EUROPEAN COLLABORATIVE ACTION

INDOOR AIR QUALITY & ITS IMPACT ON MAN

Environment and Quality of Life

Report No 16

Determination of VOCs emitted from indoor materials and products

Second interlaboratory comparison of small chamber measurements

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

1995

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(formely COST project 613)

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Second interlaboratory comparison of small chamber measurements

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Abstract

ECA (European Collaborative Action "Indoor Air Quality and its Impact on Man"), 1995.
Determination of VOCs emitted from indoor materials and products - Second interlaboratory comparison of small chamber measurements. Report No 16, EUR 16284 EN.
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The results of the first interlaboratory comparison, carried out in 1991-92 in the framework of the European collaborative Action "Indoor Air Quality and Its Impact on Man", showed unacceptable interlaboratory discrepancies in the case of a thin layer fast decreasing source. A second interlaboratory comparison was subsequently organized and, in order to improve the agreement, the design included: (1) control of the chamber air velocity; (2) control of the source layer thickness; (3) adoption of both dilution and sink mathematical models. The concentrations of 2-(2-butoxyethoxy)-ethanol and of the two Texanol isomers emitted from a water-based paint had to be determined over 13 days to derive the initial emission factor. The results of the 18 participating laboratories from 10 countries can be summarized as follows. The preparation of the paint sample contributed markedly to the variance, because of differences in the paint film thickness. The impact of the chamber itself on the results, if any, was less evident: in fact, a satisfactory agreement of the results has been obtained with chambers of widely different features (capacity range 35 cm^3 to 1.5 m^3). Despite the use of calibration solutions prepared from the same batch of pure compounds, the analysis of the compound concentrations contributed markedly to the variance, as confirmed by the results of an analytical comparison carried out in parallel with the main comparison. Model fitting has produced a reasonably good description of the data sets, apparently accounting also for the sink due to chamber wall adsorption. The maximun ranges of the estimated emission factors, expressed as a ratio of the highest to the smallest reported value, are 52, 9 and 9 respectively for 2-(2-butoxyethoxy)-ethanol, Texanol-1 and Texanol-2; however, the scattering is markedly reduced if only results obtained with the same GC detector (*FID*) and from paint samples within a narrow thickness range (50.8-70.6 μm) are considered.

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1. Introduction

The production of less polluting materials for indoor use, which comply with the hygiene and health requirements as defined in the Construction Product Directive (*89/106/EEC*), requires that sufficiently validated test methods be available for the measurement of pollutant emissions from materials. A Guideline concerning the measurement of VOCs has been issued by the European Collaborative Action "Indoor Air Quality and Its Impact on Man" [1] and was subject to a validation by a 1st Interlaboratory comparison in 1991-92 [2]. The conclusion of this comparison experiment left two major questions unanswered: (1) what caused the discrepancies observed for most laboratories between the measured and the expected emission rate (on a weight loss basis) of a constant n-dodecane source and (2) how the interlaboratory agreement could be improved to an acceptable level, especially when dealing with thin layer fast decreasing sources [2,3].

There are strong indications that sorption on the internal surfaces of the test chambers is the answer to question (1) in most cases [4]. In some cases errors in flow measurements may also have contributed. The experiment described here was intended to answer question (2), by the introduction of three main steps compared with the 1st Interlaboratory comparison. These are: (a) the control of the air speed in the chamber; (b) the control of the source layer thickness; (c) the adoption of a second model (sink model), in addition to the simpler dilution model, to correct any important distortion of the data due to adsorption on the chamber walls (see question (1) above). Moreover, a 24 h delay has been introduced after the sample preparation and before the start of measurements, in order to allow for the evaporation of the most volatile fraction and in particular of water, and, hence, to reduce discrepancies due to analytical difficulties.

The Environment Institute at the Joint Research Centre of the European Commission (Ispra, Italy), which co-ordinated the 1st Interlaboratory Comparison Experiment, has also been coordinator of the 2nd Experiment.

2. Experimental design

Eighteen laboratories, from 10 countries and from the European Commission, took part in the experiment (see *Appendix 1*). Some features of the chambers used, including air speed measurements, are reported in *Table 1*.

The material selected for the experiment was a water-borne styrene/acrylic paint, which was applied onto stainless steel or aluminium plates, with a standardized coating device (see *Appendix 2*), at a nominal wet thickness of 200 µm and with a chamber loading factor of 0.5 $m^2.m^{-3}$. Chamber parameters were maintained at 23°C for temperature, 45% for relative humidity, 1 h^{-1} for air exchange rate and 10 $cm.s^{-1}$ for air speed.

The concentrations of 2-(2-butoxyethoxy)-ethanol, of the two monoisobutyric esters of 2.2.4-trimethyl-1.3-pentanediol and of TVOC produced by the paint sample(s) in the test chamber had to be measured at preset times up to 312 hours (13 days). Pure compound vials were distributed to the participants by the co-ordinating laboratory. The two ester isomers were only available as a mixture with the commercial name Texanol® registered by Eastman Chemical Company. The same detector response factor was adopted for both isomers and the mass of each of them was derived in proportion to the GC peak area. The isomer esterified in position 3 is henceforth named Texanol-1 and the one esterified in position 1 Texanol-2. A gas-chromatogram of a chamber air sample is shown in *Figure 1.*

Further details on the experimental conditions for the emission measurements are reported in *Appendix 3.* Two emission measurements (runs) under identical conditions were requested. Before starting the 2nd run, the residual concentrations from the 1st run were measured as requested in the Directions; the values observed are reported in *Appendix 4.*

Standardization of the sampling and analysis methods was not attempted, each laboratory used the preferred one. However the participants were requested to report their methods and a summary of these is given in *Appendix 5.* An analytical comparison was carried out, in order to investigate the contribution of sampling and analysis to the total variance. For this purpose, samplers of the participating laboratories were loaded with the paint vapours at the Environment Institute, under the same conditions as those of the main experiment. The samplers were then analyzed in the laboratories of the participants. Details of this analytical comparison are given in *Appendix 6.*

3. Model calculations

The participants were requested to apply the following two models to each data set (i.e. compound and run). (a) The so-called dilution model (i.e. neglecting sink effects and the vapour pressure effect) which is described by the following equation:

$$C = k_1 \cdot A \cdot M_0 \cdot \frac{\left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t}\right)}{\left(k_2 - k_1\right) \cdot V} \qquad (1)$$

where C is the chamber air concentration (mg m^{-3}), A is the area of the source (m^2), M_0 is the initial mass per unit area (mg.m^{-2}), k_2 is the air exchange rate (h^{-1}) and k_1 the emission rate constant (h^{-1}). The dilution model had to be applied first to derive M_0 and k_1. (b) Successively, the so-called sink model (i.e. neglecting only the vapor pressure effect) had to be applied to derive the values of the same parameters again. This model includes two additional rate constants k_3 (h^{-1}) and k_4 (h^{-1}) describing the vapour adsorption and desorption rates on the chamber walls:

$$C = \frac{A \cdot M_0 \cdot k_1}{V} \cdot \left\{ \frac{(k_4 - k_1) \cdot e^{-k_1 \cdot t}}{(r_1 - k_1) \cdot (r_2 - k_1)} - \frac{(k_2 + k_3 - r_2) \cdot e^{-r_1 \cdot t}}{(r_1 - r_2) \cdot (r_1 - k_1)} + \frac{(k_2 + k_3 - r_1) \cdot e^{-r_2 \cdot t}}{(r_1 - r_2) \cdot (r_2 - k_1)} \right\},$$

$$r_2, r_1 = \left\{ k_2 + k_3 + k_4 \pm \left[(k_2 + k_3 + k_4)^2 - 4 \cdot k_2 \cdot k_4 \right]^{1/2} \right\} \cdot \frac{1}{2} \qquad (2)$$

Both models are applied to the concentration versus time data set by a non linear least squares iterative procedure described elsewhere [5]. A diskette with the software needed to carry out the calculations, has been distibuted to the participants.

The emission factor is described for both models by the following equation:

$$EF = M_0 \cdot k_1 \cdot e^{-k_1 \cdot t} \qquad (3)$$

where EF is the emission factor ($mg.m^{-2}.h^{-1}$) at time t and the product of M_0 and k_1 denotes the initial emission factor EF_0 ($mg.m^{-2}.h^{-1}$).

Almost all the participants supplied, as requested, the estimates for M_0 and k_1, using the dilution and sink models. However, due to experience gained in the 1st Interlaboratory Comparison Experiment and also to exclude calculation errors as a source of variance, regression calculations were also carried out at the Environment Institute for all the data sets and, in the case of the "sink" model also with different initial guesses ("*tuning*"). With the latter model, in fact, the parameter estimates are frequently different with different initial guesses; this is due to the fact that, because of the greater complexity of the equation, there may be local minima of the least squares function, which may be mistaken as the absolute minimum. This fact is better understood looking at the example reported in *Table 2*, which shows parameter estimates obtained for one single data set (Texanol-1 in run 1 of lab. no. 9) with different initial guesses and both models. Whereas the estimates of M_0 and k_1 obtained with the dilution model with widely varying initial guesses were virtually constant, large variation of the parameter estimates occurred using the sink model. The recalculation of the parameter estimates at the Environment Institute highlighted the need for the careful consideration and application of modelling.

For 2-(2-butoxyethoxy)-ethanol as an example (for the other compounds the situation is very similar), this work, in addition to providing the missing calculation results for some 8 data sets, issued in parameter estimates different from those reported as follows: out of 115 M_0 and k_1 estimates, 11 were different by 1 to 10% and 15 were different by more than 10%. In addition, many very large differences were obtained for the k_3 and k_4 estimates through the sink model "tuning".

The criteria adopted for the selection of the best estimates were the following: (a) equivalent parameter estimates are obtained with at least two different initial guesses; (b) the associated standard errors are less or not much larger than the estimates themselves for all four parameters; (c) the errors are minimum; (d) there is no overparameterization, i.e. the parameters are really independent from each other (as indicated by the correlation matrix). It may happen that not all these conditions are met simultaneously. In this case, it is left to the statistician-modeller's personal judgement to decide. For instance, in the example of *Table 2* for the sink model, the minimum of the sum of squares was obtained in the 3rd trial, but the corresponding estimates were not accepted because of the large value of M_0 and because of the large error associated with k_4. The estimates accepted are those obtained in the 1st and 5th trials.

The best regression result obtained with the sink model has been compared with the result of the dilution model by the "*extra sum of squares F test*" for the significance of the difference between two variances. This test involves the following mathematical formula:

$$F(p_2 - p_1, n - p_2) = \frac{(S_1 - S_2)/(p_2 - p_1)}{S_2/(n - p_2)} \qquad (4)$$

where S_1 and S_2 are the residual error sums from the regression analyses of the same experimental data onto the models 1 and 2, p_1 and p_2 represent the respective number of parameters, and the subscripts refer to the specific models. To use Eq. (4) model 2 should be a generalization of model 1. In our case, models 2 and 1 correspond to the sink and to the dilution model, respectively. To distinguish between the two models one should compare the value of the $F(n,p)$ ratio in Eq. (4) with the corresponding entry (n,p) in the F tables at a certain percentage value of confidence level α (e.g., 95%). If the variance obtained with the sink model turned out significantly (95% confidence level) smaller than that obtained with the dilution model, the former has been considered more adequate to describe the particular data set. Consequently, its parameter estimates were used for the interlaboratory comparison. If no significant variance reduction was obtained with the sink model, the parameter estimates obtained with the dilution model were used for the comparison.

In the example in *Table 2* the residual sum of squares of four out of five trials with the sink model are very significantly smaller than the corresponding value for the dilution model; thus the parameter estimates from the sink model have been used for the comparison. *Figure 2* shows an example of fitting one data set with the two models, where the sink model remarkably improves the fitting (the residual sum of squares of the dilution and sink models were 456190 and 12446, respectively). The model which provided the best estimate adopted is indicated in *Tables 6a*, *7a* and *8a* for each data set. The calculated F values and the F values tabulated for the corresponding number of degrees of freedom are reported in *Table 3*.

For the analysis of variance of the M_0, k_1 and EF_0 results, the values obtained with the dilution or with the sink model have been pooled together. The one-way analysis of variance has been carried out to estimate the "*between*" and the "*within*" laboratory variance and to test the significance of the difference between groups of data: those obtained with different detectors (*FID* and *MS*), with different paint film thickness, etc.

The "*sink*" constants k_3 and k_4 have not been included in the statistical treatment, because they refer to chamber properties and not to source properties.

4. Results and discussion

In general the laboratories complied with the requested values for temperature, relative humidity, air exchange rate, air speed and loading factor. In particular, the reported mean values of air speed (*Table 1*), except in a few cases, are reasonably close to the value requested (10 $cm.s^{-1}$), but the fluctuations between minimum and maximum were generally high. This could be expected considering that, in general, the operation of a fan is intended to cause turbulence in the chamber.

The final dry film thickness expected for the paint samples was roughly 60 μm. This reduction, compared with the 200 μm slit of the application device, is explained by two facts: (1) the shearing stress, which depends on the coating speed, reduces the effective wet layer thickness to about 2/3 of the nominal thickness; (2) the loss of water and of the other volatile ingredients which leaves roughly 45% by weight dry residue. *Table 4* reports the paint film thickness in terms of average weight per unit area (determined by the laboratories) and in terms of measured thickness by a microprocessor controlled film gauge. The latter determinations, which were carried out at the Environment Institute (see *Appendix 2*) show a mean value reasonably close to the expected thickness (overall mean 66 μm), but a number of samples deviate quite remarkably.

To give the reader a more immediate perception of what was going on in the test chambers, the concentrations measured by each laboratory at three selected times are reported in *Table 5*. The shortest time (3h) corresponds roughly to the maximum concentration. The chamber background concentrations, measured before the 2nd run, to ckeck for a possible "memory effect" from the 1st to the 2nd run (*Appendix 4*) are mostly zero or close to zero; only a few of concentrations exceed 1-2% of the maximum concentration in the 2nd run and one is close to 10% (2-(2-butoxyethoxy)-ethanol from *FLEC*); overall, this background may hence be neglected in an attempt to explain the variance of the results.

The best parameter estimates for 2-(2-butoxyethoxy)-ethanol, for Texanol-1 and for Texanol-2 are reported respectively, in *Tables 6a* and *6b*, *7a* and *7b*, *8a* and *8b*. It may be observed, in *Table 6a*, that out of 34 data sets, 19 (56%) are best described by the sink model and 15 (44%) by the dilution model. The corresponding observation for Texanol-1, in

Table 7a, shows that out of 32 data sets, 20 (63%) are best described by the sink model and 12 (37%) by the dilution model. Finally, the comparison between the two models for Texanol-2 *in Table 8a*, indicates that out of 32 data sets, 23 (72%) are best described by the sink model and 9 (28%) by the dilution model. So, from 2-(2-butoxyethoxy)-ethanol through Texanol-2, i.e. going from the more volatile to the less volatile compounds, there is a tendency of an increasing number of chambers apparently suffering from the sink effect.

