Identifying and quantifying VOC emissions from Brazilian paints: methodology

K.L. Uemoto*, V. Agopyan

Department of Civil Construction Engineering, Escola Politécnica, Universidade de São Paulo, São Paulo, SP, Brazil

ABSTRACT
This paper presents the preliminary results obtained in a study aiming to investigate the environmental impact of architectural paints in Brazil and also discusses the methodology used to identify and to quantify the volatile organic compound (VOC) emissions of alkyd enamel and latex paints collected from the market. The emissions were determined by gas chromatography, via headspace sampler, coupled to mass spectrometry on liquid paint and on 'free films' with 24 and 168 h of drying time. The preliminary results obtained show that the paints contain ingredients that are detrimental to the indoor air quality and can also cause occupational health effects to workers in buildings under construction.

INDEX TERMS
Paint; VOC; Gas chromatography; Environment; Occupational health

INTRODUCTION
Building construction generates atmospheric pollution and wastes and, in the case of polymeric building materials, the emission of VOCs is a serious source of air pollution (Yu and Crump, 1998; Kasenen *et al.*, 2000; Senitkova, 2000; Tham *et al.*, 2000; Yang *et al.*, 2001). The main products used for painting buildings are latex and alkyd enamel paints. These architectural paints usually have four main constituents, the binder or resin, the inert fillers and pigments, the solvents or dispersants and, finally, additives such as stabilizers, surfactants, and thickeners to provide modifications in their properties. VOCs are ingredients present in these products that evaporate during the application and drying process, and are responsible for paint odour and emissions of solvents in the atmosphere. Almost all common solvents have a deleterious effect on the atmosphere; some, besides the environmental impact, also have neurotoxical effects on workers during painting work.

The alkyd resin paints require high levels of petroleum-based solvents and the latexes are thinned with water, but they still contain considerable amounts of VOCs constituted by products to improve freezing resistance (glycols) and film formation (coalescents). The VOC emission from paints can last 6 months after application.

The need to reduce VOC emissions has been influencing the development of new painting products, in case of more environmentally friendly paints, having lower VOCs and reduced odor. Significant changes were observed in the formulation, production and application of paints. Several technologies have successfully been adopted such as: formulation of products with high solid contents, reduction of aromatic solvents content in the paints, use of oxygenated solvents or production of powdered paints, change of solvent-based products to emulsion-based products, use of new coalescents or elimination of coalescing solvents and glycols in latex paints.

This paper presents the preliminary results obtained in a study whose objective is to investigate the environmental impact of architectural paints in Brazil. These data will allow to

* Corresponding author. E-mail: kai.uemoto@poli.usp.br

provide support to the paint manufacturer for improving their products in the optimization of paint formulations with lower environmental impact, as well as to guide designers and constructors to select less toxic products, to alert constructors, workers and consumers against the adverse health effects caused by VOCs emissions during the construction phase and indoor air during occupation.

METHODS

The VOC characterization was carried out in latexes and alkyd enamel paints collected from the consumer market of the City of São Paulo. Their basic compositions were characterized determining the nonvolatile content by drying the sample at 105°C and the pigment content drying at 450°C. The resin content was estimated through the difference between non-volatile content and pigment content.

The VOCs were analysed by gas chromatography, via headspace sampler, coupled with mass spectrometry (GC-MS) (Shimadzu HSS-4A). The GC-MS is a current technique for analysis of solvents and VOCs determination (Simonsick, 1992) and the headspace sampler is an accessory specific to determine volatile compounds. This technique is recommended in cases where the sample cannot be diluted with a solvent, as in this study (Young, 1992).

The tests were realized on liquid paint and on dry paint films with 24- and 168-h drying, maintained in a laboratory with constant temperature of 23°C and relative humidity of 50%, with normal air changes. The films were obtained applying the liquid paint on a Teflon plate with a film applicator with a nominal wet thickness of 600 μm. After each drying time, the films were separated from the Teflon plate. The VOCs emitted by the liquid paint and the films were separated in the gas chromatography column and then identified by mass spectroscopy based upon computerized library comparison searches: NIST 107, NIST 21 and WILEY 229.

Chromatographic Conditions

The operating parameters during the test are:

30 m × 0.25 mm DB-5 Column

Oven temperature: held at 60°C for 3 min, raised to 10°C/min and then raised to final temperature of 250°C/10 min

Injection volume: 0.4 ml, via headspace analysis

Sample preparation: without dilution and internal standard. Approximately 2 g in a 30 ml vial crimped with septum top and thermostated at 80°C.

