5 minutes and must be reported. The very strict sampling times given for the first 30 minutes are necessary for an adequate description of the portion of the curve of the more volatile compounds which are rising steeply.

The concentrations of α -pinene, linalool, geraniol, α -cedrene and TVOC must be determined. The emission factors (EF)₀ at t₀ and the relative k values must be calculated by a fitting equation (9) reported in Section 6c of the abovementioned European Guideline (Report EUR 13593 EN).

The results must be reported using the attached forms. In addition, a concentration-time graph (even a very rough one) with the fitting curve, if available, would be very useful.

In view of the large number of data in this case, I would ask you to help us by also writing the results onto a diskette (any kind of 3.5 or 5.25 cm diskette would be suitable) in ASCII format. The following example shows how the results should be reported therein. First a title line containing identifiers, sampling time, sampling duration, compound names (in the same order as the result reporting form) and name of the laboratory. Data for time and concentration (µg m⁻³) lie in successive columns (no fixed column width is required), each data in the row being separated from the other by one or more spaces. Missing values, if there are any, should be expressed as -1E30. Files of this kind can easily be prepared by any editor or word processor or spreadsheet as they can be saved as unformatted (i.e. ASCII) files.

Example data file:

time(h) dt(min) compound1 compound2 compound3 compound4 TVOC LabName

.083 4.98 141 2722 858.7 810.2 6414

.183 5.05 147 2985 1445 1029 7027

.283 4.78 143 2985 1666 1138 7355

.5 5.3 118 2568 1769 1119 6704

1 4 1 71 6 1673 1580 911 3 4718

2 4.98 27.5 757 1322 500.2 2625

5 5.1 2.3 86.2 563.9 93.5 426

8 5.3 1.2 32.9 377.9 41.1 273

24 5.07 1.0 2.6 36.3 7.4 78.9

FileNames could be RUN1.DAT and RUN2.DAT.

Interlaboratory Chamber Experiment Results of test n. 3 : liquid wax Run n.

laboratory	
chamber volume (m³) chamber wall material measured air exchange rate (h-1)	
measured temperature (°C)	
date material arrived from Ispradate and hour material was placed in the chamber (t _o) wax volume used (cm ³)	

time after	duration of sampling	Concentration (µg m ⁻³)							
(hours)	(mins)	α-pinene	linalool	geraniol	α-cedrene	TVOC			
0.083			· · · · · · · · · · · · · · · · · · ·						
0.167									
0.25									
0.50									
1.0						A. A. B.			
2.0									
3.0									
5.0									
7.0									
24									
(EF) _ο (μg	.h ⁻¹ m ⁻²) ⁽²⁾								
K (l	1 ⁻¹) ⁽²⁾					<u>, A</u>			

- (1) sampling starts at this time
 (2) see attached directions for the calculation of this parameter.

APPENDIX C

INTERNATIONAL COMPARISON EXPERIMENT ON THE DETERMINATION OF VOC EMITTED FROM INDOOR MATERIALS THROUGH SMALL TEST CHAMBERS

Draft minutes of the meeting of the European participants Ispra, 28-29 September 1992

1. Discussion of the draft report on the experiment prepared by M. De Bortoli and A. Colombo.

In the discussion on the discrepancies observed in the 1st test, some colleagues shared the results of supplementary tests they carried out to understand the discrepancies: a compound like C15, less volatile than C12, showed an even greater discrepancy; more volatile compounds (butanol and toluene) showed smaller discrepancies. One test carried out by laboratory 5 (see Table 3 in the report) at a much higher air exchange rate than the standard test yielded no discrepancy at all. These are considered signs that the discrepancies may be caused by some kind of sink, i.e. losses on the walls of the chamber. Tests of these types (compounds of different volatility, preferably homologous, and different air exchange rates) should be repeated by all the participants who reported remarkable discrepancies. Correction: in Table 3, laboratory 1 had fan on.

The results of the **2nd test** are considered acceptable by the participants: in particular the agreement on TVOC was positively surprising, in view of the little degree of standardization adopted (the response factor of toluene had to be used, but no definition was given of the precise volatility range considered, nor of the minimum peaks integrated). However the agreement observed in this test cannot be extended to other situations, without testing.

