DEVELOPMENT AND VALIDATION OF A NOVEL SURFACE EMISSION SAMPLER FOR IN-SITU CHARACTERIZATION OF SOURCES OF INDOOR AIR POLLUTION IN NON-INDUSTRIAL MICROENVIRONMENTS

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Abstract

Similar to passive exposure to cigarette smoke, building occupants, in homes and in offices, are passively exposed to volatile organic compounds that are being emitted form surfaces of interior finishes and furnishings. Identifying emissions from surfaces of interior finishes and furnishings requires in-situ sampling. Interior finishes and furnishings used in homes and offices are many and varied. Current available methods used for sampling surface emissions from interior finishes and furnishings require the use of environmental chambers in laboratory settings. The in-situ applications of these lab-based chambers are limited. A novel method for in-situ surface emission sampling is needed. This thesis presents the development and validation of a novel surface emission sampler, the Kappa. Emissions from an interior carpet sample were captured using three different samplers, an ASTM-based chamber, a Field and Laboratory Emission Cell (FLEC) and the novel Kappa. Results were compared qualitatively and quantitatively. Based on the results obtained, the Kappa and the FLEC were comparable in their relative responses with each other and against the ASTM chamber. The Kappa, however, sampled emissions in-situ, whereas the ASTM and the FLEC sampled emissions under laboratory settings. As an in-situ surface emission sampler, the Kappa was able to estimate the contribution of an interior finish such as a carpet to indoor air pollution in real indoor conditions. The Kappa could thus provide representative, appropriate and necessary field data that are required to justify implementation of site-specific remedial action. The latter would help reduce the burden of, and occupants' exposure to emissions from interior finishes and furnishings in non-industrial microenvironments.

Résumé

De manière similaire à l'exposition passive à la fumée de cigarette, les occupants de bâtiments, maisons et bureaux, sont exposés de manière passive à des émissions provenant de produits domestiques, de finitions intérieures et des ameublements. Plusieurs de ces matériaux émettent des composés organiques volatils (VOCs). Quelques VOCs d'intérieur proviennent principalement des surfaces de finitions intérieures. L'échantillonage in situ est nécessaire pour l'identification d'émissions provenant de telles surfaces. Les finitions intérieures sont variées en grand nombre. La méthode disponible courante employée pour l'échantillonage d'émissions de surface requière surtout des chambres environnementales de laboratoire. Les applications in situ de telles chambres sont limitées. Une méthode originale pour l'échantillonage d'émissions de surface in situ est présentée. Cette thèse présente le développement et la validation d'un nouvel échantillonneur d'émissions de surface, le Kappa. Des émissions provenant d'échantillons de tapis d'intérieur ont été captées par l'entremise de trois échantillonneures d'émissions différents: une chambre à base ASTM, une cellule d'émission FLEC (Field and Laboratory Emission Cell) et le nouveau Kappa. Les émissions ont été comparées en qualité et en quantité. Selon les résultats obtenus, le Kappa et la cellule FLEC auraient des résultats comparables en opposition à ceux de la chambre à base ASTM. Par contre, le Kappa a échantillonné les émission in situ, tandis que la chambre à base ASTM et la cellule FLEC ont échantillonné les émissions selon un protocol de laboratoire. En tant qu'échantillonneur d'émissions de surface in situ, le Kappa a pu ainsi estimer la part des finitions intérieures et des ameublements dans la pollution d'air intérieure dans des conditions réelles et fournir des données expérimentales afin de justifier l' emploi d'actions réparatrices spécifiques selon le lieu, lesquels aideraient à réduire la nuisance des émission provenant de surfaces d'intérieur dans les microenvironnements intérieurs non-industriels, ainsi que l'exposition passive des occupants à celles-ci.

