

CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS FROM CONSTRUCTION PRODUCTS

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ABSTRACT

Non negligible amounts of organic vapors are released into indoor air from a variety of decorating and building materials. Exposure to these products may have long-term health effects ranging from discomfort to illness. Little data now exist concerning health risks as well as characterization of the products themselves. This is partly due to the complexity of the problem : variability of emitted compounds in space and time along with low concentration levels.

Cleaner indoor air can be obtained by reducing vapor sources and optimizing ventilation systems. Many architects, designers, building owners and tenants may now wish to control indoor air quality (IAQ) through a careful choice of materials used in building and decorating.

Environmental chamber technology in conjunction with harmonized protocols have been developed for accurately characterize the emission of volatile organic compounds from building related materials.

Three kind of chamber experiments including solid and wet material testings have been performed in a 1 m³ environmental chamber following the european guideline. Chemical identification of the compounds, emission rate calculation and time variation of the results are presented for each material.

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INTRODUCTION

Building related materials, consumer products and office equipments have been shown to be a major source of volatile organic compounds in non-industrial environment. About 50 to 300 volatile organic compounds are usually found in such indoor environment with concentration often higher (2 to 10 times) than those sampled in outside air. However the maximum level observed for each component is far (100 to 1000 times lower) from the occupational threshold values (TLV's) generally established in various industrial countries. Exposure to these substances is reported as showing several health effects from discomfort (odor) to more acute effects like eyes and mucous irritation (Molhave 1991) and is often discussed as a possible factor of sick building syndrome.

The first step towards controlling indoor air quality is tracking pollutants to their sources along with improving ventilation efficiency. A comprehensive IAQ evaluation of materials used in building therefore would be necessary to influence the selection of appropriate products for buildings and thus to reduce the exposure of human to toxic substances. This includes chemical emission study, mathematical modeling of the dispersion of the emitted substances and comparison of estimated indoor concentrations to available toxicological and epidemiological data.

The method for evaluating emission rate and composition of those emissions is now reasonably well developed. Insulation products, partitions, paints, wax, floor and wall covering can be tested in conditions similar to those found in offices and residential settings with the use of small emission chamber. The identification and concentration of volatile organic pollutants are determined by chemical analysis using thermal desorption/gas chromatography/mass spectrometer detector. The specific emission factors are then mathematically calculated for one or all of the components and used in indoor and exposure models to respectively predict the chemical impact of a product on the indoor air and estimate the population exposure.

The procedure has been successfully used for a test experiment on three different kinds of materials (known source, solid material and wet material). The description of the methodology and results are developed in this paper.

ENVIRONMENTAL CHAMBER TECHNOLOGY

The emission of chemical substances from materials to the air involves different mechanisms (diffusion, evaporative mass transfert) that are highly dependant on environmental parameters, on the type of the material (solid or wet material, microstructure of the material etc.) and on the substances themselves (molecular size and structure). As a result, forecasting the emission of individual chemical from a product made from several raw materials and additives is not an easy task. The methodology requires a precise control of the parameters which may have a direct effect on the results. Moreover it must provide realistic simulation of building performance, product loading and environmental exposure in order to closely estimate the IAQ impact of the material.

The need for an harmonized protocol describing the method and procedures for determining emission rates of VOC from indoor building related products in view of interlaboratory comparison has led to the developpement of international guidelines. The US Environmental Protection Agency (US EPA) has published a guide (Tichenor 1989) later on adopted as an ASTM standard (1990). In Europe, a "guideline for the characterization of volatile organic compounds emitted from indoor materials and products using small test chambers" (CEC 1991) has been developed by the working group 8 of the EC Concerted Action "Indoor Air Quality and its Impact on Man" on the basis of the US EPA work. The study presented in this paper was done following this european guideline.