Concerning the 3rd test, the following factors were pointed out in the discussion, as contributing to the very great dispersion of the results: the preparation of the wax layer, the surface air velocity and the model used. The description of standardised methods for the uniform and reproducible distribution of a liquid on a solid support and the determination of the film thickness will be supplied by A. Grove. Concerning the model used, D. Crump suggested that a comparison be made of the results without using any model, to have an idea of the intrinsic variation of the data. We have carried out a calculation of the mean and standard deviation on the concentrations measured 2 hours after to; the output of such a calculation is reported in the attached table. Based on the proportionality between concentration and emission factor (at steady state, see equation 5 of the Guideline; the proportionality constant, in fact, is the same for all laboratories), the calculated standard deviations may be compared with the standard deviations of the emission factor of the PVC tile results as indicated inTable 10 of the report. From the comparison it appears that whereas for the

PVC tile the relative standard deviation is roughly \leq 45%, for the concentration after 2 hours produced by the wax it lies between 45 and 160%. This is, almost certainly, already a favourable case, because at shorter times after t₀ greater variations have to be expected; and the model, of course, takes into account all the data.

An independent measurement of the **content of linalool in the wax sample** (one sealed vial was still available) was carried out at Ispra by direct injection of the wax on Tenax. The content thus found is $10.740 \pm 703 \,\mu g \,m^{-2}$ (4 measurements), which is not far from the 75th percentile of M_0 in both runs (see Table 18 in the report).

A revised version of the "Conclusions" will be prepared, including several points from the discussion above; moreover the FLEC chamber will be mentioned in the statement on equivalence of chambers.

A questionnaire, distributed to all the participants (including USA) attached to these minutes, has been devised in order to collect supplementary information which could help in understanding the results. Such information will be included in the final version of the report.

The revised report will be published as a EUR report, whereas a condensed version will be presented at INDOOR AIR '93.

The view seemed to arise during the meeting that the first concentration data (those included, say, in the first 15 minutes of the wax experiment) were presumably perturbed and should not have been considered for modelling. We do not share such a view as those data, in very general terms and especially for rapidly emitted compounds, may contain significant information concerning the rising part of the concentration/time curve and are therefore needed to define the curve shape and to obtain reasonable estimates of (EF)₀ and K. Their elimination can produce model overparametrization and/or unrealistic results for these parameters (see Addendum).

2. Corrections to the Guideline

At least the two following items should be addressed in the Guideline: a) the recovery of the chamber should be checked through tests with known sources of pure compounds of different volatility and polarity, the results of such tests being requested when reporting emission data; b) for experiments aiming at the determination of emission parameters of rapidly exhausting products more detailed recommendations should be given, including the model to be used. The definition of such recommendations should follow further experimental work (see below).

3. Next interlaboratory comparison

The participants unanimously recognized the need for a further experiment and expressed their intention to take part in it. It was decided that, after approval by the Steering Committee of the European Collaborative Action, the experiment could be started in autumn 1993 with the following features:

- a) emitting materials, with known content of the compounds to be determined, would be a paint (P. Wolkoff could arrange to have it supplied by a manufacturer) and a linoleum (same, H. Gustafsson); these materials have been choosen in order to have an emission decreasing more slowly than the wax of the past experiment (10-15 days) and because of the possibility of knowing their composition;
- b) the paint should be applied and the final thickness of the applied layer should be determined using standardized methods (see above);
- c) the air velocity on the evaporating surface should be measured (method to be defined);
- d) the model to be used should be evaluated very carefully in advance;
- e) the pure compounds to be determined will be supplied to the participants in a calibration solution.

MDB 23rd October 1992

Run 2

mean	(38.62)	18.17	1016	171.1	29.46	2130
std.dev.	(74.25)	9.18	1647	195.8	13.20	1640
% std.dev.	(192)	50.5	162	114	44.8	77.0

(1) In brackets results from all the data; the second column refers to data after removal of laboratory n.12

CONCENTRATIONS FROM WAX TWO HOURS AFTER to means of the different laboratories

Run 1

	α - pinene ⁽¹⁾	linalool	geraniol	α - cedrene	TVOC
mean	(30.41) 14.97	995.5	219.9	51.80	2863
std.dev.	(62.36) 8.97	1523	240.0	48.27	2538
% std.dev.	(205) 59.9	153	109	93.2	88.7

ADDENDUM

In order to evaluate the effect of discarding the initial concentration data, we did best fits by Eq. 9 of the Guideline (EUR 13593 EN) to simulated concentration data sets, generated by Eq. 9 itself at the foreseen experiment sampling times, with L = 0.4, N = 1, (EF)₀ = 3000 and three K values, i.e., 3, 6 and 15 (5 data sets for each K value).