The values in *Tables 6a, 7a* and *8a*, after discarding the outliers, have been submitted to a one-way analysis of variance with the conclusions reported in *Table 9*. This Table shows that, for M_0, the variance due to interlaboratory differences ("*between*") is larger or much larger than the variance due to fluctuations inside the laboratory ("*within*").

The values of the initial emission factor EF_0 (i.e. the product of M_0 and k_1) are represented graphically in *Figures 3-5* to visualize the inter- and intra-laboratory variability. In addition, they are reported in *Tables 6b, 7b* and *8b* in order to compare their distribution with the distribution of M_0 and k_1. Values in the Tables are ranked by size and not by run number. Therefore values in one row usually do not refer to the same run. A compensation effect (i.e. large M_0 values combined with small k_1 values and vice versa) does only occurs in a few cases (e.g. for runs 1 and 2 of the same laboratory), but the overall dispersion of the EF_0 values remain similar and even larger than that of M_0 and k_1.

The interlaboratory variance includes two factors which contribute significantly to the overall variance, these are the thickness of the paint film and the *GC* detector used. A graphic presentation of the influence of paint thickness on M_0 is given in *Figures 6*, *7* and *8*, which show, for 2-(2-butoxyethoxy)-ethanol, Texanol-1 and Texanol-2, the correlation between the two variables, respectively. The correlation is highest if only the M_0 values obtained with the *FID* detector are considered.

Figures 6-8 also highlight the different contributions to variance of the *FID* and *MS* detectors. The variances of the two groups of M_0 data obtained with the *FID* and *MS* detectors have been subject to the *F-test* after normalization for thickness. The normalization was carried out dividing each M_0 value by the ratio between the actual thickness of the corresponding paint sample and the smallest thickness measured (39.1 μm). As a result of this test, the variance of the *MS* results is significantly greater ($p < 0.01$) than that of the *FID* results.

The impact of the detector type on the results is also shown in *Table 10*; here the means and standard deviations of M_0, k_1 and EF_0 are shown separately for *FID* and *MS* results. Only data obtained from paint specimen within a narrow film thickness interval (50 to 70.6 μm) have been used for this comparison in order to minimize the influence of the paint thickness on the variance. The 18 samples falling within this arbitrarily defined range have a mean thickness of 60.3 ± 6.3 μm, with a reduction of the standard deviation from 30%, for the whole data set, to 10%. The coefficients of variation reported in *Table 10* for M_0

and EF_0 must be looked upon together with the respective means, to perceive the real difference, roughly a factor of 2.

It is also interesting to compare the initial masses M_0 of the two Texanol isomers estimated from the chamber test data with the amount of Texanol added to the paint by the manufacturer (only the sum of the two isomers has been given), namely 0.3 ± 0.006 % of the total paint weight. Using experimental data for the mean dry weight of paint per unit area and considering that the dry matter of the paint accounts for 46 % of the fresh paint weight (see *Appendix 2, Table A*), initial total Texanol masses of 789 mg/m^2 and 887 mg/m^2 result respectively (see *Appendix 7*). These values may be compared with the sum of the initial masses of Texanol-1 and Texanol-2 determined by means of the FID and the MS detector as reported in *Table 10*: 217 mg/m^2 respectively 396 mg/m^2. Obviously, during the 24 h conditioning period most Texanol evaporated. A quantitative check of this deduction, carried out at the Environment Institute repeating the experiment with a *FLEC* chamber, showed that of the total Texanol evaporated between 1 and 312 hours after the paint sample preparation, about 55% evaporated in the period of 1 - 23 hours and 45% successively (see *Appendix 8*).

4.1 TVOC

Considering the results of the analysis carried out on the data of the three individual compounds and that they represent by far the largest fraction of the total emission, hence that any analysis of the TVOC data cannot add much, only a very limited effort has been carried out thereon.

The initial mass (M_0) estimated by the laboratories for TVOC (dilution model, except laboratory n.5, which reported estimates for the sink model only), was compared with the sum of the best estimates (*Tables 6-8*) of M_0 for the three compounds. This comparison is legitimate if the sum of the individual compounds corresponds to the total signal (no other compounds are detected) or if the fraction of the total signal due to other compounds is constant. Inspecting the chromatograms obtained at the Environment Institute, it appears that, under "normal" integration conditions, the sum of the three compounds totals approximately 85% of the *FID* signal. However, if the integration conditions are changed also to integrate very small peaks, the contribution due to the three compounds may decrease to 65%. Consequently, the above mentioned condition may not be met in all cases.

Anyhow, the comparison is presented in *Table 11* and in *Figure 9*, in the form of a linear correlation. The correlation is poor (correlation coefficient 0.40), because of largely scattered data, which also means that no individual value can be discarded as an outlier (*Dixon's Q* test on the ratio). However, the slope has exactly the value, 0.60, expected on the basis of the relative *FID* responses of Texanol and toluene (reference compound for

TVOC) at the Environment Institute. The relative response of 2-(2-butoxyethoxy)-ethanol is 0.45, but the contribution of this compound to TVOC, is small compared with Texanol. The large scattering (the ratio TVOC over the sum of the three compounds ranges between 0.035 and 2.09) may have different contributions such as: (1) different integration conditions, as mentioned above; (2) different response factors for Texanol relative to toluene and hence to TVOC; (3) errors in the M_0 estimate for TVOC.

4.2 Analytical comparison

A comparison of the analytical performance of 10 out of the 18 participating laboratories was carried out as described in more detail in Appendix 6. One or two air samples per laboratory were collected from a chamber with a paint sample at the Environment Insitute, using samplers of the participating laboratories. The results are summarized in Table 12. The two runs correspond to two air samples which were collected from the chamber on two successive days, so that the paint emission rate and hence the concentrations decreased from the 1st to the 2nd run. Two aspects are evident from these results: the variance is important for all three compounds and for 2-(2-butoxyethoxy)-ethanol there is an additional variance compared with the Texanol isomers. This excess of variance may be due to a different interaction of the compound with the various analytical systems of the laboratories, also including sampling of the vapours from the air. A striking example thereof are the results from Laboratory n.8 obtained with two different sampler tubes. Results obtained with charcoal adsorption and solvent elution are consistently lower than those obtained with Tenax adsorption and thermal elution. If the values of the coefficient of the variation of the concentrations in this comparison (*Table 12*) are compared with those of the emission factor for selected data (*FID* detector, *Table 10*), it appears that they constitute a very important fraction thereof, roughly 50%. This confirms that sampling and analysis contribute substantially to the total variance of the intercomparison results.

5. Conclusions

The experiment has been very positive from the point of view of experience gained and understanding of the topics which deserve further research. Despite a remarkable progress in reducing the dispersion of the results compared with the 1st Interlaboratory comparison (see *Figure 10*), the experiment shows that there is still a gap between the state of the art of material emission measurements and the industrial needs in this field. Progress is being made in order to fill this gap. The European Committee for Standardization (CEN) has set up a working group (WG 7 within Technical Committee 264) whose task it is to define a test chamber method for the determination of the "emission of chemical substances from building materials". A group of research institutes, including the Environment Institute, and industries manufacturing flooring materials and paints have proposed a research project, called VOCEM, to be funded by the Standard, Measurement and Testing

programme of the EU, aimed at an improved control of the factors, which, from the experiment described here, mainly result in contributing to the still too high variance of the results of emission measurements. These factors are highlighted below in the following more detailed conclusions.

The experiment may be regarded as being composed of four parts: (1) the preparation of the paint source; (2) the chamber operation and interaction with the source; (3) the chemical analysis, i.e. sampling of the vapours and their quantitative determination; (4) the model calculations.

The preparation of the sample has markedly contributed to the variance of the results, as shown by the wide differences in the paint thickness of some samples and by the correlation between M_0 and thickness. Considering the standardization effort introduced in this step and the fact that the mean thickness is very close (~ 10%) the one expected, it may be argued that the differences are mainly due to different skills in applying the paint at the different laboratories. However, a group of a few laboratories show consistent capability in preparing reproducible films of the desired thickness. There is a clear need for further standardization in the sample preparation and for the definition of the way and the time needed for sample conservation between preparation and the start of testing.

For the chamber test itself, the first interlaboratory comparison experiment (ECA, 1993) had already demonstrated that chamber sinks and the surface air velocity or turbulence were the factors mainly influencing the reproducibility or variance of the test results. Chamber sinks have been accounted for in this experiment by modelling. Applying two models (dilution and sink model) to all data sets selecting the most appropriate for each data set by an objective procedure (*F-test*), yielded in general good fitting of the data points, even in the tailing portion of the concentration versus time curves (see *Figure 2*). This represents a remarkable progress compared to the 1st experiment where only the dilution model has been applied. However, the successful application of the sink model to the prediction of emission rate constants and emitted masses critically depends on the assumption of a simple exponential decrease of the emission rate. If more complex emission processes should occur, e.g. emission from two compartments with two different exponential decrease rates as observed by Chang and Guo [6], application of the sink model may lead to erroneous results.

The problem of surface air velocity has been addressed in this experiment by requesting its measurement, prescribing a measurement position and urging the participants to arrange air circulation/mixing in such a way that the average air speed, at the point of measurement be as close as possible to 10 $cm.s^{-1}$. The reported values of the surface air velocity did not show any correlation with the emission test results (M_0, k_1). Therefore, apparently, the surface air velocity has caused no evident bias of the results. However, the measured air velocities show large fluctuations, cannot be controlled well in many chambers

and it is uncertain how representative the values measured in the prescribed position are for the average air velocity. Moreover, the measurements were started when a solid film had already been formed at the paint surface in order to reduce the influence of surface air velocity. For all these reasons, the control of the surface air velocity needs further attention.

The analytical step, despite the use of calibration solutions prepared from the same batch of pure compounds, heavily contributes to the variance of the results; this is shown by the evident and significant differences due to the detector employed (*FID* or *MS*). This problem has been further investigated by means of the analytical comparison, which confirms the important contribution of the errors in this step to the overall dispersion of the results.

The phase of model fitting has issued reasonably good descriptions of the data sets, by the fact that two models were used (dilution and sink), the most appropriate for each data set being objectively (*F* test) selected.

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Table 1. Chamber capacity and air speed

Laboratory	Chamber volume (ℓ)	Chamber wall material[1]	Air speed[2] ($cm.s^{-1}$)			Notes[3]
			min	*max*	*aver.*	
1	85.1	SS	7.4 7.4	14.2 14.2	10.2 10.2	FR FR
2	51.0	SS	5 5	15 15	10 10	FR FR
3	1000	SS	0 0	56 41	9 9	FR FR
4	53	SS	7 7	9 9	8 8	FR FR
5	180	SS	3 6	20 20	10 14	FR FR
6	92.35	SS	9.6 9.2	17.6 17.2	13.8 13.4	FR FR
7	1475 0.035	SS SS	5 5 NR NR	15 15 NR NR	10 10 0.31 0.31	FNR FNR FLEC FLEC
8	1000	SS	6 6	17 17	12 12	FR FR
9	280	SS	5 5	15 15	10 10	FR FR
10	100	SS	NR NR	NR NR	NR NR	FR FR
11	953	SS	47	59	53	FR 2nd run failed
12	970	SS	7.95 7.57	10.35 10.71	9.15 9.14	FR FR
13	985	SS	NR NR	NR NR	16.2 16.2	FR FR
14	1000	GLASS	NR 5	NR 20	3 10	FNR FR
15	1000	SS	NR	NR	30	1st run failed FR
16	225	SS	--- ---	22 14	10 10	FR
17	250	GLASS	8	14	10	FR FR
18	53	SS	0	17.8	8.6	FR - one run only

(1) ss = stainles steel
(2) NR = not reported
(3) FR = fan running; FNR = fan not running

Table 2. Example of parameter estimate sensitivity to variations in the initial guesses

Texanol-1, run 1, laboratory no. 9

a. "dilution" model

guesses	parameter estimate	std. error	R^2	residual sum of squares
M_0 = 1 k_1 = 1	M_0 = 74364 k_1 = 0.022738	5166 0.001948	0.98120	18388
M_0 = 100 k_1 = 100	M_0 = 74372 k_1 = 0.022734	5166 0.001948	0.98120	18388
M_0 = 1 k_1 = 100	M_0 = 74364 K_1 = 0.022738	5166 0.001949	0.98120	18388
M_0 = 0.1 k_1 = 10,000	M_0 = 74367 K_1 = 0.022736	5166 0.001948	0.98120	18388

b. "sink" model

guesses	parameter estimate	std. error	R^2	residual sum of squares
M_0 = 74364 k_1 = 0.022738 k_3 = 1 k_4 = 1	M_0 = 79296 k_1 = 0.035629 k_3 = 0.79095 k_4 = 0.033225	2209 0.002202 0.10686 0.0044392	0.99898	995.30
M_0 = 74364 k_1 = 0.022738 k_3 = 1 k_4 = 0.1	M_0 = 144289 k_1 = 0.019846 k_3 = 0.84187 k_4 = 6.42×10^{-7}	not reported " " " " " "	0.99892	1056.8
M_0 = 74364 k_1 = 0.022738 k_3 = 0.1 k_4 = 1	M_0 = 140041 k_1 = 0.020284 k_3 = 0.82309 k_4 = 0.00028	111720 0.000519 0.55961 0.01714	0.99903	946.35

Table 2. (cont.d)

guesses	parameter estimate	std. error	R^2	residual sum of squares
M_0 = 74369 k_1 = 0.022733 k_3 = 1 k_4 = 1	M_0 = 74796 k_1 = 0.022397 k_3 = 0.02919 k_4 = 0.01345	21018 0.00571 0.3429 0.17013	0.98172	17877
M_0 = 74369 k_1 = 0.022733 k_3 = 0.3 k_4 = 0.03	M_0 = 79296 k_1 = 0.035629 k_3 = 0.79096 k_4 = 0.033223	2096 0.00222 0.10858 0.00446	0.99898	995.30