Chamber testing

Environmental chamber technology has been developed for measuring the volatile organic compounds emission from building related products. Real life conditions are simulated in a 1 m³ dynamic test chamber under highly controlled environmental conditions (temperature, relative humidity, air exchange rate). Special attention is taken in minimizing chemical interaction of the chamber with the product being tested by using inert materials (electropolished stainless steel, glass or Teflon) in the purified air channel as well as in the chamber itself. The chamber testing methodology includes the control of experimental conditions such as sample collection and conditioning, loading factor (i.e. area of the product to the volume of the chamber), physical parameters (temperature, humidity, air exchange rate, internal chamber mixing) and clean air generation. The standard environmental control of the chamber is as followed :

Temperature : 23° C

Relative humidity : 45%

Air exchange rate : 1.0 h⁻¹

Sample collection

Organic compounds are collected over time from the air exiting the chamber by pulling a portion of the chamber air through a sampling glass tube filled with non specific synthetic polymer (Tenax TA). These pre cleaned sorbant tubes permit the collection and the desorption of a range of very low concentrated compounds from very light (C₃) through semi-volatile (C₁₈). The sampling rate of 0.1 liter per minute is controlled by a calibrated mass flow controller which is installed inline between the sample cartridge and the sampling pump. After the sampling, the sorbant tubes are hermetically sealed and stored inside glass tubes in a refrigerator at 4° C prior to analysis.

Sample analysis

Volatile organic compounds are thermally desorbed from the sampling cartridge at 250° C under high purity helium to a cryogenic trap cooled at - 100° C by liquid nitrogen before being flash desorbed to the capillary column of a gas chromatograph. A mass spectrometry detector is used for mass spectral identification and quantification of the compounds. Selected compounds are being seldom quantified using internal standard method. Moreover the total volatile organic compounds (TVOC) is determined for each material by multiplying toluene response factor by total area count of each chromatogram.

Emission factor

The measured chamber concentrations are mathematically related to emission factor according to the type of materials to be tested.

In the case of material with a relatively constant emission rate over the test period (i.e. solid material), the chamber concentration will reach a constant equilibrium value that can be used for the calculation of the emission factor usually expressed in micrograms of substance per m² of material surface and hour. Taking into account an ideal chamber with no sink effect (adsorption or desorption of pollutants on the chamber), this factor is :

$$EF = Q c / A \quad (1)$$

where :

EF = Emission factor, mg m⁻² h⁻¹

c = chamber concentration, mg m⁻³

Q = flow through chamber, m³ h⁻¹

A = sample area m²

For a source presenting decreasing emission rate over the test period (i.e. wet sources), chamber concentration versus time data are used to calculate the emission rate. Physical and empirical models have been developed to provide this emission factor (Dunn and Tichenor 1988, Colombo et al. 1990). Although the first type of model relies explicitly on physical effects, the empirical one is based on a mathematical description of the chamber emission phenomenon. The general empirical model developed by Colombo et al. has been used in the following study.

RESULTS AND DISCUSSION

Three different tests of increasing complexity have been performed following the CEC guideline.

Known source (dodecane)

The aim of this test was to validate the whole procedure chamber-sampling-analysis by comparing the emission rate of a single compound (pure n-dodecane solution) to the calculated emission rate determined by the weight loss of the substance in a defined time interval. Duplicate air samplings have been collected respectively 24, 48 and 72 hours after the introduction of the vial containing the substance inside the chamber. The results are presented in the Table 1.

The comparison of the n-dodecane emission rates over time as calculated from the concentrations in the chamber (measured value) and from the weight loss (expected value) shows a general discrepancy between these two values. Indeed the measured minus expected emission rates as percentage of the expected value are respectively -42%, -37% and -23 % for the three samplings. This difference could be partly explained by an adsorption of the pure substance on the wall of the chamber called as sink effect.

Moreover although the chamber concentration might have reached a constant equilibrium value before sampling, increasing concentrations are observed over the test period. This was aimed at highlighting possible reversible sink effect releasing the adsorbed substance

from the chamber's walls to the air and leading to higher concentrations over time and thus artificially increasing emission rate values.

Further test experiments with different kind of compounds would improve the knowledge of the behavior of the chamber as regards the sink effect.

Solid material

The second test concerns the characterization of a solid material (PVC tile) with a constant pollutant emission rate. The loading factor of $0.4 \text{ m}^2/\text{m}^3$ chosen for the experiment takes into consideration both the front and the back of the flooring material. The PVC tiles were placed on cleaned stainless steel support inside the chamber under environmental conditions described above. Two duplicate samples were collected after 48 and 72 hours respectively. An other run was performed with a second set of PVC tiles with a sample collection at 48 hours. An exemple of chromatogram from the chamber effluent is presented in the Figure 1.