To simulate the perturbation, a normal random error of mean zero and standard deviation equal to 6% of the theoretical concentration maximum (c_{max}) was added to the first three data of each set (i.e., those within the first 15 minutes), whereas to the other seven ones the added normal random error had standard deviation reduced at 3% of c_{max} (the latter value was choosen from the alphapinene and linalool results of chambers 14a and 14b, whose fits appear not markedly affected by sink effects). Note that for given L, N and K, c_{max} is directly proportional to (EF)₀, so that we would have obtained similar results even by selecting an (EF)₀ value other than 3000.

For each selected K value, the table below collects the results of the 5 fits, expressed as mean and standard deviation. Figures in brackets refer to results after elimination of the first three data from each set.

(EF) ₀ (min)	Κ	c _{max}	tmax
3000	3	230.9	33.0
2983 ± 267	2.98 ± 0.33		
(2984 ± 226)	(2.96 ± 0.18)		
3000	6	139.8	21.5
2905 ± 269	5.88 ± 0.61		
(5832 ± 7030)	(10.8 ± 12.2)		•
3000	15	65.9	11.6
2907 ± 415	14.6 ± 2.4		
(4164 ± 3342)	(19.9 ± 15.5)		

The table shows that data elimination can be unquestionably negative for rapidly emitted compounds, i.e., those for which t_{max} , the time at which t_{max} occurs, is small and lies before non-eliminated sampling data. As $t_{max} = [Ln(N/K)]/(N-K)$, this condition should occur as easier as K, or N or both are larger.

Note that we carried out best fits also by Eq. 11 of the Guideline, obtaining for (EF)₀emp results quite similar to those given above.

APPENDIX D

SUPPLEMENTARY INFORMATION ON CHAMBERS AND ANALYSIS FEATURES

Information	Lab.1	Lab.2	Lab.4	Lab.5	Lab.6	Lab.7	Lab.8
chamber wall material	SS (304 S15)	SS	SS	glass	glass	SS	SS
internal surface area (m²)	~7.7	8.2(2)		-	-	-	6.4
electropolishing (process)	no	no	-	-	-	-	no
air velocity in chamber(1) (ms-1)	0.41	0.2	~0.3	<0.1	•	-	-
chamber air flow measurement	anemometer	anemometer	<u>-</u>	-	bubble- meter	flow meter ⁽⁴⁾	flow meter ⁽⁴⁾
device permanently installed at	outlet	outlet	inlet	inlet	outlet	inlet	outlet
vapour sampling on	Tenax	Tenax TA	Tenax TA	act.charcoal ⁽³⁾	Tenax TA	Tenax TA	Tenax TA
desorption	250°C	225°C		CS ₂ ⁽³⁾	thermal	thermal	250°C
thermal desorption apparatus	PE ATD-50	-	•	•	<u>.</u>	PE ATD-50	Chrompack
GC column	BP10,25m	DB-1, 60m	<u>-</u>	unpolar capil.	-	-	DB-1,30m OV-1701,50m
detector	FID	FID	FID	FID	MS	FID	FID
TVOC range	C ₆ -C ₁₈	C ₆ -C ₁₂	70-320°C	-	-	C ₅ -C ₁₈	C ₆ -C ₁₆

- dashes indicate the misssing data
 (1) communicated for the 1st test (n-dodecane)
 (2) with recirculation 16,2m²
 (3) in the 3rd test Tenax and thermal desorption
 (4) calibrated with bubble meter

SUPPLEMENTARY INFORMATION ON CHAMBERS AND ANALYSIS FEATURES (Cont'd)