RESULTS AND DISCUSSION

Table 1 shows the basic composition of a latex paint and an alkyd enamel sample of the study, chosen as an example for illustration. Table 2 shows the main VOC compounds contained in these samples determined by GC-MS technique. Figures 1 and 2 show the chromatograms of typical solvents (VOCs) emitted by the liquid paint (Figures 1a and 2a) and on dry paint films obtained after 24 h of drying time (Figures 1b and 2b) and 168 h of drying time (Figures 1c and 2c) in a controlled condition.

Table 1 Characteristics of the paints

Paint sample	Determinations			
	Total volatile content (%)	Resin content (%)	Pigments (%)	VOC (%)
Alkyd enamel	30	29	41	30
Latex	58	15	27	2

According to this analysis, the solvents of alkyd enamel paint are usually a mixture with more than 60 compounds. Latex paints emit much less VOCs than alkyd enamel paints. The identification in this study was done only on compounds with higher proportions. Some of them, in spite of their low proportion in the sample, are considered hazardous air pollutants and present toxic and irritating characteristics such as the glycol ethers, ketones, aromatic and hydrocarbons.

Dry paint films, after 24 h of drying time, in ambient with controlled conditions, show chromatograms with much lower concentrations in solvents; for alkyd enamel samples approximately 1% of VOCs and for latex paint 2.5% VOCs. The VOC content was obtained integrating the peaks of compounds with higher proportions in the chromatograms. Dry paint films, after 7 days of drying time show chromatograms with much lower concentrations in solvents; for both paints only some solvent residue is observed.

The results obtained on films with 24 h of exposure show that this period is sufficient to eliminate almost all the solvent present in the paint film. However, it is necessary to confirm this result by applying the paint onto a porous substrate normally used in building constructions to confirm these data.

The materials emission rates are usually measured in a small-scale test chamber under different environmental parameters. Most tests were carried out in glass or stainless steel chamber under controlled temperature and relative humidity, with controlled air circulation (airflow). In the present study, gas chromatography was used, via headspace sampler, coupled to mass spectrometry (GC-MS). This technique is specific for analyzing solvents and volatile compounds. The emission rates were estimated by the difference obtained between liquid paint and films with pre-fixed drying time, in controlled conditions.

The method proposed seems to be useful as a screening test. It can be used as a fast way to obtain emission databases or to develop paint formulations. The method can help paint manufacturers to improve their products as well as to guide designers to select the least toxic or non-toxic paints. The small-scale chamber test method presents more complex procedure compared to this test methodology. Besides, the chamber also has its limitations. The tests for this study must be repeated using different environmental parameters and its results correlated with the small-scale chamber test results, determined according to ASTM D 5116-97.