About 30 peaks were observed in the chromatogram. The compounds identified consisted of alkanes, aromatics and phenol. The concentrations of four compounds (phenol, 1,2,4-trimethylbenzene, n-decane and n-dodecane) as well as the TVOC value have been measured (Table 2).

A good reproductibility of the analytical system is observed when comparing the duplicate samples values. Moreover the comparison of concentration and emission rate data between the two runs concerning the 48 hours sampling shows a good agreement of the results. This is representative of a good homogeneity of the material itself. Moreover a general decreasing trend of the emission factor is observed between the 48 and 72 runs.

Wet material

The third test consisted in a wet material (floor wax) which presented a decreasing emission rate over the test period. The 20 cm^3 of wax spread on a glass support represented a loading factor ($0.4 \text{ m}^2/\text{m}^3$) simulating a full coverage of the floor in a room with a 2.4 m height

ceiling. The product was then placed inside the chamber for a 24 hours experiment. Ten air samples were collected over time from the chamber and analysed following the guideline. This experiment was repeated twice.

Among the 25 components observed on chromatograms, 9 substances have been identified as toluene, a pinene, 1-phenyl ethanone, linalool, camphor, 4-methyl-1(1methyl ethyl)3-cyclohexene lol, geraniol and a cedrene. Figure 2 presents a concentration profile over time (experimental data and empirical model fitting) for both alpha pinene, geraniol and alpha cedrene . Emission factor parameters including the initial emission factor (EF_0) and the decay constant (k) are presented in Table 3 for the above compounds as well as for linalool and TVOC.

The three compounds present similar behavior as regards the concentration profile : very high concentrations after the start of the experiment followed with exponential decrease with time. Contrary to the previous experiment with solid material, most of these substances reach very rapidly (3-4 hours) low levels of concentration limiting their chemical impact on the indoor air. Moreover the experiment shows the differences in the behavior of individual compounds released in different amounts and with different time dependencies.

A large discrepancy of the data is observed between the two runs for each compound. It shows the difficulty in controlling the repeatability of the test procedure. First of all the emission of a wet product shows a high variability in the concentration and the composition of the compounds over time. As evaporation seems to be mostly involved in this kind of emission, it implies that air velocity is an important parameter that is quite difficult to controlled due to the very low values of air velocity recommended in the test procedure to simulate real conditions (around 0.4 m/sec). Moreover problems may also rise from the difficulty in controlling the conditioning methodology prior to introduce the product inside the chamber (handling and spread method, time for the sample preparation, etc.).

More experiments have to be carried out with wet products providing that a better control of the parameters that seems to influence the measure is respected.

CONCLUSION

Environmental chamber testing has been shown to be a performant method for IAQ characterization of building related materials.

The validation of the whole chamber-analytical methodology has been performed by testing a known calibrated emission source. Discrepancy between the measured and expected emission rate over the test period may be partly explained by sink phenomenon.

The testing of a constant emission source material such as PVC tiles has shown good agreement between the set of products.

As concerned the wet material, difficulties have been observed concerning the repeatability of the test. This might be due to the difficulty in controlling the whole test procedure and especially the conditioning of the wet product prior to its introduction inside the chamber.

More experimental chamber testing are to be conducted to improve the methodology that will give useful results for the evaluation of building related products as regards the chemical impact on the indoor air. Low emitting materials that minimize adverse comfort and health effects would thus be likely to be developed.

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Table 1
Results of the n-dodecane test

Run	concentration ($\mu\text{g}/\text{m}^3$)	measured emission rate ($\mu\text{g}/\text{h}$)	emission rate comparison*
24 h	35,57 40,62	34,70 39,70	- 42%
48 h	41,79	40,83	- 37%
72 h	43,32 56,13	42,30 54,80	- 23%

* measured minus expected emission rate as percentage of the expected value ($64 \mu\text{g}/\text{h}$).