Table 3. Model discrimination based on the extra sum F-test

Lab	2-(2-butoxyethoxy)-ethanol		Texanol-1		Texanol-2	
	$F_{exp.}$	$F_{tab\ (0.05)}$	$F_{exp.}$	$F_{tab\ (0.05)}$	$F_{exp.}$	$F_{tab\ (0.05)}$
1	$F_{(2,22)} = 1.106$ $F_{(2,20)} = 4.791$	$F_{(2,22)} = 3.44$ $F_{(2,20)} = 3.49$	$F_{(2,22)} = 0.205$ $F_{(2,20)} = 21.33$	$F_{(2,22)} = 3.44$ $F_{(2,20)} = 3.49$	$F_{(2,22)} = 0.52$ $F_{(2,20)} = 18.40$	$F_{(2,22)} = 3.44$ $F_{(2,20)} = 3.49$
2	$F_{(2,5)} = 7.34$ (a)	$F_{(2,5)} = 5.79$ (a)	$F_{(2,8)} = 38.77$ (a)	$F_{(2,8)} = 4.46$ (a)	$F_{(2,8)} = 13.04$ $F_{(2,16)} = 21.40$	$F_{(2,8)} = 4.46$ $F_{(2,16)} = 3.63$
3	$F_{(2,6)} = 18.71$ $F_{(2,6)} = 5.496$	$F_{(2,6)} = 5.14$ $F_{(2,6)} = 5.14$	$F_{(2,6)} = 28.34$ $F_{(2,6)} = 87.17$	$F_{(2,6)} = 5.14$ $F_{(2,6)} = 5.14$	$F_{(2,6)} = 18.12$ $F_{(2,6)} = 137.0$	$F_{(2,6)} = 5.14$ $F_{(2,6)} = 5.14$
4	$F_{(2,6)} = 83.44$ $F_{(2,8)} = 72.43$	$F_{(2,6)} = 5.14$ $F_{(2,8)} = 4.46$	$F_{(2,7)} = 7.755$ $F_{(2,8)} = 2.157$	$F_{(2,7)} = 4.74$ $F_{(2,8)} = 4.46$	$F_{(2,7)} = 25.63$ $F_{(2,8)} = 4.93$	$F_{(2,7)} = 4.74$ $F_{(2,8)} = 4.46$
5	$F_{(2,8)} = 2.65$ $F_{(2,8)} = 0.298$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 5.248$ $F_{(2,8)} = 2.092$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 0.91$ $F_{(2,8)} = 2.45$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$
6	$F_{(2,6)} = 7.04$ $F_{(2,8)} = 23.74$	$F_{(2,6)} = 5.14$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 77.26$ $F_{(2,8)} = 142.6$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 3.41$ $F_{(2,8)} = 47.74$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$
7	(b) $F_{(2,8)} = 17.77$ $F_{(2,9)} = 0.228$ (g) $F_{(2,9)} = 0.0016$ (g)	(b) $F_{(2,8)} = 4.46$ $F_{(2,9)} = 4.26$ $F_{(2,9)} = 4.26$	$F_{(2,9)} = 0.024$ $F_{(2,8)} = 25.44$ $F_{(2,9)} = 6E\text{-}6$ (g) $F_{(2,9)} = 9E\text{-}7$ (g)	$F_{(2,9)} = 4.26$ $F_{(2,8)} = 4.46$ $F_{(2,9)} = 4.26$ $F_{(2,9)} = 4.26$	$F_{(2,9)} = 0.054$ $F_{(2,8)} = 36.57$ $F_{(2,9)} = 0.0$ (g) $F_{(2,9)} = 15.82$ (g)	$F_{(2,9)} = 4.26$ $F_{(2,8)} = 4.46$ $F_{(2,9)} = 4.26$ $F_{(2,9)} = 4.26$
8	(c) $F_{(2,14)} = 11.78$	(c) $F_{(2,14)} = 3.74$	(c) $F_{(2,14)} = 5.831$	(c) $F_{(2,14)} = 3.74$ (d)	(c) $F_{(2,14)} = 69.11$	(c) $F_{(2,14)} = 3.74$
9	$F_{(2,4)} = 719.4$ $F_{(2,5)} = 914.7$	$F_{(2,4)} = 6.94$ $F_{(2,5)} = 5.79$	$F_{(2,9)} = 78.46$ $F_{(2,11)} = 54.49$	$F_{(2,9)} = 4.26$ $F_{(2,11)} = 3.98$	$F_{(2,9)} = 125.53$ $F_{(2,11)} = 115.4$	$F_{(2,9)} = 4.26$ $F_{(2,11)} = 3.98$
10	$F_{(2,8)} = 10.95$ $F_{(2,10)} = 9.14$	$F_{(2,8)} = 4.46$ $F_{(2,10)} = 4.10$	$F_{(2,8)} = 2.483$ $F_{(2,8)} = 1.515$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 0.274$ $F_{(2,8)} = 0.081$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$
11	$F_{(2,6)} = 0.069$ (d)	$F_{(2,6)} = 5.14$ (d)	$F_{(2,6)} = 29.32$ (d)	$F_{(2,6)} = 5.14$ (d)	$F_{(2,4)} = 10.13$ (d)	$F_{(2,4)} = 6.94$ (d)

Table 3. (cont.d)

Lab	2-(2-butoxyethoxy)-ethanol		Texanol-1		Texanol-2	
	$F_{exp.}$	$F_{tab\ (0.05)}$	$F_{exp.}$	$F_{tab\ (0.05)}$	$F_{exp.}$	$F_{tab\ (0.05)}$
12	$F_{(2,8)} = 13.54$ $F_{(2,3)} = 0.630$	$F_{(2,8)} = 4.46$ $F_{(2,3)} = 9.55$	$F_{(2,8)} = 9.746$ $F_{(2,5)} = 9.141$	$F_{(2,8)} = 4.46$ $F_{(2,5)} = 5.79$	$F_{(2,8)} = 17.22$ $F_{(2,5)} = 8.52$	$F_{(2,8)} = 4.46$ $F_{(2,5)} = 5.79$
13	$F_{(2,10)} = 22.11$ $F_{(2,10)} = <<<1$	$F_{(2,10)} = 4.10$ $F_{(2,10)} = 4.10$	$F_{(2,10)} = 13.84$ $F_{(2,10)} = <<<1$	$F_{(2,10)} = 4.10$ $F_{(2,10)} = 4.10$	$F_{(2,10)} = 18.18$ $F_{(2,10)} = 0.226$	$F_{(2,10)} = 4.10$ $F_{(2,10)} = 4.10$
14	$F_{(2,8)} = 1.625$ $F_{(2,9)} = 73.77$	$F_{(2,8)} = 4.46$ $F_{(2,9)} = 4.26$	$F_{(2,8)} = 2.959$ $F_{(2,8)} = 8.996$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 12.19$ $F_{(2,8)} = 6.12$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$
15	(d) $F_{(2,9)} = 23.58$	(d) $F_{(2,9)} = 4.26$	(d) $F_{(2,21)} = 231.8$	(d) $F_{(2,21)} = 3.47$	(d) $F_{(2,21)} = 263.9$	(d) $F_{(2,21)} = 3.47$
16	$F_{(2,8)} = 1.071$ $F_{(2,8)} = 0.474$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 31.25$ $F_{(2,8)} = 24.78$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$	$F_{(2,8)} = 24.19$ $F_{(2,8)} = 33.17$	$F_{(2,8)} = 4.46$ $F_{(2,8)} = 4.46$
17	$F_{(2,9)} = 2.74$ $F_{(2,10)} = 1.976$	$F_{(2,9)} = 4.26$ $F_{(2,10)} = 4.10$	(e)	(e)	(e)	(e)
18	$F_{(2,8)} = 2.43$ (f)	$F_{(2,8)} = 4.46$ (f)	$F_{(2,8)} = 0.95$ (f)	$F_{(2,8)} = 4.46$ (f)	$F_{(2,8)} = 7.88$ (f)	$F_{(2,8)} = 4.46$ (f)

(a) no raw data exist
(b) for the 1st run, the results of the sink model were rejected because not reliable
(c) not reliable results (only decreasing concentration raw data)
(d) run failed
(e) Texanol isomers not separated
(f) one run only was carried out
(g) FLEC

Table 4. Thickness of the paint samples

Laboratory	Dry weight of paint [1] ($mg.cm^{-2}$)	Paint thickness [2] (μm)	
		mean	std. dev.
1	NR NR	46.3 40.8	6.2 6.5
2	15.3 13.5	89.5 [3] 83.5 [3]	--- ---
3	10.8 10.1	53.0 56.1	6.5 5.4
4	8.2 7.4	39.1 SNR	4.7 ---
5	31 33	107 123	15 16
6	10 13	43.4 65.6	5.3 9.2
7	17.6 17.3 15 15	58.7 50.8 56.9 52.1	3.3 3.5 1.6 1.4
8	NR NR	80.8 59.0	13.5 7.8
9	12.5 9.5	60.8 52.2	4.5 5.5
10	30 30	103 SNR	13 ---
11	51.7 ---	56.0 ---	5.5 ---
12	8.4 9.0	65.2 65.0	8.9 4.9
13	10.3 10.2	68.6 60.2	2.4 2.7
14	11.5 11.5	69.3 64.7	4.9 4.5
15	--- 28.9	--- SNR	--- ---
16	21 22	SNR SNR	--- ---
17	12.3 ---	SNR ---	--- ---
18	26.8	70.6	18.0
Mean of all runs *Mean of selected runs* [4], [5]	*18.9 ± 11.6* *12.1 ± 2.9*	*60.5* [4]	

(1) reported by the participants; NR = not reported
(2) measured at the Environment Institute (Ispra) by digital film gauge; SNR = sample not received
(3) glass plate, measurement by material profiling technique
(4) runs for which the mean paint thickness was in the range between 50.8 and 70.6 μm
(5) with exception of the two values reported by laboratories ns. 11 and 18, which are outliers

Table 5. Concentrations measured at selected times in the test chambers ($\mu g.m^{-3}$)

Lab	2-(2-butoxyethoxy)-ethanol			Texanol-1			Texanol-2		
	3h	78 h	240 h	3 h	78 h	240 h	3 h	78 h	240 h
1	2194 3395 1993 1500	34.4 122 19.5 32.4	0 8.6 0 5.1	978 1299 1174 1121	174 383 161 146	10.9 35.0 9.0 12.5	1195 1901 1683 1576	360 709 349 355	24.0 59.8 30.4 32.3
2	556 -	- -	9.0 -	1030 -	674 -	188 -	- 900	- 811	- 89.4
3	487 461	2.9 5.4	- -	1499 1248	250 454	- -	1240 1108	227 416	- -
4	563 443	0 0	0 0	929 550	167 84.4	0 5.2	1210 849	187 108	0 7.3
5	1037 1673	105 143	11.3 7.9	656 983	353 382	126 110	1019 1477	572 868	404 192
6	283 727	- 0	0 0	1968 1333	513 635	0 98	1003 1705	619 746	31 143
7	247 164 101 83.5	46.5 18.2 25.6 19.2	8.0 7.3 18.5 19.2	288 252 351 312	124 116 80.3 45.5	37.9 30.5 5.1 4.0	472 424 549 521	191 190 132 76.0	58.1 47.1 8.1 6.5
8	- 441	97 [c] 58 [d]	6 10	- 666	511 271	93 57	- 1047	844 443	150 94
9	534 353	13.4 [c] 0.8 [d]	- -	728 709	190 [b] 78.5	10.6 2.9	1037 1056	282 [b] 129	17.3 4.8

Table 5. (cont.d)

Lab	2-(2-butoxyethoxy)-ethanol			Texanol-1			Texanol-2		
	3h	78 h	240 h	3 h	78 h	240 h	3 h	78 h	240 h
10	2219 2092	134 118	0 0	1840 1860	440 427	67 59	1272 1234	544 518	143 128
11 [a]	360	-	13	1216	-	4.2	864	-	-
12	296 209	20 0	16 -	249 460	96 199	11 -	602 826	234 331	24 -
13	1160 960	13 26	0 0	870 820	140 250	6 11	1220 1160	220 370	9 17
14	2970 1760	415 92	49.9 11.9	1660 1030	637 301	137 44.1	1450 1360	833 384	181 55.6
15 [a]	3819	736 [b]	16	1651	699 [b]	210	2615	1247 [b]	449
16	65.2 98.2	5.7 13.3	1.8 2.9	322 331	136 187	20.5 23.8	351 362	148 203	26.0 28.3
17	315 816	12 29 [e]	0 14	-- --	-- --	-- --	-- --	-- --	-- --
18 [a]	181	32.0	0	304	127	0	270	108	0

0 below detection limit
(-) no measurements reported
(--) Texanol isomers not separated
(a) one run only
(b) concentration at 72 h
(c) concentration at 73 h
(d) concentration at 80 h
(e) concentration at 74 h

Table 6a. 2-(2-butoxyethoxy)-ethanol parameter estimates selected[1] for the comparison

Laboratory	Run	M_0 (mg.m^{-2})	k_1(h^{-1})	model [2]
1	1	106	0.0632	d
	2	61.1	0.119	s
2	1	56.4	0.0307	s
	2[3]	32.1	0.0427	s
3	1	18.7	0.0665	s
	2	17.5	0.0788	s
4	1	21.1	0.0760	d
	2	14.9	0.0801	s
5	1	90.2	0.0289	d
	2	144	0.0248	d
6	1	8.19	0.173	s
	2	37.5	0.0547	s
7	1	4.81	0.214	d
	2	15.1	0.0919	s
	FLEC1	19.3	0.0165	d
	FLEC2	12.1	0.0233	d
8	1[4]	---	---	---
	2	40.4	0.0445	s
9	1	21.3	0.118	s
	2	10.1	0.157	s
10	1	108	0.0538	s
	2	99.6	0.0614	s
11	1	34.3	0.0230	d
	2[5]	---	---	---
12	1	12.8	0.0725	s
	2	10.1	0.0471	d
13	1	52.2	0.112	s
	2	33.7	0.0644	d
14	1	199	0.0347	d
	2	63.1	0.158	s
15	1[5]	---	---	---
	2	728	0.0258	s
16	1	4.81	0.0393	d
	2	9.74	0.0302	d
17	1	11.4	0.0651	d
	2	44.1	0.0437	d
18	1[6]	22.1	0.0253	d

(1) according to minimum error and other criteria (see the section "Model calculations").
(2) d = dilution, s = sink.
(3) value reported by the laboratory (no raw data available).
(4) rejected because no concentration data was available for the first 28 hours.
(5) run failed.
(6) one run only.

Table 6b. 2-(2-butoxyethoxy)-ethanol ranked parameter estimates

M_0 (mg.m^{-2})	k_1 (h^{-1}) (x1000)	EF_0 (mg.m^{-2}.h^{-1})
4.81	16.5	0.189
4.81	23.0 MS	0.281
8.19 MS	23.3	0.294
9.74	24.8	0.319
10.1	25.3 MS	0.474 MS
10.1 MS	25.8 *	0.559 MS
11.4 MS	28.9	0.741 MS
12.1	30.2	0.787 MS
12.8	30.7 MS	0.925
14.9	34.7 MS	1.03
15.1	39.3	1.19
17.5	42.7 MS	1.24
18.7	43.7 MS	1.37 MS
19.3	44.5	1.38
21.1	47.1	1.39
21.3	53.8	1.41 MS
22.1 MS	54.7 MS	1.59
32.1 MS	61.4	1.60
33.7	63.2 MS	1.73 MS
34.3 MS	64.4	1.80
37.5 MS	65.1 MS	1.93 MS
40.4	66.5	2.05 MS
44.1 MS	72.5	2.17
52.2	76.0	2.51
56.4 MS	78.8	2.61
61.1 MS	80.1	3.58
63.1 MS	91.9	5.80
90.2	112	5.85
99.6	118	6.12
106 MS	119 MS	6.70 MS
108	157	6.91 MS
144	158 MS	7.27 MS
199 MS	173 MS	9.94 MS
728 *	214	18.8 *

* outliers (Dixon's *Q* test).