Table of Content

List of Figures

List of Tables

Citation Method

The citation/referencing system used in this thesis is based on the Vancouver referencing method—with an adaptation to electronic publishing. The Vancouver method, endnote numbering system, is mostly used in medical journals. The Harvard method, in-text referencing by author and date, is mostly used in engineering journals. The textual presentation style of the former may be less disruptive to flow of text and hence readability. The chronology of continuity in endnote numbering as recommended by the Chicago system is also implemented. In the classical Vancouver method, one number is reserved for a unique and specific reference. In this dissertation, and in line with the Chicago system, a new number is automatically generated in a chronological sequence for each citation as a superscript endnote format regardless of it being a new reference or a recurring one. This arrangement is used in response to the limitations associated with cross-referencing algorithm used in most word processing software during cut-and-paste, editing, and rearranging texts from one section to another. In addition, using a new reference number for each endnote facilitates back-chain referencing. Back-chain referencing is useful for a reader who wishes to trace citations from the endnote section back to the text. Furthermore, the ibid abbreviation was not used in this dissertation, favoring full citation of consecutively repeated reference. The latter arrangement avoids misplacement of references during editing operations.

Contribution of Co-authors

These are the list of publications, conference proceedings, as related to this research project. The contribution of each co-author is explicitly stated.

1) Rastan, S., Doudier, E., Haghighat, F. & Farant, J-P 2005, 'The influence of airflow and humidity on surface emissions'. Indoor Air 2005, Conference Proceedings, Beijing, China.

Soheil Rastan: Principal investigator and author.
Mr. Emmanuel Doudier (co-op student / Concordia University): Under the direction of Dr. Farant and Dr. Haghighat, and with the immediate supervision of the author, Mr. Doudier has assisted in the preparation of samples collected during the FLEC/Kappa/REM-X sampling campaign.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

2) Rastan, S., Haghighat, F. & Farant, J-P 2004, 'A palm size chamber for a do-it-your-self emission sampling of VOCs from interior finishes and furnishing in non-industrial microenvironments', CIB World Building Congress 2004, Toronto, Canada.

Soheil Rastan: Principal investigator and author.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

3) Rastan, S., Horton, A., Murray, F., Farant, J-P, & Haghighat, F 2003, 'On diffusive badges and VOC sampling in IAQ investigations', Healthy Buildings 2003, Singapore.

Soheil Rastan: The principal author
Mr. Anthony Horton (Master student / Murdoch University, Australia): Prepared Table C-1 / Appendix C, titled: *VOC concentrations in homes and offices….*
Dr. Frank Murray (Thesis Supervisor of Anthony Horton): Review of table C-1 / Appendix C.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.

4) Rastan, S., Haghighat, F. & Farant J-P 2003, 'A reference emitting materials for VOC emission testing', International Conference on QA/QC in the Field of Emission and Air Quality Measurement, Harmonization, Standardization and Accreditation , Phara, Czech Republic.

Soheil Rastan: Principal investigator and author.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

5) Rastan, S., Brodie, T., Farant, J-P. & Haghighat, F 2003, 'A comparative study between a small environmental chamber, the FLEC and the Kappa for sampling VOC emissions from a building material', Cold Climate HVAC 2003, Trondheim, Norway.

Soheil Rastan: Principal investigator and author.
Ms. Trisha Brodie (M.A.Sc student / McGill University): Under the direction of Dr. Farant and Dr. Haghighat, and with the immediate supervision of the author, Ms. Brodie has assisted in conducting sampling and chemical analysis during the carpet sampling campaign.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

6) Rastan, S., Brodie, T., Bouchard, D., Kozinski, J., Haghighat, F. & Farant, J-P 2002, 'A comparative study of the FLEC (Field and Laboratory Emission Cell) and a small environmental chamber using a novel Reference Emitting Material (REM)'. Indoor Air 2002, Monterey, California, USA.

Soheil Rastan: Principal investigator and author.
Ms. Trisha Brodie (M.A.Sc student / McGill University): Under the direction of Dr. Farant and Dr. Haghighat, and with the immediate supervision of the author, Ms. Brodie has assisted in the preparation of the sampling setup for the ASTM/FLEC REM sampling campaign.
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Dr. Januz Kozinski (Thesis advisor / McGill University): Advisory role.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

7) Rastan, S, Farant, J-P. & Haghighat, F 2000, 'A calibration device for environmental chambers', Healthy Building 2000, Helsinki, Finland.