Table 2
**PVC tiles test : concentrations and
emission rates at 48 and 72 hours**

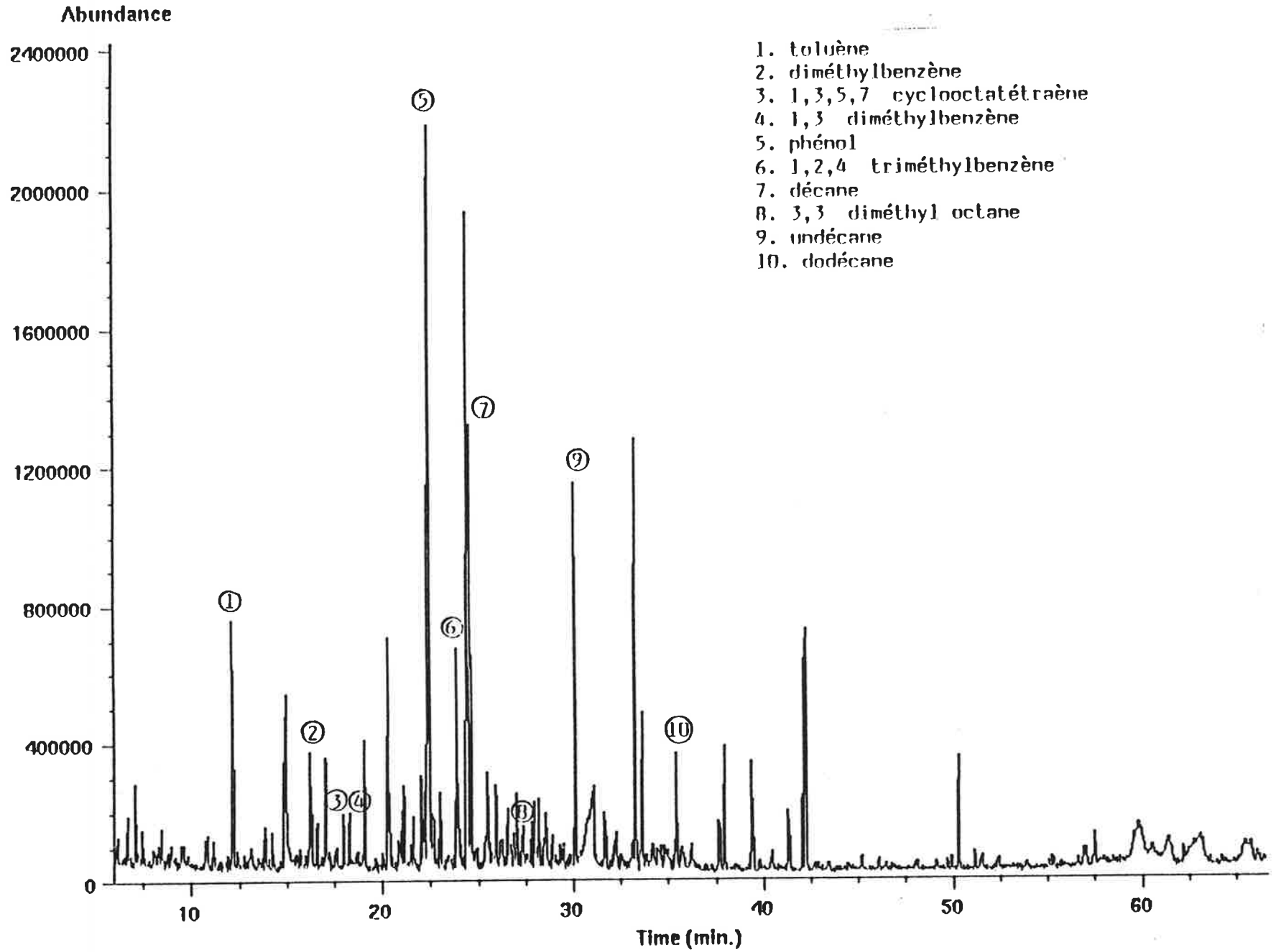
pollutants	concentration ($\mu\text{g}/\text{m}^3$)			emission rate ($\mu\text{g}/\text{h}$)		
	48 h		72 h	48 h		72 h
	run 1	run 2		run 1	run 2	
Phenol 1st sampling 2nd sampling	381	358	337	384	354,4	339,7
1,2,4-triméthylbenzène 1st sampling 2nd sampling	33,9 32,0	29 31	31,3 28,2	34,2 32,3	28,7 30,7	31,6 28,4
n-decane 1st sampling 2nd sampling	94,5 91,8	90,5 93,5	85,8 77,2	95,3 92,5	89,6 92,3	86,5 77,8
n-dodecane 1st sampling 2nd sampling	20,6 19,6	20,6 21,5	16,1 17,2	20,8 19,8	20,4 21,3	16,2 17,3
TVOC 1st sampling 2nd sampling	1 756 1 179	925 944	1 068 972	1 770 1 180	916 737	1 077 980