Table 7a. Texanol-1 parameter estimates selected [1] for the comparison

Laboratory	Run	M_0 (mg.m^{-2})	k_1 (h^{-1})	model [2]
1	1	138	0.0190	d
	2	96.5	0.0566	s
2	1	332	0.0084	s
	2[3]	304	0.0065	d
3	1	176	0.0229	s
	2	192	0.0181	s
4	1	81.7	0.0260	s
	2	47.6	0.0268	d
5	1	202	0.0100	s
	2	240	0.0093	d
6	1	226	0.0233	s
	2	253	0.0168	s
7	1	57. 3	0. 0114	d
	2	93.6	0.0109	s
	FLEC 1	74.1	0. 0180	d
	FLEC 2	54.4	0.0203	d
8	1[4]	---	---	---
	2	118	0.0146	s
9	1	79.3	0.0356	s
	2	52.9	0.0439	s
10	1	191	0.0214	d
	2	190	0.0230	d
11	1	138	0.0265	s
	2[5]	---	---	---
12	1	37.3	0.0163	s
	2	64.8	0.0194	s
13	1	78.8	0.0346	s
	2	90.4	0.0183	d
14	1	305	0.0106	d
	2	116	0.0705	s
15	1[5]	---	---	---
	2	355	0.0255	s
16	1	73.2	0.0165	s
	2	103	0.0140	s
17	1,2[7]	---	---	---
18	1[6]	42.4	0.0210	d

(1) according to minimum error and other criteria (see the section "Model calculations")
(2) d = dilution, s = sink
(3) value reported by the laboratory (no raw data available)
(4) rejected because no concentration data was available for the first 28 hours
(5) run failed;
(6) one run only;
(7) only the sum of Texanol-1 and Texanol-2 reported.

Table 7b. Texanol-1 ranked parameter estimates

M_0 (mg.m^{-2})	k_1 (h^{-1}) (x 10^3)	EF_0 (mg.m^{-2} h^{-1})
37.3	6.5 MS	0.608
42.4 MS	8.4 MS	0.653
47.6	9.3	0.890 MS
52.9	10.0	1.02
54.4	10.6 MS	1.10
57.3	10.9	1.21
64.8 MS	11.4	1.26 MS
73.2	14.0	1.28
74.1	14.6	1.33
78.8	16.3	1.44
79.3	16.5	1.65
81.7	16.8 MS	1.72
90.4	18.0	1.98 MS
93.6	18.1	2.02
96.5 MS	18.3	2.12
103	19.0 MS	2.23
116* MS	19.4 MS	2.32
118	20.3	2.62 MS
138 MS	21.0 MS	2.73
138 MS	21.4	2.79 MS
176	22.9	2.82
190	23.0	3.23 MS
191	23.3 MS	3.48
192	25.5*	3.66 MS
202	26.0	4.03
226 MS	26.5 MS	4.09
240	26.8	4.28 MS
255 MS	34.6	4.37
304 MS	35.6	5.27 MS
305 MS	43.9	5.46 MS
332 MS	56.6 MS	8.18* MS
355*	70.5* MS	9.05*

* outliers (Dixon's *Q* test)

Table 8a. Texanol-2 parameter estimates selected [1] for the comparison

Laboratory	Run	M_0 (mg.m^{-2})	k_1 (h^{-1})	model [2]
1	1	238	0.0152	d
	2	158	0.0450	s
2	1	346	0.00883	s
	2[3]	300	0.0111	s
3	1	167	0.0213	s
	2	177	0.0174	s
4	1	91.6	0.0340	s
	2	65.7	0.0328	s
5	1	436	0.00604	d
	2	410	0.00821	d
6	1	236	0.00945	d
	2	308	0.0150	s
7	1	88.9	0.0121	d
	2	167	0.0114	s
	FLEC 1	123	0.0170	d
	FLEC 2	81.8	0.0341	s
8	1[4]	---	---	---
	2	193	0.0143	s
9	1	116	0.0383	s
	2	82.6	0.0497	s
10	1	220	0.0124	d
	2	216	0.0129	d
11	1	99.2	0.0338	s
	2[5]	---	---	---
12	1	89.6	0.0175	s
	2	115	0.0178	s
13	1	117	0.0339	s
	2	135	0.0172	d
14	1	327	0.0164	s
	2	164	0.0564	s
15	1[5]	---	---	---
	2	707	0.0234	s
16	1	80.4	0.0163	s
	2	105	0.0148	s
17[7]	1	---	---	---
	2	---	---	---
18	1[6]	67.1	0.0544	s

(1) according to minimum error and other criteria (see the section "Model calculations");
(2) d = dilution, s = sink;
(3) value reported by the laboratory (no raw data available)
(4) rejected because no concentration data was available for the first 28 hours;
(5) run failed;
(6) one run only;
(7) only the sum of Texanol-1 and Texanol-2 reported.

Table 8b. Texanol-2 ranked parameter estimates

M_0 (mg.m^{-2})	k_1 (h^{-1}) (x 10^3)	EF_0 (mg.m^{-2}.h^{-1})
65.7	6.04	1.08
67.1 MS	8.21	1.31
80.4	8.83 MS	1.55
81.8	9.45 MS	1.57
82.6	11.1 MS	1.90
88.9	11.4	2.05 MS
89.6	12.1	2.09
91.6	12.4	2.15
99.2 MS	12.9	2.23 MS
105	14.3	2.32
115 MS	14.8	2.63
116	15.0 MS	2.73
117	15.2 MS	2.76
123	16.3	2.79
135	16.4 MS	2.79
158 MS	17.0	3.06 MS
164 MS	17.2	3.08
167	17.4	3.11
167	17.5	3.33 MS
177	17.8 MS	3.35 MS
193	21.3	3.37
216	23.4 *	3.56
220	32.8	3.62 MS
236 MS	33.8 MS	3.65 MS
238 MS	33.9	3.97
300 MS	34.0	4.11
308 MS	34.1	4.44
327 MS	38.3	4.62 MS
346 MS	45.0 MS	5.36 MS
410	49.7	7.11 MS
436	54.4 MS	9.25 MS
707 *	56.4 MS	16.5 *

* outlier (Dixon's *Q* test)

Table 9. Contribution of the "between laboratory" and the "within laboratory" variances to the total variance (%)

	M_0*		k_1*		EF_0 *	
	"between"	*"within"*	*"between"*	*"within"*	*"between"*	*"within"*
2-(2-butoxyethoxy)-ethanol	60	40	not significant difference		85.8	14.2
Texanol-1	94.7	5.3	not significant difference		75.4	24.6
Texanol-2	84	16	not significant difference		not significant difference	

* The significance of the difference between the two variances is always at the 0.01 confidence level

Table 10. Mean and standard deviation of estimates (paint film thickness 50-70.6 µm)

		M_0 (mg.m^{-2})			k_1(h^{-1}) x 10^3			EF_0 (mg.m^{-2}.h^{-1})		
		mean	std. dev.	c.v. (%) [1]	mean	std. dev.	c.v. (%) [1]	mean	std. dev.	c.v. (%) [1]
2-(2-butoxyethoxy) - ethanol	FID[2]	20.6	13.6	66	85.1	54.9	65	1.61	1.44	89
	MS[3]	71.2	73.0	103	59.1	56.7	96	4.05	4.17	103
Texanol-1	FID[2]	89.9	46.7	52	21.9	10.0	46	1.90	1.09	57
	MS[3]	171	107	63	18.7*	6.72*	36	4.05	2.64	65
Texanol-2	FID[2]	127	38.0	30	23.2	11.8	51	2.75	1.04	38
	MS[3]	225*	111*	49	30.4*	19.3*	64	5.25	2.38	45

(1) Coefficient of variation: (standard deviation / mean) x 100;
(2) 13 individual values;
(3) 5 individual values except * where there are only 4 values

Table 11. Comparison between initial mass of TVOC [(1)] and the sum of the initial masses of the three individual compounds (best estimates in *Tables 6-8*)

		M_0 (mg.m^{-2})				
Lab	**Run**	*2-(2-butoxyethoxy)-ethanol*	*Texanol-1*	*Texanol-2*	*Sum*	*TVOC*
1	1	106	138	238	482	274
	2	61.1	96.5	158	316	210
2	1	56.4	332	346	734	78.7
	2	32.1	30.4	300	363	172
3	1	18.7	176	167	362	138
	2	17.5	192	177	387	125
4	1	21.1	81.7	91.6	194	142
	2	14.9	47.6	65.7	128	111
5	1	90.2	202	436	728	240
	2	144	240	410	794	374
6	1	8.2	226	236	470	175
	2	37.5	255	308	601	220
7	1	4.8	57.3	88.9	151	103
	2	15.1	93.6	167	276	9.9
	FLEC1	19.3	74.1	123	216	34.0
	FLEC2	12.1	54.4	81.8	148	140
8	1					
	2	40.4	118	193	351	212
9	1	21.3	79.3	116	217	168
	2	10.1	52.9	82.6	146	147
10	1	108	191	220	519	1068
	2	99.6	190	216	506	1056
11	1	34.3	138	99.2	272	---
	2					
12	1	12.8	37.3	89.6	140	144
	2	10.1	64.8	115	190	66.5
13	1	52.2	78.8	117	248	104
	2	33.7	90.4	135	259	221
14	1	199	305	327	831	---
	2	63.1	116	164	343	---
15	1					
	2	728	355	707	1790	653
16	1	4.8	73.2	80.4	158	---
	2	9.7	103	105	218	---
17	1					
	2					
18	1	22.1	42.4	67.1	132	---
	2					

(1) reported by the laboratories, dilution model

Table 12. Analytical comparison: concentrations found sampling from the same test chamber ($\mu g.m^{-3}$)

Laboratory	2-(2-butoxyethoxy)-ethanol		Texanol-1		Texanol-2	
	run-1	run-2	run-1	run-2	run-1	run-2
3	34.6 37.4	--- ---	1291* 1473*	784* ---	1165 1347	678* ---
5	212	92.3	581	288	886	452
6 MS	159	30.2	2483*	961*	4414*	1783*
7	160	81.6	--	157		334
8	172 36	46 < 16	397 413	157 273	688 751	324 425
9	127	41.7	454	233	663	352
11 MS	100	45.7	404	273	351	253
12	145 109	41.8 ---	454 362	202 ---	829 638	354 ---
13	77.5 75.8 87.6	--- --- ---	275 294 281	--- --- ---	403 440 419	--- --- ---
15	207	70	546	273	881	457
mean *std. dev.* *c.v. %*	116.0 59.04 50.9	51.70 24.70 47.8	405.5 101.1 24.9	232.0 53.89 23.2	727.8 299.1 41.1	368.9 70.70 19.2

* outlier (excluded from the mean)