Soheil Rastan: Principal investigator and author.
Dr. Fariborz Haghighat (Thesis supervisor / Concordia University): Supervisory role.
Dr. Jean-Piere Farant (Thesis supervisor / McGill University): Supervisory role.

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Soheil Rastan: Principal investigator and author.
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To the one who shares every atom of indoor air I breathe, to the radiance of her love that created the healthy environment in which I wrote this thesis, my wife, and to my Parents, whose love has been and will always remain unconditional, I dedicate this thesis.

"Every progress depends on two things, knowledge and practice. First acquire knowledge, and, when conviction is reached, put it into practice."

From Baha'i writings

Chapter One

Introduction

Indoor air quality studies conducted so far suggest that the quality of indoor air in non industrial indoor environments such as office buildings and homes is affecting the health of the indoor population at large.[1,2,3] Review of a number of cross-sectional and case-control studies have indicated that symptoms such as eye irritation, respiratory discomfort, headache, and feeling of lethargy are partly associated with the quality of indoor air.[4] The magnitude of each effect has been found to correlate with the time spent indoors.[5] In office buildings, the quality of indoor air was found to impact the performance and productivity of building occupants.[6] Although productivity is indeed considered a silent attribute, a construct that is difficult to measure, it nevertheless presents an untapped human capital that amounts to billions of dollars of lost resources. In office buildings alone, there are 10 times more money per square meter per year that is being spent on salaries than on heating, cooling, lighting, furnishings, cleaning and maintenance, all combined. An increase in the productivity of employees by a mere 1% produces savings that exceeds the entire operational bill of any office building.[7]

In a National Institute of Standard and Technology (NIST) study, it has been estimated that building related illnesses cost some $60 billion annually in medical expenses and lost workers productivity.[8] The results of several building investigations suggest that the materials used in buildings could act as primary and secondary sources of harmful chemical emissions.[9] Most of these materials emit volatile organic chemicals (VOCs). Over 900 VOCs have been identified in non-industrial indoor environments, including homes and offices.[10] Concentrations of VOCs in non-industrial indoor environments are several times higher than those found outdoors.[11] The US Environmental Protection Agency (EPA) has recently estimated the annual direct medical cost of non-industrial indoor exposures to indoor VOCs. Their estimate, based on some assumptions, totaled 125 million US dollars per year, which has been translated into an annual productivity loss of half-a-billion US dollars.[12] Building materials such as interior finishes and furnishings typically used in non-industrial indoor environments are considered to be one of the major sources of indoor VOCs.[13]

To place the topic of this research in the framework of occupational and population health risk assessment, it suffices to mention that a risk assessment process includes a) hazard identification, b) exposure assessment, c) dose-response assessment, and d) risk characterization. This research focuses only on the former, hazard identification. It reviews and studies the issue of VOC emissions in non-industrial microenvironments. It analyzes the current available systems to sample sources of indoor VOCs with emphasis on fleecy interior finishes and furnishings such as carpets.

In response to current limitations in the methods available to conduct VOC emission sampling from surfaces of materials and the difficulties associated with sampling VOC emissions from interior finishes in situ, the fundamental objective of this research project thus became the development of a new in-situ surface emission sampler. Named after the profile of its cell, Kappa, a novel surface emission sampler was designed, developed and validated to demonstrate a simpler, a more economical and a more practical approach to surface emission sampling. It is anticipated that the Kappa, due to its simplicity and low cost, would encourage facility managers and building owners to conduct their own in-situ emission sampling and identify the sources of the most potent indoor VOCs among the plethora of other indoor sources.