Table 3
**Floor wax test : summary of emission decay parameters
(initial emission rate EF_0 , decay constant k)**

pollutants	run 1		run 2	
	EF_0	k	EF_0	k
alpha pinene	1 784,2	15,06	820,25	12,13
linalool	55 429	12,44	125 895	34,14
geraniol	1 600,8	3,49	1 488,23	3,86
alpha cedrene	1 263,7	8,98	1 259,78	12,56
TVOC	14 255	0,54	152 727	12,28

Figure 1

PVC tile chromatogram

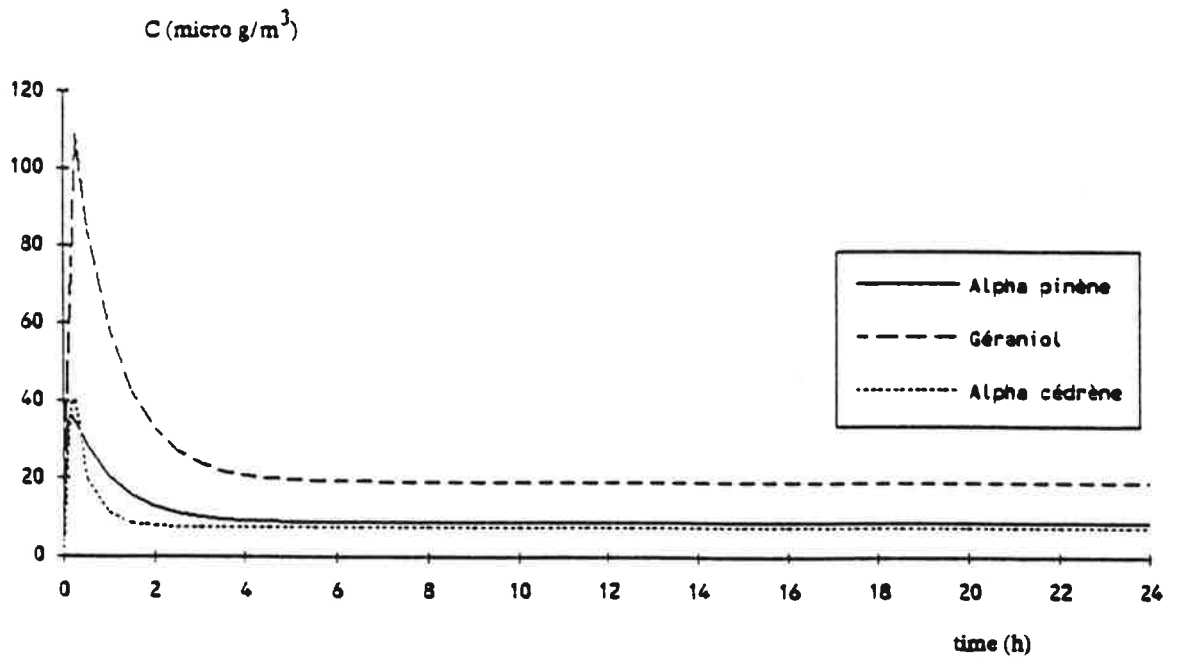


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- 1. toluène
- 2. diméthylbenzène
- 3. 1,3,5,7 cyclooctatétrène
- 4. 1,3 diméthylbenzène
- 5. phénol
- 6. 1,2,4 triméthylbenzène
- 7. décane
- 8. 3,3 diméthyl octane
- 9. undécane
- 10. dodécane

Figure 2

Fluor wax test : concentration versus time



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