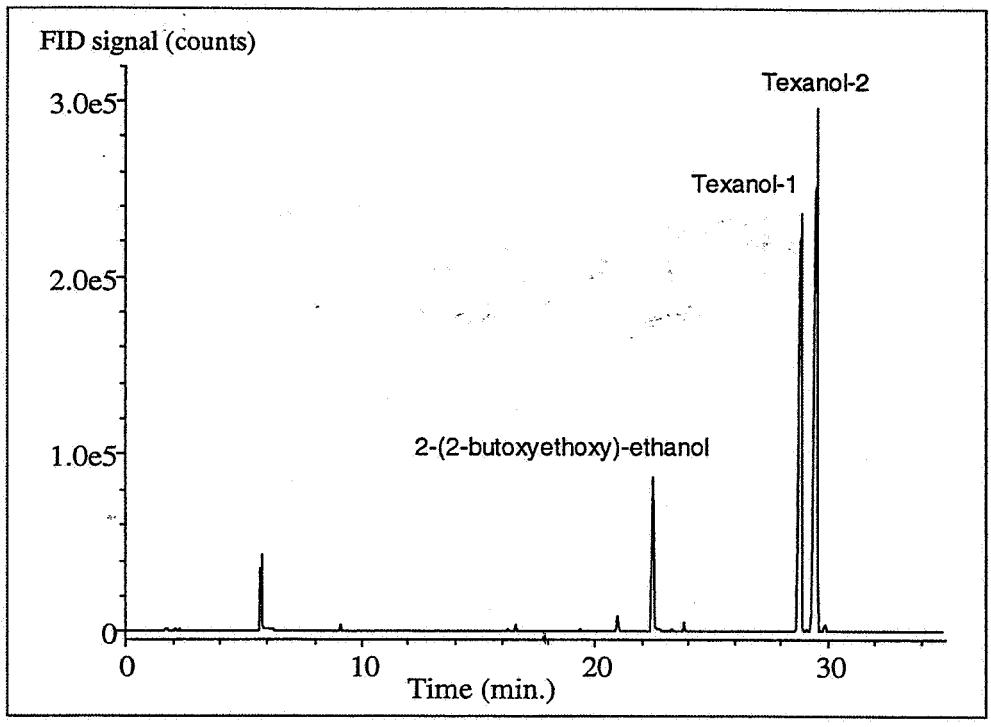

Figure 1. Gas - chromatogram of chamber air sample

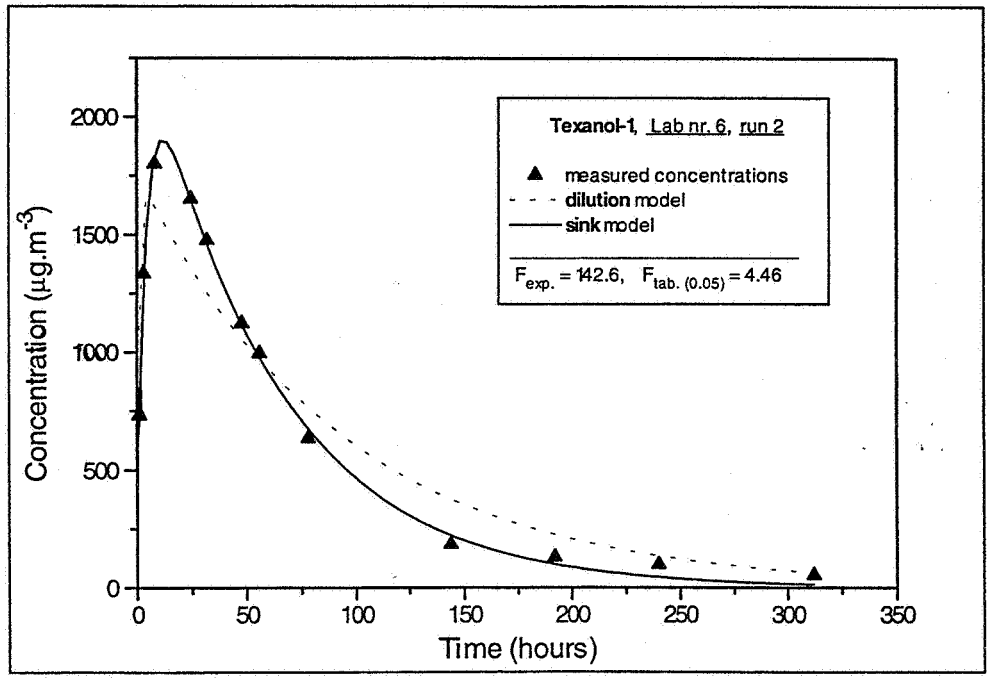

Figure 2. Concentration versus time data with model fitting

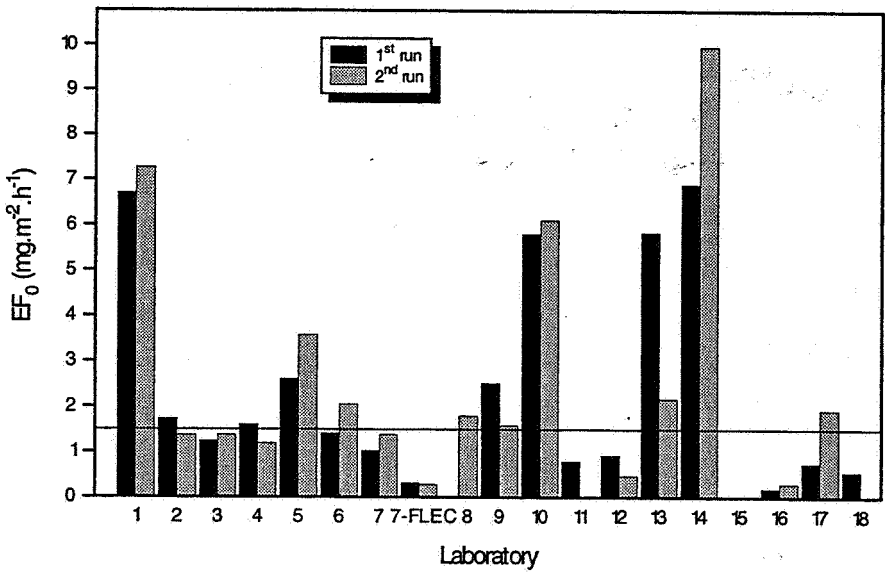

Figure 3. Individual values of EF_0 for 2-(2-butoxyethoxy)-ethanol

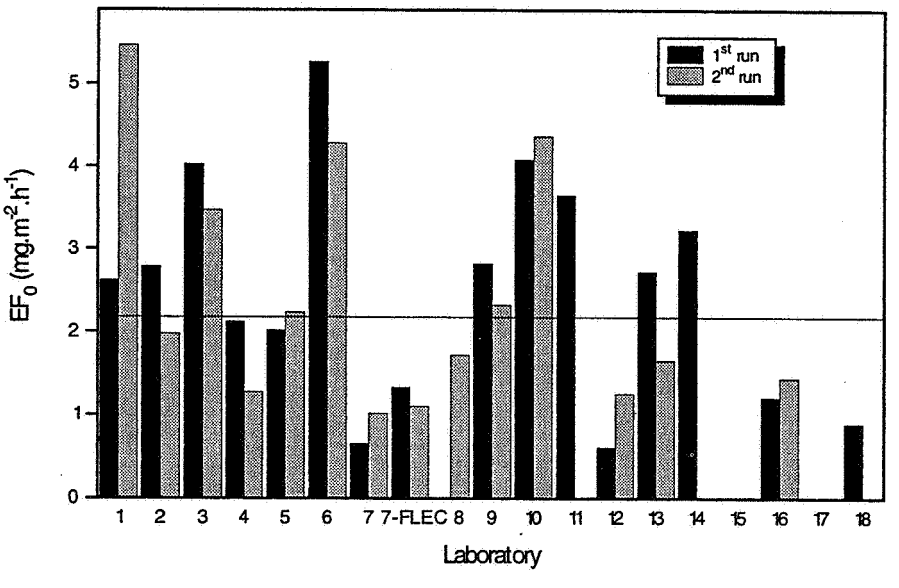

Figure 4. Individual values of EF_0 for Texanol-1

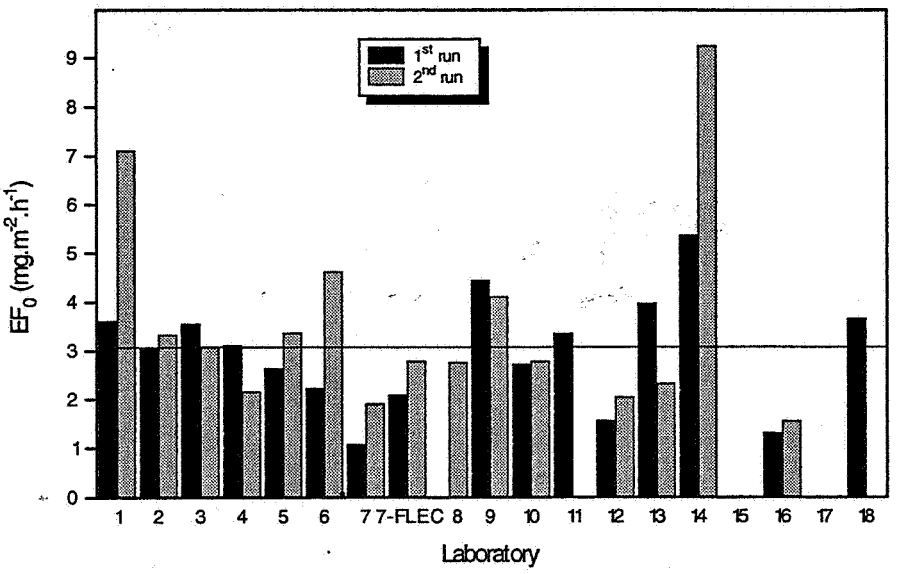

Figure 5. Individual values of EF_0 for Texanol-2

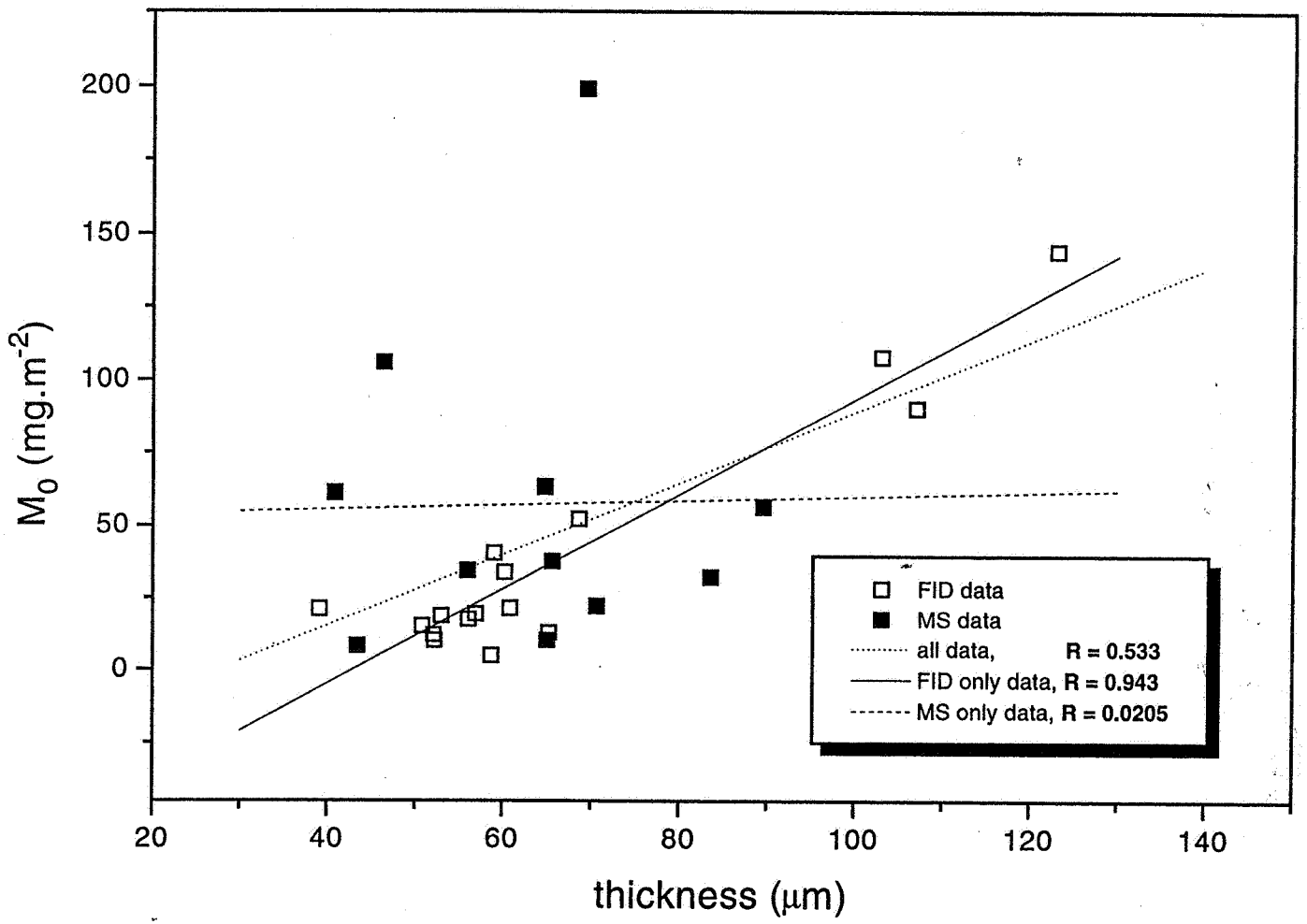

Figure 6. Effect of paint layer thickness on M_0 for 2-(2-butoxyethoxy)-ethanol

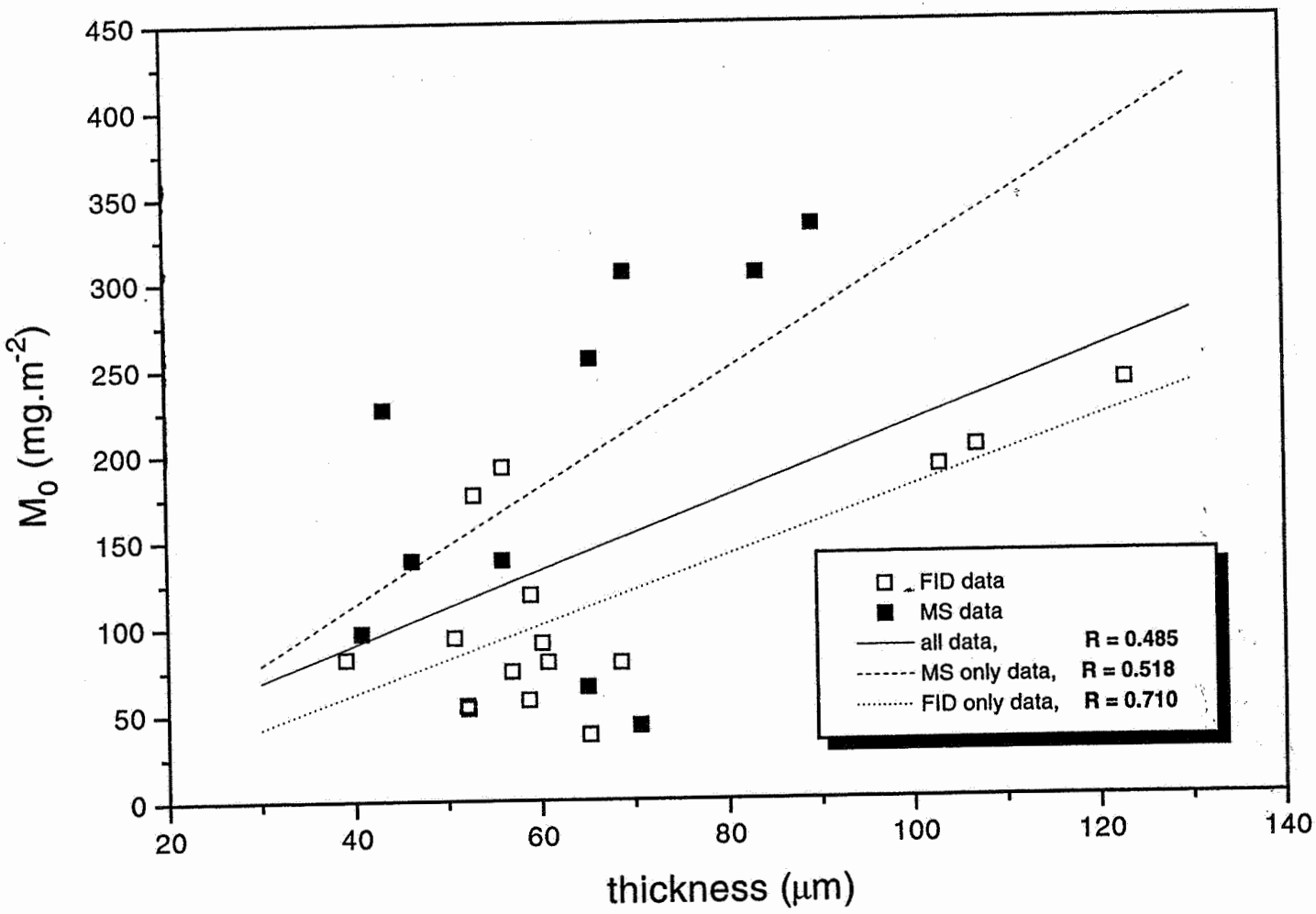

Figure 7. Effect of paint layer thickness on M_0 for Texanol-1

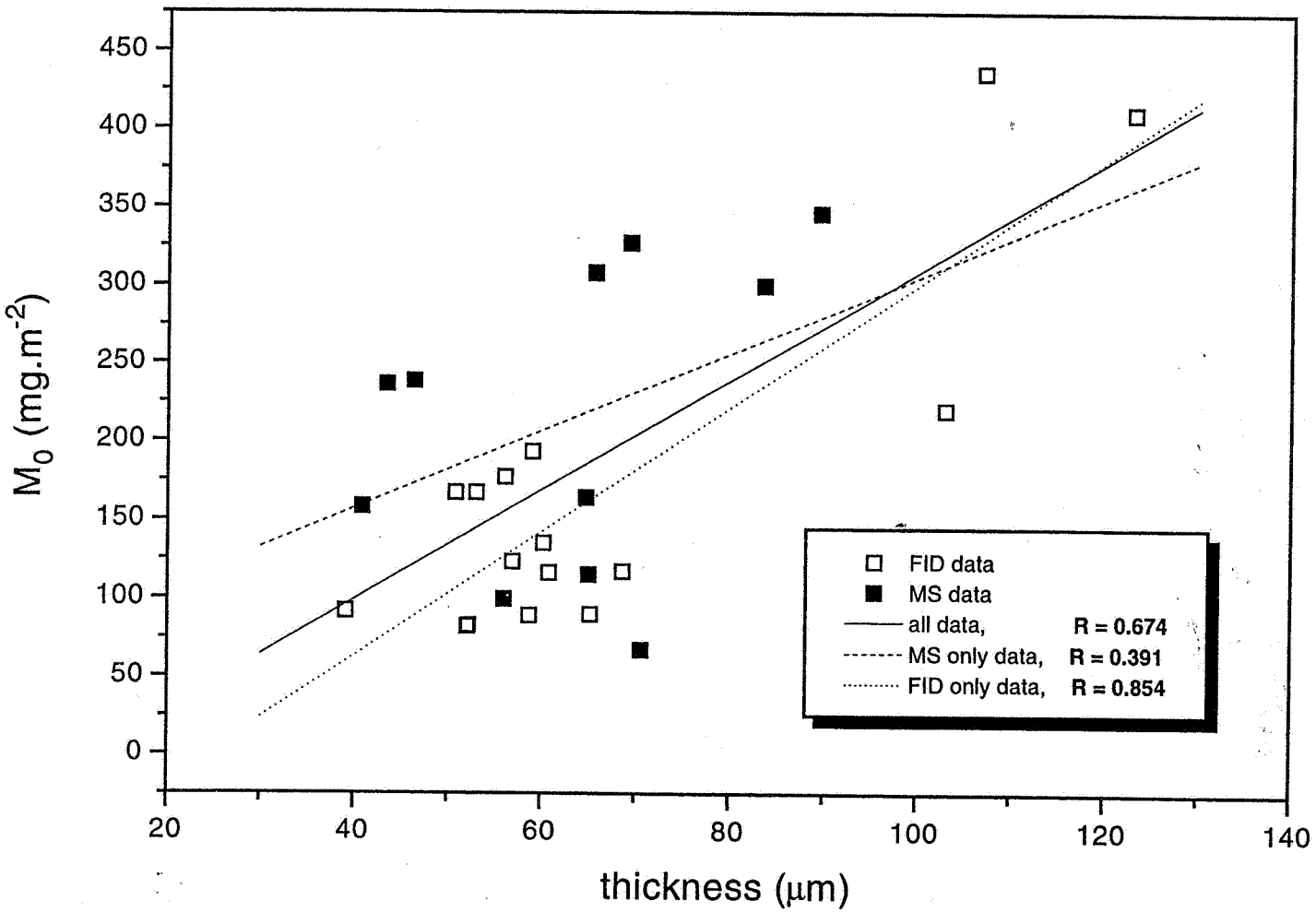

Figure 8. Effect of paint layer thickness on M_0 for Texanol-2

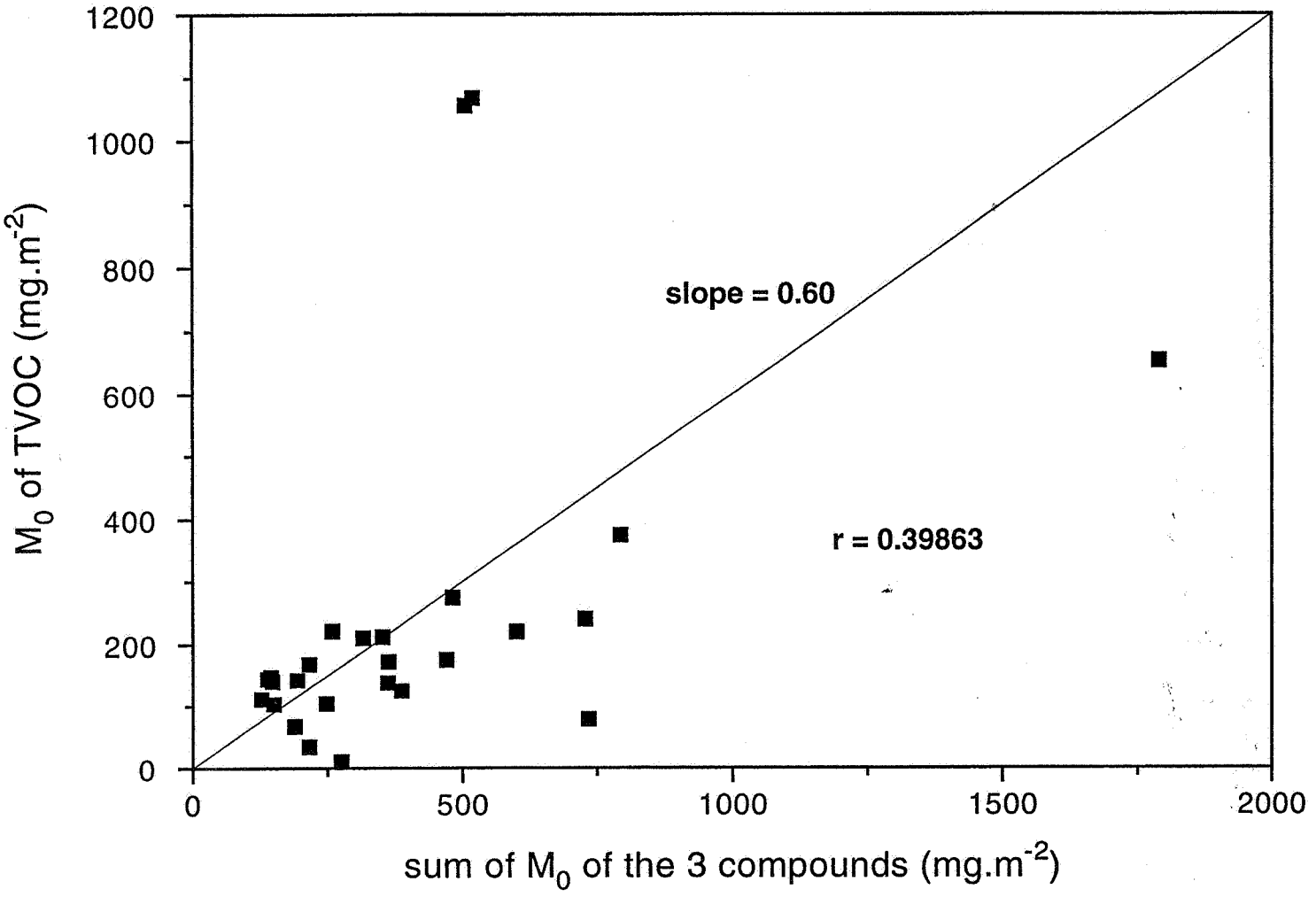

Figure 9. Correlation between initial mass of TVOC and the sum of the initial masses of the three compounds

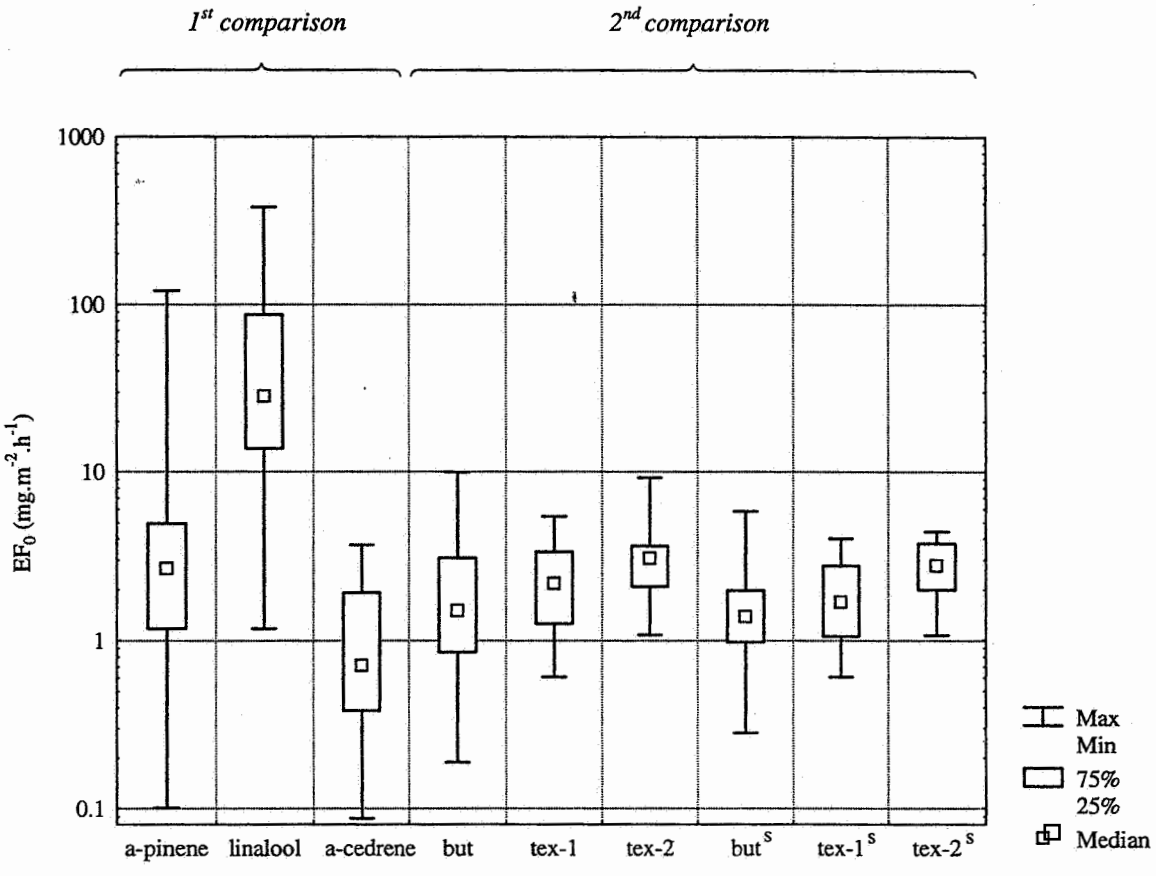

Figure 10. Distribution of the initial emission factors EF_0 in the two interlaboratory comparisons (s= distribution of selected data: FID detector only and film thickness in the range 50-70µm).

APPENDICES

APPENDIX 1

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APPENDIX 2

Paint characteristics and film thickness

The material selected for the experiment was a water-borne styrene/acrylic paint, supplied by the firm Flügger A/S, Rodovre (Denmark). The data on composition, density and dry residue obtained by the manufacturer are reported in *Table A* of this Appendix. After application, the paint becomes touchable-dry very rapidly (one hour), but full hardening takes several days.

The paint has been supplied in plastic bottles containing very reproducibly (± 1%) 450 g of paint. Two such bottles have been shipped to each participating laboratory. A test for paint homogeneity has been carried out at the JRC Environment Institute in the following way. Six out of 60 bottles have been selected at random by a Random Number Generator and a paint plate 9x38.5 cm has been prepared from each under the same conditions requested for the experiment (see *Appendix 3*). The concentration of the three target compounds emitted into the test chamber by each of the six plates was measured 3 h after introduction (when the peak concentration occurred). The concentrations of 2-(2-butoxyethoxy)ethanol were not considered because too variable; the concentrations of Texanol-1 and Texanol-2 presented a variability of 12.3% and 11.3%, respectively, in terms of coefficient of variation. After normalizing the concentrations for the plate to plate difference in the paint film thickness (see below), the two coefficients of variation became 9.7% and 8.7%, respectively. Considering all sources of variance involved, these figures indicate a very small, if any, variability from bottle to bottle, as far as the two Texanol isomers are concerned. The concentrations of the third compound, 2-(2-butoxyethoxy)-ethanol, presented a coefficient of variation of 27%.