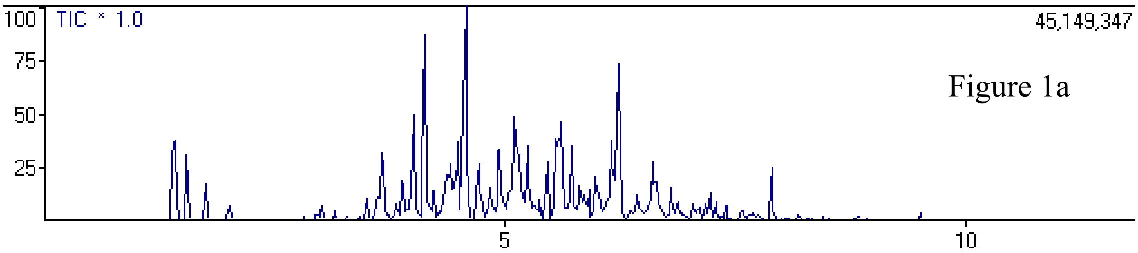

Figure 1a

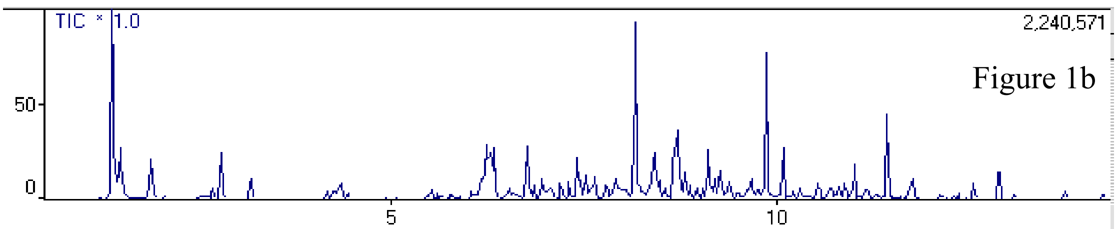

Figure 1b

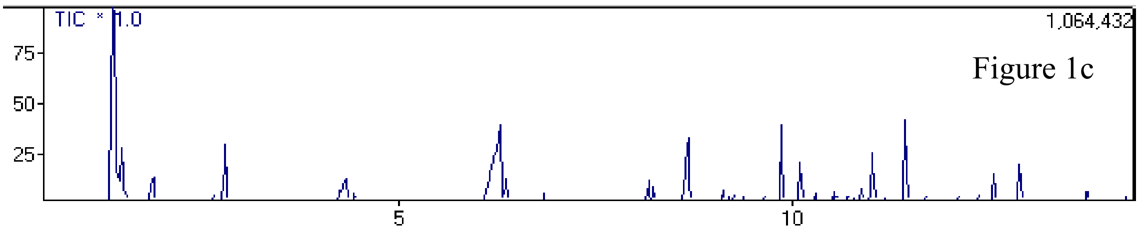

Figure 1 Chromatograms of alkyd enamel paint: (a) presents the VOCs of the liquid paint, (b) presents the VOCs of the film after 24 h of drying time and (c) presents VOCs of the film after 7 days of drying time in controlled temperature.

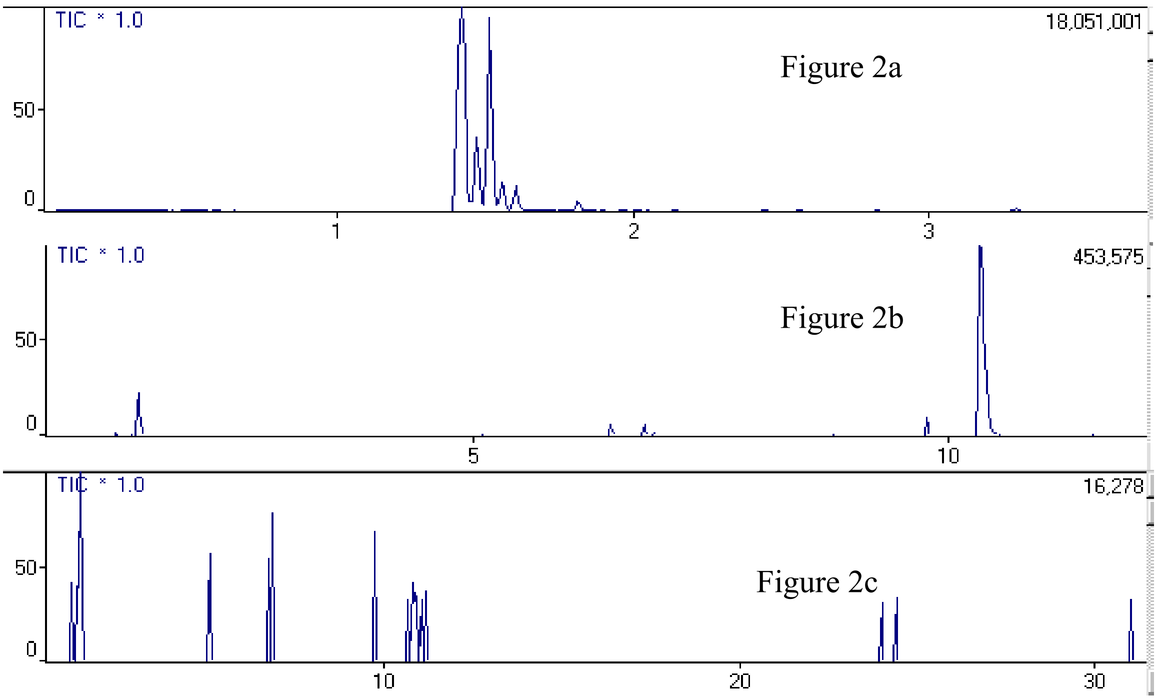

Figure 2 Chromatograms of latex paint: (a) presents the VOCs of the liquid paint, (b) presents the VOCs of the film after 24 h of drying time and (c) presents the VOCs of the film after 7 days of drying time in controlled temperature**.**