Information	Lab.9	Lab.10	Lab.11	Lab.12	Lab.13 ⁽⁷⁾	Lab.14	Lab.22
chamber wall material	SS	glass	SS	. SS	SS	SS	SS
internal surface area (m²)	*	-	-	-	-	~2.75	-
electropolishing (process)	-	-	-	-	no	yes	yes (basic)
air velocity in chamber(1) (ms-1)	0.5	-	0.01	-	-	0.4-0.5	-
chamber air flow measurement	gas meter	mass flow contr.	rotameter ⁽⁵⁾	rotameter ⁽⁵⁾	bubble- meter ⁽¹⁾	mass flow contr. ⁽⁴⁾	mass flow contr. ⁽⁴⁾
device permanently installed at	outlet	inlet	outlet	-	inlet/outlet	inlet	inlet
vapour sampling on	Tenax TA	act.charcoal	act.charcoal	act.charcoal ⁽⁶⁾	Tenax TA	Tenax TA	multi-sorbent
desorption	thermal	CS ₂	CS ₂	organic solvent	thermal	250°C	thermal
thermal desorption apparatus	Chrompack	-	•	-	PE ATD-50	Chrompack	Envirochem
GC column	HP-1,50m	-	***	-		OV-1,25m	DB-624
detector	-	FID	FID	MS	FID	FID	FID
TVOC range	C ₆ -C ₁₇	C ₆ -C ₁₈	-	=	C ₅ -C ₁₈	C6-C18	*

⁽⁵⁾ not permanently installed(6) silica gel for phenol(7) FLEC

APPENDIX E

TESTS ON THE EFFECT OF TEMPERATURE, AIR CHANGE RATE AND COMPOUND VOLATILITY ON THE EMISSION RATE MEASURED BY CONCENTRATION

Laboratory 12 (0.18 m³ chamber)

	t = 23°C, RH =45% N = 1 h ⁻¹			= 23°C, RH = 45% $t = 50$ °C, RH = 45% $N = 1 h^{-1}$ $N = 1 h^{-1}$			t = 23°C, RH = 45% N = 0,5 h ⁻¹		
	E _c [µgh ^{-1]}	E _w [µgh ^{-1]}	<u>Ec-Ew</u> -E _w [%]	E _c [μ g h ⁻¹]	E _w [µ gh -1]	<u>E_c-E_W</u> E _W [%]	E _C [μ gh -1]	E _W [µgh ⁻¹]	E _c -E _w E _w [%]
n-dodecane	30.5	120	-75	123	272	-55	21.5	88	-76
1-butanol	4557	5146	-11	5071	5710	-11	840	919	-9
toluene	5890	6018	-2	19586	20205	-3	4765	5241	-9

 $E_{\rm W}^{\rm C}={\rm emission}$ rate determined by concentration; mean of duplicate measurements $E_{\rm W}^{\rm C}={\rm emission}$ rate determined by weight loss

Laboratory 10 (0.9 liter chamber) t = 24°C, $N = 65 h^{-1}$, n-dodecane

test n.	duration (h)	E _c [µ g h ⁻¹]	E _w [μ g h ⁻¹]	E _c -E _w E _w [%]
1	22.4	43.3	43.8	-1.1
2	44.2	41.4	43.8	-5.5
3	1.0	39.0	43.8	-11
4	1.0	38.8	43.8	-11
5	1.0	39.8	43.8	-9.1
6	1.0	38.4	43.8	-12

APPENDIX **F**

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EUR 15054 - European collaborative action "Indoor air quality and its impact on man" (formerly COST project 613): Determination of VOCs emitted from indoor materials and products Interlaboratory comparison of small chamber measurements

The Concertation Committee

Luxembourg: Office for Official Publications of the European Communities

1993 - I-VII, 100 pp., fig., tab., - 21.0 x 29.7 cm

Environment and quality of life series

EN

CL-NA-15054-EN-C

An interlaboratory comparison using three materials has been organized to assess the agreement among laboratories undertaking tests to characterise the emission of volatile organic compounds from indoor materials and products using small test chambers. The twenty participating laboratories showed the following main results. Chambers of different materials (glass and stainless stell) and of widely different capacity (0.035 to 1475 ℓ) appeared equally suitable. The repeatability of duplicate measurements (including sampling) within each laboratory was good. The test with a known n-dodecane source showed, for most laboratories, an unexpected and yet unexplained discrepancy. The interlaboratory agreement appeared reasonable (coefficient of variation 26-42%) when testing a PVC tile, but for a wax the scatter was very high.