The participants were requested to prepare the paint film employing a scraper film applicator (Erichsen GMBH & Co KG, Hemer, Germany and subsidiary companies abroad), with a recess height of 200 µm and a lenght of 90 mm, corresponding to the width of the paint stripe (see *Appendix 3*). This type of applicator has been chosen after comparison with a spiral type coater: the latter, more suited for non-rigid surfaces, yielded less uniform layers, due to the permanence in the dry layer of the thread tracks and to the frequent presence of reliefs at the ends of the stripe.

A control of the effective layer thickness and homogeneity has been carried out in two ways, after completing the emission measurements. Each participant was requested to report the weight of the dry paint layer normalized to the coated area ($mg.cm^{-2}$, see "Form n.2 Sample features" in *Appendix 3*): these data are reported in *Table 4*. It may be noticed that the values of this parameter show a high dispersion: mean and standard deviation are

18.9 and 11.6 (61%) $mg.cm^{-2}$, respectively. However, this variability is not intrinsic to the method; infact, if a single operator prepares the plates, the dispersion of the paint area density is much smaller: with the 14 plates prepared at the Environment Institute for the experiment and for the homogeneity test (see above), the mean and standard deviation of the paint area density are 10.2 and 1.57 (15%) $mg.cm^{-2}$, respectively (see *Table B*).

The second mode for controlling the effective layer thickness on the paint plates has been measuring the thickness by means of a microprocessor controlled film gauge (Erichsen Model Duo-Check ST-2). This instrument has two probes, one working on the principle of magnetic induction (for magnetic supports), the other on the principle of eddy currents (for non-magnetic metal supports). The mean thickness and standard deviation obtained through about 25 point measurements distributed at random over each coated sample received are reported in *Table 4*. Again, the dispersion obtained with the plates prepared by a single operator is much smaller and is shown in *Table B* of this Appendix.

The agreement between the weight per unit area measured by the participants and the film thickness determined by the Environmnet Institute is evidenced in the correlation in *Figure A*. The correlation coefficient is low as could be expected from the high dispersion of the weight per unit area values (see above); however, the least squares line of the correlation has a slope only 10% higher than the slope (0.225) corresponding to the dry paint density, determined by the picnometric method (2.25 $g.cm^{-3}$, see *Appendix 7*).

The thickness of two paint samples on glass supports has been determined by a mechanical material profiling instrument (Tencor Instruments) available at the Institute for Advanced Materials (JRC, Ispra). The response of the latter has been compared with that of the microprocessor film gauge by measuring with both instrument plate n.8 (see *Table B*). The result of the comparison is the following:

a. the microprocessor film gauge gave a mean thickness and standard deviation of 50.7 ± 2.0 µm;
b. the profiling instrument gave the following mean readings on two tracks (3 cm lenght, minimum and maximum in brackets): 49.7 (45-55) mm and 52.5 (48-57) mm.

The agreement is satisfactory.