Table 2 Compounds emitted by alkyd enamel and latex paints

Paint sample	Compounds	Proportion in VOCs (%)
	2-Propanol	1.89
	2-Butanone	0.93
	Octane, 2-methyl	1.44
	Cyclohexane, ethyl	2.02
	Cyclohexane, 1,2,4 trimethyl	2.58
	Hexane, 2,3,4 trimethyl	5.75
	Benzene, (3,3 dimethylbutyl)	8.89

	o-Xylene	1.27
	Nonane	2.94
	Cyclohexane 1,1,4,4-tetrametyl	2.07
	Cyclohexane 1-ethyl, 4-methyl	3.67
	Cyclohexanepropanol	10.20
Alkyd enamel	Cyclooctane, 1,4-dimethyl	0.53
	Cyclohexane 1-ethyl, 4-methyl	1.13
	Cyclohexapropanol	3.50
	Cyclohexane, 2-methylpropyl	5.02
	1-Octanol, 2-methyl	3.62
	1-Octanol, 2-butyl	2.76
	Cyclohexane, 1,1,2,3 tetrametyl	3.79
	Octane, 3,5-dimethyl	3.02
	1-Iodo-2-methylundecane	4.11
	Benzene, 1,3,5-trimethyl	3.46
	Cyclopentane, 1,2-dimethyl-(1-methylethyl)	2.32
	Benzene, 1,2,3-trimethyl	5.34
	n-Decane	7.47
	Decane, 4-methyl	1.69
	Benzene, 1,3,5-trimethyl	1.30
	Cyclohexane, 2-methylpropyl	0.89
	Undecane	1.82
	Acetaldehyde	11.0
	Ethyl alcohol	28.7
Latex	2-Propanone	4.5
	Hydrazine	3.6
	Acetic acid ethyl ester	1.2

CONCLUSIONS

The study showed that a wide range of VOCs can be emitted by the Brazilian architectural paints, mainly for the alkyd enamel paints. These products are important sources of VOC emissions on buildings under construction besides the chance of causing adverse effects to the environment such as:

- occupational health effects to workers during construction phase;
- indoor environment leading to symptoms of ‘Sick Building Syndrome’ to occupants in freshly painted internal ambient and during the maintenance period of the building.

Several compounds emitted by the paints of the study such as butanone, cyclohexane, xylene, nonane, trimethylbenzene, etc., affect the yes, skin, the respiratory system, the central nervous system, blood, etc according to NIOSH Pocket Guide to Chemical Hazards. The results obtained from the study will help the Brazilian paint industry to develop voluntary VOC regulations and the government to adopt VOC legislation. The methodology used in the study is useful to estimate emission rates of paints and other ‘wet’ polymeric building materials.

ACKNOWLEDGEMENTS

This project was jointly supported by FINEP—Sponsor of Studies and Projects, CNPq—National Council for Scientific and Technological Development and ABRAFATI- Brazilian Paints Producers Association.

REFERENCES

ASTM (1997). ASTM D 5116-97: Standard guide for small-scale environmental chamber determination of organic emissions from indoor materials/products.

Kasenen, J.P., Villberg, K., Saarela, K., Pasanen, P. and Kalliokoski, P. (2000). Airway irritation of VOC mixtures based on the emissions of the finishing materials—PVC floorings and paints. *Proceedings of Healthy Buildings 2000*, Finland, Vol. 1, pp.101–106.

Senitkova, I. (2000). Ranking of selected indoor chemical pollutants. *Proceedings of Healthy Buildings 2000*, Finland, Vol. 1, pp. 109–114.

Simonsick, W.J., Jr. (1992). Mass spectrometric techniques for coatings characterization. analysis of paints and related materials: current techniques for solving coatings problems. *ASTM STP 1119*, pp. 105–124. Philadelphia, PA: American Society for Testing and Materials.

Tham, K.W., Sekhar, S.C., Cheong, K.W., Wong, N.H., Lee, H.K. and Amanullah, M. (2000). Identifying, quantifying and controlling VOCs in an air-conditioned office building—a Singapore case study. *Proceedings of Healthy Buildings 2000*, Finland, Vol. 1, pp. 449–454.

Yang, X., Chen, Q., Zhang, J.S., Magee, R., Zeng, J. and Shaw, C.Y. (2001). Numerical simulation of VOC emissions from dry materials. *Building and Environment* **36**, 1099–1107.

Young, F.X. (1992). Practical applications of gas chromatography in the paint and coating industry. Analysis of paints and related materials: current techniques for solving coatings problems. *ASTM STP 1119*, pp. 105–124. Philadelphia, PA: American Society for Testing and Materials.

Yu, C. and Crump, D. (1998). A review of the emission of VOCs from polymeric materials used in buildings. *Building and Environment* **33** (6), 357–374.