This thesis is divided into six chapters. Following this introductory chapter, the next chapter, chapter two, reviews the literature on indoor air quality with emphasis on indoor VOCs, sources and sampling methods. The chapter also examines the difficulties associated with available methods for sampling VOC emissions from interior finishes and furnishings and identifying sources of indoor air pollution. Chapter three puts forward the question statement of this research, outlines its objectives and presents the experimental setup to be used towards achieving the objectives of this research. The contents of the ensuing two chapters, chapters four and five, constitute the core of this dissertation. The methods used, the experimental setup developed and the results obtained during the course of this study are presented in these two chapters.

Parts from the contents of these two chapters, chapter four and five, are published in peer-reviewed proceedings. The first two published papers were in the proceedings of the International Academy of Indoor Air Sciences Conference (Indoor Air 1999; Edinburgh, UK) and the International Society of Indoor Air Quality and Climate Conference (Healthy Buildings 2000; Helsinki, Finland). The results obtained in these two papers have significantly contributed towards shaping and narrowing down the focus of this research. The former shed light on the challenges of sampling sources of indoor VOCs, in-situ. The latter addressed the need for an appropriate standard reference emitting material for quality control during source emission sampling. Chapter four describes the design and development of the new reference standard, the Reference Emitting Material (REM). Further manuscripts from this chapter were published in the proceedings of the International Academy of Indoor Air Sciences Conference (Indoor Air 2002; Monteray, California, USA), the International Conference on Harmonization, Standardization and Accreditation by the European Commission on Quality Control and Quality Assurance in the Field of Emission and Air Quality Measurements (QA/QC 2003; Prague, Czech Republic), and the International Academy of Indoor Air Sciences Conference (Indoor Air 2005; Beijing, China).

Chapter five presents the central theme and the key deliverable of this thesis. It outlines the development and demonstration of a novel material emission sampler named the Kappa after the profile of its inner sampling cell. The Kappa is developed to screen and identify sources of VOCs in non-industrial indoor settings. The Kappa is compared against two standard emission samplers, the ASTM-based small scale emission chamber and the European-based Field and Laboratory Emission Cell (FLEC). Emissions from both the REM and a newly installed office carpet are used to compare the three samplers. Manuscripts from this chapter are published in the proceedings of the International Conference on Cold Climate Heating, Ventilating and Air-Conditioning (Cold Climate HVAC 2003; Trondheim, Norway), the International Society of Indoor Air Quality and Climate Conference (Healthy Buildings 2003; Singapore), and the International Council for Research and Innovation in Building and Construction Conference of the *Conseil International du Bâtiment* (CIB World Building Congress 2004; Toronto, Canada). The principal elements of both the REM and the Kappa are submitted to the Office of Technology Transfer (OTT) of McGill University as Reports of Invention (ROI).

Chapter six concludes this thesis. It collates the findings of this research study, outlines its implications and presents the limitations and the lessons learned. The REM and the Kappa has so far shown promising applications and provided the answers to the question statement of this research. The deployment of the Kappa in both laboratory and field settings have demonstrated a simplified approach to in-situ emission sampling from interior finishes and furnishings. Currently the Kappa is being used for carpet emission sampling at several office buildings in Montreal and Ottawa under an innovations and solutions program of the real property services of Public Works and Government Services Canada.[14]

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Chapter Two

Literature Review

It was during the early 70's that the U.S. Environmental Protection Agency (EPA) expanded its mandate to examine the relative risk of some specific environmental problems such as environmental tobacco smoke (ETS) in indoor public places. The latter brought about the issue of indoor air quality (IAQ) in non-industrial microenvironments including office buildings and residential dwellings. In response, the committee on relative risk reduction strategies of EPA's science advisory board conducted analysis of relative environmental risks that are associated with non-industrial indoor environments. From this analysis, two resulting reports, *Unfinished Business: A Comparative Assessment of Environmental Problems*[1] and *Reducing Risk: Setting Priorities and Strategies for Environmental Protection,*[2] ranked indoor air pollution among the top five environmental risks to public health. The other top risks, depending on the region where the EPA studies were conducted, were pesticides; outdoor air toxics and particulates; radon, ozone; lead; few criteria air pollutants, radiation other than radon, and carbon monoxide. Indoor air quality risk classification was based on ecological, human health and economical factors. Excluding radon and ETS, indoor air had a combined risk category ranking of 1, which is a top combined risk rank category.[3]

The US congressional commission on risk assessment and risk management has highlighted the fact that indoor air pollution poses substantial health risk to building occupants.[4] The findings of these reports identified indoor environmental pollution as a great risk to human health.