Table A. Paint characteristics [1]

Constituent	Weight %
binder	9.1
propylene glycol	1.7
white spirit	0.6
Texanol	0.3
water	42.4
dry matter	45.9
TOTAL:	**100.0**

(1) by the manufacturer

Table B. Area density and thickness of the paint specimens prepared at the Environment Institute

		Thickness (μm)		
Plate no.	**Paint area density ($mg.cm^{-2}$)**	*mean*	*standard dev.*	*c.v. %*
1	11.7	63.1	9.1	14.4
2	12.3	66.6	3.8	5.7
3	12.9	55.4	3.0	5.4
4	13.1	58.1	2.3	4.0
5	9.1	48.2	5.4	11.2
6	10.0	60.0	5.5	9.2
7	9.4	49.8	8.9	17.9
8	9.4	50.7	2.0	3.9
9	9.45	53.4	5.2	9.7
10	8.88	51.8	2.6	5.0
11	9.16	51.9	3.8	7.3
12	10.0	58.8	4.3	11.0
13	8.59	47.2	5.3	11.2
14	9.16	47.8	4.9	10.3
mean:	10.2	54.5		
std. dev.:	1.57	6.03		

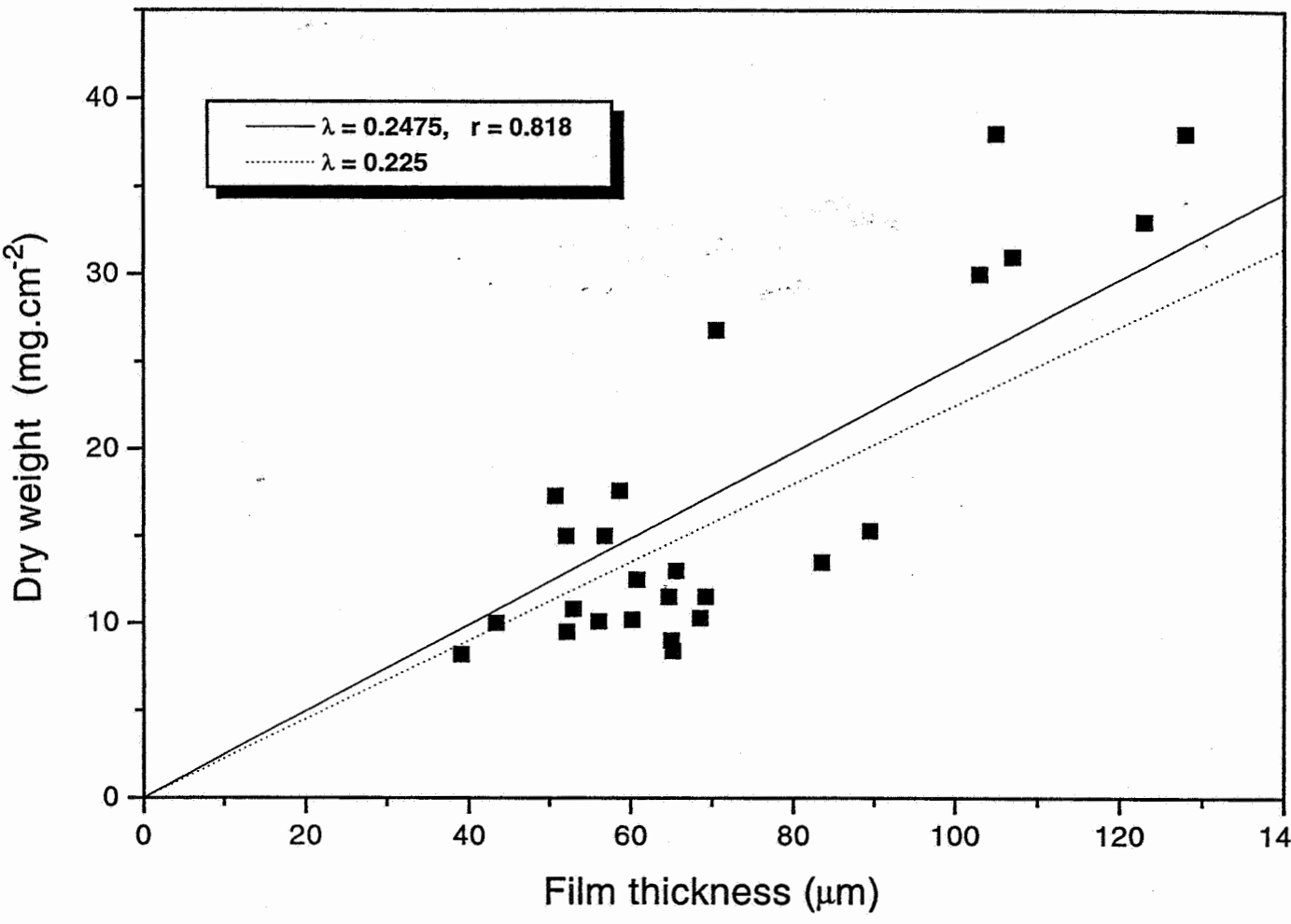

Figure A. Paint samples: Correlation between the dry weight per unit area determined by the laboratories and the film thickness determined by electronic gauge at the Environment Institute

APPENDIX 3

2nd Interlaboratory Comparison Experiment on VOC emitted from Paint

Directions given to the participants

Chamber and Analytical Methods

Describe the chamber through the attached Form no.1 and any relevant information. Describe the technique used for sampling vapours in the chamber and for the subsequent *GC* or *GC-MS* analysis, using the attached Form no.1 and any relevant additional information.

Air speed

Experience shows that air speed at the surface of an evaporating layer plays a very important role in determining the emission rate. Therefore, the air speed in the chamber should be measured: the common hot wire anemometer, with its small probe, fits the need for punctual measurements. The measurement should be performed about 1 cm above and approximately in the centre of the paint surface; the average and the range should be reported. Moreover, in order to have comparable results, air circulation/mixing in the chamber should be arranged so that the average air speed, at the point of measurement, be as close as possible to 10 $cm.s^{-1}$. The effectively measured air speed should anyhow be reported (see Form no.1): failure to do so would mean to be excluded from the experiment. Only in the case of the very small chambers (e.g., *FLEC*), may the air speed be derived from the measured air flow rate.

Paint

The amount of paint you have received is largely sufficient for training in the coating operation and for testing. Each bottle contains roughly 450 g of paint; as the wet layer will weigh about 300 $g.m^{-2}$, this amount will be sufficient to coat roughly 1.5 m^2.

It is recommended that, for training purposes, one bottle only be open and the other one be kept closed until starting the experiment and should be used therein. This paint is stable for several months; due to its water content, it should be stored at temperature >5°C.

Paint support, loading factor and coating

The material to act as support for the paint should be stainless steel or aluminium, sufficiently thick to avoid bending (consider that the larger the area the greater the risk of bending).

A loading factor of 0.5 $m^2.m^{-3}$ should be used: this will require, e.g., for the 1 m^3 chambers, a paint source of 5000 cm^2, which can be composed of e.g., 6 bands 9 x 92.6 cm. The support must be weighed (with the most sensitive balance compatible with its size) before use and the weight recorded (Form no.2).

The spreading of the paint should be carried out through the slit paint applicator already described (letter MDB of 29th October 1993), with a 200 mm slit. This is probably the most delicate operation in the whole experiment, so some preliminary training is highly recommended. Before sampling, the paint should be thoroughly stirred. After the last VOC sampling in the chamber, the plate with the dry paint layer is weighed again and the weight recorded (Form no. 2). Finally, the plate or an aliquot (e.g. 10 x 10 cm or 10 cm in diameter) should be mailed to the Environment Institute, Ispra for the film thickness determination.

Preliminary conditioning

Immediately after preparation, the paint layer should be introduced in a chamber for 24 hour conditioning, ideally under the same conditions of the experiment (see below). In particular, the air speed during this step is very important. In the case that a second chamber is not available, the conditioning may be carried out in a room with temperature and humidity as close as possible to those requested; a fan should be used to increase air speed.

Chamber conditions during the experiment

At the end of conditioning, the sample is transferred into the chamber where VOC sampling will take place: the introduction time wil be time 0. The following conditions should be maintained in this chamber:

temperature 23 ± 0.5 °C;
relative humidity 45 ± 5%;
air exchange rate 1 ± 0.05 h^{-1};
air speed 10 $cm.s^{-1}$; as specified above.

Compounds to be measured and VOC sampling

The concentration of the following compounds should be determined on each sample:

2-(2-butoxyethoxy) ethanol;
the two monoisobutyrric esters of 2.2.4-trimethyl-1.3-pentanediol;

These two isomers, in the proportion resulting from the manufacturing process, are commercially named **Texanol.** We shall name them **Texanol 1** and **Texanol 2:** the former elutes first from a non polar column, with a smaller peak area than the latter. **In addition, the concentration of TVOC should be determined: therefore an overall of four concentration values at each sampling time must be reported.** For the purpose of this experiment, TVOC is defined as the FID signal integrated between C6 and Texanol (included), converted to mass through the toluene response factor.

The solutions of the pure compounds received with the paint bottles should be used for calibration.

Sampling should be carried out at the following **times (hours) after time 0** (time of introduction into the measurement chamber): 1, 3, 8, 24, 32, 48, 56, 78, 144, 192, 240, 312. If conditioning is started on Monday (8-9 a.m.) all these sampling times fall within normal working hours. For a good determination, the air volume sampled should be increased after the first week.

Model adopted and reporting data

The diskette you have received contains software and directions to carry out the calculations following Dunn's dilution and sink models. A printed copy of the directions (*DILSINK.DOC* on the diskette) is attached herewith. Everyone has thus the possibility to derive, for each compound and for TVOC, the requested parameters, i.e., the initial mass M_0 and emission constant k_1 for the dilution model, the same two parameters and the two sink constants k_3 and k_4, for the sink model, if this is used.

However, every participant should **report data on a diskette, possibly 3.5", containing, for each compound, a file with sampling times** (including 1/2 of the sampling interval, if this is not negligible compared with elapsed time from t_0) **and concentrations** (see example in *DILSINK.DOC*). The values below the lowest measurable concentration should be reported as 0. **In addition to the diskette, please provide a print-out of the calculation results and of the plots.**

Duplicate run

A second complete run, under conditions identical to the first run (hence in the same chamber), should be carried out in order to enable the evaluation of the "*within laboratory*" variance, as distinguished from the "*between laboratory*" variance.

It is known that the target compounds may present a marked sink effect; consequently the blank in the chamber air should be determined before starting the second run and reported (Form no.2).

The results from the 1^{st} and 2^{nd} run, respectively, should be clearly labelled when reporting them.

Form no. 1 **Chamber and analytical features**

Laboratory .....

Run no. .....

Chamber

wall material .....

volume (*litres*) .....

height (*cm*) .....

width (*cm*) .....

length (*cm*) .....

measured temperature (*°C*) .....

measured RH (*%*) .....

measured air changes per hour (h^{-1}) .....

fan running: yes / no

air speed (*average*, *min.*, *max.*, $cm.s^{-1}$)* .....

.....

* at the point indicated in the directions

Sampling

adsorbent (*type* and *amount*) .....

sampling flow ($cm^3.min^{-1}$) .....

desorption (if thermal, *apparatus* and *temperature*) .....

.....

Analysis

analytical column .....

detector .....

calibration .....

.....

Form no. 2 **Sample features**

Laboratory .....

Run no. .....

Support material. .....

Support weight (g) .....

Support + paint weight (g) .....

Net paint weight (g). .....

Area effectively coated ($cm.cm$) .....

Specific weight of the film ($g.cm^{-2}$) .....

Blank concentrations in the chamber before the 2nd run:

2-(2-butoxyethoxy) ethanol ($mg.m^{-3}$). .....

Texanol isomer no. 1 ($mg.m^{-3}$). .....

Texanol isomer no. 2 ($mg.m^{-3}$). .....

APPENDIX 4

Chamber blank concentrations before the 2nd run ($\mu g.m^{-3}$)

Lab	2-2(-butoxyethoxy)-ethanol	Texanol-1	Texanol-2
1	0	0	5.3
2	< 7	< 7	6
3	2.9	19.2	17.6
4	0	0	0
5	< 1	2	5
6	0	0	0
7	2.1 9.3	5.8 1.9	7.2 2.6
8	9	1	2
9	< 1	< 1	< 1
10	< 0.1	< 0.1	< 0.1
11	*	*	*
12	0	0	0
13	0	0	0
14	33.1	14.3	16.6
15	< 10	< 10	< 10
16	0	0	0
17	20.3	12.3**	**
18	d	d	d

* below detection limit
** sum of Texanol-1 and Texanol-2
d not reported

APPENDIX 5

Summary of sampling and analysis methods used by the laboratories in the comparison experiment

Laboratory	Sampling	Desorption	GC-Column	Detector
1	Tenax	thermal, (250°C)	methyl-silicone	MS [1]
2	multibed (incl. Tenax)	thermal, (285°C)	methyl-phenyl (5%)-vinyl (1%)-silicone	MS
3	Tenax	thermal, (250°C)	methyl-phenyl-cyanopropyl-silicone	FID
4	multibed (incl. Tenax)	thermal, (250°C)	polyethene glycol	FID
5	charcoal	solvent, (CH_2Cl_2+5% CH_3OH)	methyl-silicone	FID
6	Tenax	thermal, (290°C)	methyl-silicone	MS [1]
7	Tenax	thermal, (225°C)	methyl-silicone	FID
8	charcoal	solvent, (CS_2+5% CH_3OH)	methyl-silicone	FID
9	Tenax	thermal, (250°C)	methyl-silicone	FID
10	Tenax	thermal, (?)	methyl-silicone	FID
11	charcoal	solvent (CH_2Cl_2+5% CH_3OH)	polyethene glycol	MS [1]
12	Tenax	thermal, (260°C)	polysiloxane	FID [3]
13	Tenax	thermal, (250°C)	methyl-phenyl (5%)-silicone	FID
14	Tenax	thermal, (250°C)	methyl-phenyl (5%)-vinyl (1%)-silicone	MS

Appendix 5. (cont.d)

Laboratory	Sampling	Desorption	GC-Column	Detector
15	Tenax	thermal, (250°C)	methyl-silicone	FID
16	Tenax	thermal, (250°C)	(a) methylsilicone (b) polyeth. glycol	FID
17	Tenax	thermal, (220°C)	methyl-silicone	MS [2]
18	multibed (Carbotrap)	thermal, (275°C)	methyl-phenyl (5%) - silicone	MS

(1) mass selective detector
(2) ion trap detector
(3) 1st run only, 2nd run by MS, mass selective detector

APPENDIX 6

Interlaboratory comparison on sampling and analysis

This exercise was realized on occasion of a meeting at the Environment Institute (Ispra, 26-27 January 1995) where all the European and one USA participants convened to discuss the results of the chambers experiment.

Participants in the meeting had brought at least two samplers from their laboratories. One of the samplers from each laboratory was used as blank whereas the other(s) were loaded with air from a 0.28 m^3 chamber, where paint plates had been introduced the day before, under conditions identical to those o the experiment. Pumps and flowmeters of the Environment Insitute have been used for sampling. The sum of the air flow rates to the different samplers did never account for more than 50% of the air flow rate through the chamber. The air flow was measured by integration gas meters, which had been previously controlled by the water drop and weighing technique and found accurate within 2%, with an overall standard deviation of 1.3% (n = 24). Not all samplers could be loaded simultaneously and moreover, charcoal samplers requested a much longer sampling time than Tenax and multibed samplers. Therefore, throughout the entire experiment duration, the Environment Insitute made frequent measurements of the chamber concentration which were used to correct for the concentration decay over time.

The loaded samplers along with the blank samplers were analyzed by the participants in their respective laboratories. The analytical method adopted was the same as in the experiment: the detector employed (*FID* or *MS*) is indicated in *Table 12.*

APPENDIX 7

Comparison of the initial mass M_0 (mg.m^{-2}) of Texanol found with the mass introduced in the paint formulation

Texanol in the paint is 0.3 ± 0.006 % by (wet) weight; to convert this wet weight fraction to dry weight per unit area, the values reported by the laboratories for the 18 paint samples within a narrow range of measured thickness (50-70.6 mm, see *Tables 4* and *10*) have been used. Excluding the two outliers (laboratories n. 11 and 18), the mean is 12.1 ± 2.9 (24%) mg cm^{-2} or 12.1 x 10^4 mg.m^{-2}. As the dry weight is 46% of the wet weight (see *Appendix 2, Table A*), the intial mass M_0 of the two Texanol isomers per unit area is:

$$(12.1 \times 10^4 \times 3 \times 10^{-3}) / 0.46 = 789 \text{ mg.m}^{-2}$$

A considerable fraction of this amount must have been emitted during the first 24 hour conditioning period; the mass remaining is the M_0 determined in the experiment. For example, the mean of the *FID* values reported for M_0 in *Table 10* of 217 mg.m^{-2} would correspond to a residue after 24 hours of 28 % of the initial mass per unit area (217 / 789).

The mean dry weight per unit area has been checked independently measuring the density of the dry paint (picnometer method) which is 2.25 g.cm^{-3} and multiplying this figure by 60.3 μm, mean thickness of the selected samples above: the result is 13.6 mg.cm^{-2}. If this number is used instead of 12.1, the total amount of Texanol initially present in the paint is 887 mg.m^{-2}.

APPENDIX 8

Estimate of Texanol losses during 24-hour conditioning

This investigation has been carried out employing a *FLEC*, with a loading factor of 110 $m^2.m^{-3}$ (38 cm^2 paint surface) and an air exchange rate of 170 h^{-1} (100 $cm^3.min^{-1}$). Two runs have been performed, the 1st (*FLEC 1*) following exactly the sampling scheme requested in the comparison (i.e. with the 24-hour delay after sample preparation) and the 2nd (*FLEC 2*) anticipating 23-hour, i.e., with 1-hour delay after sample preparation.

The following results were obtained (units are the same used throughout the report, the dilution model has been used):

	FLEC 1			FLEC 2		
	M_0	k_1	EF_0	M_0	k_1	EF_0
2-(2-butoxyethoxy)-ethanol	12.2	0.070	0.86	52.3	0.108	5.65
Texanol-1	59.9	0.017	1.02	68.0	0.057	3.88
Texanol-2	89.8	0.015	1.34	102	0.046	4.71

These results show that reducing the delay between sample preparation and start of measurements brings about a very large increase of M_0 and modest increase of k_1 for 2-(2-butoxyethoxy)-ethanol, whereas the opposite occurs for the two Texanol isomers. We have no explanation for this behaviour. However, the initial emission factor, EF_0, shows an increase of 6.6, 3.8 and 3.5 times, respectively for the three compounds with a trend coherent with their decreasing volatility.

In order to have a mass balance to refer to the Texanol content communicated by the manufacturer, we calculated the mass to the outlet of the chamber by means of the trapezoid rule, in the two time intervals 1-24 and 24-336 hours after sample preparation. The result is the following:

time (*h*)	Texanol-1 (μg)	Texanol-2 (μg)
1-24	193	266
24-312	148	235
1-312	341	501

It appears that 57% of Texanol-1 and 53% of Texanol-2 are lost during the period of 1-24 hours.

If this finding is applied to the Texanol initial mass reported in *Table 10*, as the mean of 13 *FID* determinations on paint samples within a narrow film thickness, i.e. 217 $mg.m^{-2}$, an initial mass of 482 $mg.m^{-2}$ (= 217/0.45) one hour after sample preparation is obtained. This is 54-61% of the initial mass derived from the Texanol recipe fraction of 0.3% (see *Appendix 7*). But a further fraction must have evaporated during the 1st hour and, what is probably more important, the air speed in the *FLEC* was much smaller than the speed to which the samples prepared for the comparison have been exposed during the 24-h conditioning period. Considering all the above, the total initial mass of Texanol reported in *Table 10, FID* detector, appears reasonably compatible with the paint composition.

APPENDIX 9

Minutes of the Meeting held on 26th - 27th January 1995
Joint Research Centre, Ispra, Italy

Discussion on the experimental results

The conclusions written in the report were approved and substantially no further explanation was brought forward for the variance in the data.

Two additional pieces of information were collected during the meeting with the hope that some further understanding of the discrepancies observed could be obtained; one concerns the environmental conditions of the paint during the 24-hour drying period and a few details about the air speed measurement technique employed (see the attached table); the second concerns the technique employed for the mass spectrometry determinations in the experiment, Single Ion Monitoring (*SIM*) or Total Ion Current (*TIC*) detection (see the attached Table). However, no substantial contribution comes from the new information.

The hypothesis, put forward in the report, that a motor driven paint applicator could improve the reproducibility of the paint film seems questioned by the fact that Laboratory 14 in fact used such a device, without any evident improvement in the results (uniformity of the film and reproducibility from run to run). The topic will be investigated further, also with a view to obtaining collaboration from the paint industry.

An experiment for the comparison of the analytical performance of the laboratories was started during the meeting. Air samples from the 0.28 m^3 chamber at the Environment Institute (EI), loaded with paint samples exactly as in the test, were collected on samplers brought by the participants, but using pumps and air flow meters from the EI. The results of this exercise will be included in the final edition of the report.

The following improvements were suggested for the report. A few representative plots of concentration versus time should be included, in order to show the different fits of the dilution and sink models. The magnitude of this difference should also be reported, in some way, for every data set. Tables with the concentrations observed at selected times in the various chambers would be useful. The chamber blank values reported by the laboratories after the 1st run should also be mentioned.

The report, completed following the above guidelines, with the material provided in the meeting (graphs of M_0 versus thickness for Texanol, TVOC, etc.) and with the result of the analytical comparison will be published as soon as possible in the ECA series.

Needs and recommendations for further experiments

Sources

Emitting materials to be used for comparison exercises should be selected that require less skill in their preparation (i.e., solid materials), whose homogeneity however, has to be tested. The problem of the representativity of different sample sizes (for e.g., 1 m^3 chambers and FLEC) should be considered as well.

Once a satisfactory agreement is reached with such materials, "wet" materials like paint may be tested again. In the meantime, the techniques for obtaining reproducible and uniform films should be investigated, in collaboration with industrial laboratories. The reproducibility should not only concern the physical properties, but also the emission rate. In particular, the automobile industry has developed the capability of preparing specimens of applied paint in sealed containers, which could be distributed. This possibility will be further explored.

Aluminium should no more be used as a support for "wet" sources, because, due to its acidic character, it could react with the material applied thereon: stainless steel and glass are recommended as equally suited supports.

The adoption of "wet" materials with a known composition or at least a known content of the target compounds is regarded as being very useful. In order to benefit from the possibility of comparing the result with the recipe data, the time between sample preparation and the start of testing should be reasonably short (e.g., 1 hour).

The adoption of realistic supports, like wood, gypsumboard, etc., is not considered important within the development of the chamber method, but only if the method has to be applied to certain purposes, e.g., predicting exposure.

Chambers

Performance criteria for physical parameters (temperature, RH, air exchange rate, air speed) should be established, based on what is realistically attainable. A particular investigation is needed for air speed, concerning its measurement and its impact on emission rate; a special chamber design could turn out to be requested. Adequate recording of the physical parameters during material testing should be provided.

Sink effects in chambers should be characterized before starting emission measurements in interlaboratory exercises, by measuring the recovery of selected

compounds at appropriate concentrations. This also has to take into account any effect due to additional surfaces present in the chambers (like diffusers, baffles, fans and supports).

Appropriate cleaning procedures for chamber walls should be defined and adopted.

An interlaboratory comparison with identical chambers (e.g. *FLEC*) could be useful in order to identify variance sources other than the chamber.

Air sampling and analysis

An appropriate Quality Control/Quality Assurance programme should be designed and followed by participants (e.g. distribution and analysis of reference solutions; sampling from the same atmosphere; duplicate samplers from material testing to be analyzed by the test laboratory and by a reference laboratory, etc.).

A preliminary analytical comparison should take place amongst those intending to participate in an interlaboratory emission experiment. This exercise should be carefully designed.

Directions on analytical methods for interlaboratory experiments, if any, should be reduced to a minimum; analysts should be free to use their preferred method, provided they demonstrate the equivalence with the one recommended.

Proposal of a project for application to the Standards, Measurements and Testing Programme of the EU Shared Cost Actions (deadline 19th April 1995)

All those present at the meeting expressed their interest in participating in such a project, though to different degrees. An interest has also been expressed by other industrial companies, in addition to those represented at the meeting.

The provisional title of the project could be "Development of a method to measure VOCs emitted from building materials and products in small test chambers". On the basis of the above mentioned needs and recommendations, the project proposal should include the following.

a. Investigations on sources

Solid materials (e.g., flooring PVC tiles, carpet): sample homogeneity, selection and size, treatment of edges. "Wet" materials (e.g., paints): preparation of uniform films with reproducible thickness; standardization of supports (e.g., stainless steel); identification of materials with known content of target compounds.

b. Investigations on chambers

Definition of QC/QA criteria for physical parameters and chemical inertness; effect of air speed on emission rate for different types of sources and chamber design; recommendations for air speed control.

c. Investigations of vapour sampling and analysis

Definition of appropriate QC/QA procedures; if necessary, selection of method(s) to be used (e.g., FID detector);

d. Interlaboratory comparisons

Intercomparisons should be carried out in succession on (i) sampling and analysis of VOCs only; (ii) homogeneous solid source; (iii) "wet" source.

The secretariat of the ECA will enquire of the person responsible of the 'Standard, Measurement and Testing Programme' about the best structure to propose for the project. The outcome of this inquiry will be immediately communicated to the participants.

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Complementary information on air speed and chamber sizes

Laboratory	Conditions during the 24-hour drying period				Air speed measurements during the testing period			Chamber sizes l x w x h (cm)
	temperature (°C)	*R.H.* (%)	*air speed* ($cm.s^{-1}$)	*air change rate* (h^{-1})	*distance* (cm)	*averaging time* (min.)	*apparatus*	
1								
2	18-23	40-60	~ 10	unknown	1	1	hot wire	50.5 x 40.6 x 24.8
3	21-23	45	10	1-1.2	1	1	SOLOMAT, hot wire	86 x 95 x 122
4	23.1	50	8	1.0	1	1	B&K 1213	50.8 x 40.7 x 25.4
5	20	20-37	~ 10	unknown	1	6	TESTO 452	60 x 60 x 50
6	22.2	49	10	~ 1	2	20	hot wire	61.5 x 50 x 30
7	23	45	10	1	2	2	hot wire	100 x 100 x 100
8	23	45	unknown	1	3	1	Bruel & Kjær 1213	100 x 100 x 100
9	23	45	10-15	1	1	1	hot wire (LSI)	110 x 60 x 43
10	23	45	unknown	1	?	?	?	80 x 40 (cylinder)
11	19-20	50	170	unknown	1.2	10	Höntzsch Exact	173 x 75 x 75
12	20 ± 1	30-35	~ 10	rel. high	1	2-3	Omni sensor, hot wire	154.5 x 63.5 x 99
13	23	45	16.2	1	< 1	3	Dantec anemometer	98.5 x 100 x 100
14	23	45	5	0.5	17	2	hot wire anemometer	130 x 77 x 100
15	23	45	30	1.0	1	1	hot wire	100 x 67 x 150
16	24	50	estimated ~ 15	unknown	2-3	1	DISA, low flow speed analyzer	30 x 50 x 75
17	23	45	10	1	1	1	Testotherm-anemometer	100 x 50 x 50
18								

Mass spectrometry technique used for the quantitative determination in the experiment

(TIC = Total Ion Current; SIM = Single Ion Monitoring; numbers indicate mass range covered)

Laboratory	2-(2-butoxyethoxy)-ethanol	Texanol-1	Texanol-2	TVOC
6	TIC, 50-500	TIC, 50-500	TIC, 50-500	TIC, 50-500
11	TIC, 40-450	TIC, 40-450	TIC, 40-450	TIC, 40-450
14	45-300	45-300	45-300	---
17	TIC (ion trap)	TIC (ion trap)	TIC (ion trap)	---

APPENDIX 10

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European Commission

EUR 16284 – European collaborative action 'Indoor air quality and its impact on man': Determination of VOCs emitted from indoor materials and products

Second interlaboratory comparison of small chamber measurements

The Steering Committee

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The results of the first interlaboratory comparison, carried out in 1991-92 in the framework of the European collaborative Action "Indoor Air Quality and Its Impact on Man", showed unacceptable interlaboratory discrepancies in the case of a thin layer fast decreasing source. A second interlaboratory comparison was subsequently organized and, in order to improve the agreement, the design included: (1) control of the chamber air velocity; (2) control of the source layer thickness; (3) adoption of both dilution and sink mathematical models. The concentrations of 2-(2-butoxyethoxy)-ethanol and of the two Texanol isomers emitted from a water-based paint had to be determined over 13 days to derive the initial emission factor. The results of the 18 participating laboratories from 10 countries can be summarized as follows. The preparation of the paint sample contributed markedly to the variance, because of differences in the paint film thickness. The impact of the chamber itself on the results, if any, was less evident: in fact, a satisfactory agreement of the results has been obtained with chambers of widely different features (capacity range 35 cm^3 to 1.5 m^3). Despite the use of calibration solutions prepared from the same batch of pure compounds, the analysis of the compound concentrations contributed markedly to the variance, as confirmed by the results of an analytical comparison carried out in parallel with the main comparison. Model fitting has produced a reasonably good description of the data sets, apparently accounting also for the sink due to chamber wall adsorption. The maximun ranges of the estimated emission factors, expressed as a ratio of the highest to the smallest reported value, are 52, 9 and 9 respectively for 2-(2-butoxyethoxy)-ethanol, Texanol-1 and Texanol-2; however, the scattering is markedly reduced if only results obtained with the same GC detector (*FID*) and from paint samples within a narrow thickness range (50.8-70.6 μm) are considered.

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