Studies conducted by the National Institute for Occupational Safety and Health (NIOSH) of the United States, have shown that the majority of IAQ problems in non-industrial microenvironments are due to ETS, inadequate ventilation and chemical emissions from interior finishes and furnishings.[5]

2.1 Volatile Organic Compounds: Background Definition

Excluding ETS, presently there are limited data on the magnitude of air pollution in non-industrial indoor microenvironments. For the purpose of this thesis, a non-industrial indoor microenvironment includes both occupational and non-occupational settings, that is, office buildings and residential dwellings.

It has been acknowledged that indoor Volatile Organic Compounds (VOCs), and their reaction by-products are the major contributors to the perceived quality of indoor environments. VOCs are considered to be one of the prevalent pollutants in indoor air.[6] There are many groups of VOCs and there are several sampling and analytical techniques developed to sample and identify each. These techniques are not only based on the capability of the researcher, but are dependent on having appropriate laboratory tools and analytical equipments.

The EPA defines VOCs as compounds of carbon*, which actively participate in atmospheric photochemical reactions.[7] However, in the field of IAQ, most vapor-phase organic compounds are considered as VOCs, with the occasional exception of formaldehyde, which is often considered separately as a distinct sub-VOC-family of aldehydes.[8] The World Health Organization (WHO) has classified VOCs as those organic compounds with a boiling point ranging from 50°C to 260°C.[9,10] Organic indoor pollutants with lower boiling points are referred to as very volatile organic compounds (VVOC), and those with boiling points higher than 260°C are refereed to as semi-volatile organic compounds (SVOC). The above classification is based on a physical property of boiling point with some, though limited, association to chemical structures, toxicity and potency. Table 2.1 presents one of the most common classifications of VOCs.

Table 2.1: Example of VOC Classification.

Classification	**Abr.**	**Boiling Point Range**
Very Volatile Organic Compound	VVOC	< 0°C to 50-100°C
Volatile Organic Compound	VOC	50-100°C to 240-260°C
Semi-volatile Organic Compound	SVOC	240-260°C to 380-400°C
Organic Compounds associated with Particulate Organic Matter	POM	>380°C

Abr. = Abbreviation

Several other VOC classifications do exist in the literature. One of the more comprehensive classification schemes for VOCs has been suggested by Wolkoff.[11] According to Wolkoff, indoor VOCs should not be categorized. Wolkoff's no-categorization approach was due to the complex nature of indoor VOCs including their oxidation by-products. Accordingly, any classification of

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* Excluding carbon monoxide, carbon dioxide, carbonates, metallic carbides, carbonic acid, ammonium carbonate, and compounds that have negligible photochemical reaction activities.

indoor VOCs that are based on some physical or chemical properties may be limiting. Wolkoff has suggested that all VOCs, namely any gas-phase volatile organic compound within a boiling point range of 0°C to 400°C, have to be considered a VOC, regardless.[12] This definition, however, encompasses a wide range of physiochemical properties, and presents a major challenge to the study of indoor VOCs. Sampling and studying such a wide range indoor VOCs requires different sampling and analytical tools and equipments.

In many cases, especially in IAQ case studies, VOCs are discussed as members of groups. These groupings are based on similarities in chemical structure and physical properties. Although VOCs within each group may be similar in their chemical structure, each compound may have very different toxicological properties. It is important not to make a generalization about the effect of one chemical based on the knowledge of the effects of a similar chemical or a group of chemicals.

There are VOCs that can be traced to effluvia, i.e. emissions, from people, pets and plants. One well-known source of such VOCs is those produced by microorganisms. This specific class of VOCs, known as microbial VOCs (MVOCs), has generated a great interest in indoor air research dealing with microbial metabolites and their potential contribution to indoor air quality.[13] Many of these metabolites are toxic, allergenic and in some cases carcinogenic. Some MVOCs have been associated with specific respiratory diseases such as asthma, allergic rhinitis and hypersensitivity pneumonitis.[14] These microbial metabolites can be generated by molds that grow behind damp walls or carpets. Volatile metabolites can pass through various types of vapor barriers including polyethylene and vinyl floor coverings. Since sources of indoor VOCs may be from microbial as well as non-microbial origins, it is a challenge to attribute the presence of certain VOCs to their origins and sources. In a few cases, investigators have been able to distinguish between strains of Aspergillus by their VOC composition.[15] MVOCs are beyond the scope of this research, and hence no reference will be made to MVOCs in this investigation.

The concept of total VOCs (TVOC), and its appropriateness as a measure of indoor air quality is a debated topic among scientists and practitioners.[16] Grouping and reporting the total sum of VOCs as such simplifies comparison and analytical quantification. However, assessing and comparing the quality of indoor air on the basis of a TVOC value could be misleading. Since some VOCs have industrial permissible exposure levels (PELs) that are several times higher than others, a TVOC value may well mask the presence and potency of toxic VOCs from the less toxic VOCs.

In the absence of standardized non-industrial indoor PELs for VOCs, advocates of the TVOC concept claim that TVOC is a good comparative tool for, and an acceptable measure of the quality of non-industrial indoor air. There are several protocols for reporting and quantifying indoor TVOC. The European Commission (EC) has produced a guideline on reporting TVOC in indoor air.[17] The pioneering works of Molhave[18] and Seifert[19] on indoor VOCs, and the concept of TVOC as a whole, were central to the widespread use of TVOC as an indicator of indoor air quality by building practitioners. Practitioners need simple indicators to compare good air with poor air. However, there is insufficient toxicological knowledge for the many hundreds of indoor VOCs that constitute the TVOC observed. Molhave and Seifert have thus proposed to group at least the most relevant indoor VOCs into a single TVOC measure. Their proposal, which was followed by the EC, was widely scrutinized from the viewpoint of science.[20,21,22] As mentioned earlier, the use of indoor TVOC concentration as an indicator of "indoor health" is inappropriate because the potency of individual VOCs to elicit symptoms are highly variable. [23] Despite these limitations, it has been recognized that unusually high TVOC concentrations in non-industrial indoor air exceeding 1000 ug/m^3 do indicate the presence of strong indoor sources and hence a potential for adverse health effects.[24,25] Accordingly, practitioners, though simplistically, have used this 1000 ug/m^3 limit (1 mg/m^3) as an index to distinguish between good and poor indoor air quality. [26]

Table 2.2 presents a list of a mixture of 22 indoor VOCs deemed relevant by Molhave.[27,28] This mixture of indoor VOCs is dubbed by practitioners as "Molhave's mix". The selection of compounds was based on a Danish study of 39 modern dwellings.[29] These 22 compounds were the most common indoor VOCs that were predicted to be emitted by finishes and furnishings and were suspected mucous membrane irritants.[30]

The two most widely used methods of reporting TVOC are: 1) compound-specific TVOC, and 2) group-specific TVOC. The compound-specific TVOC method sums analytical responses of each specific VOC of interest for total VOC quantification. In other words, the concentration of all detected VOCs (TVOC) is reported by adding the concentration of each VOC in the mixture of interest. This entails generating a calibration curve for each VOC of interest.

Table 2.2: Molhave's 22 indoor VOC mix and their ratios.

Volatile Organic Compound	**Ratio**
1-Octane	0.01
n-Undecane	0.1
Cyclohexane	0.1
1,2,4-Trimethylbenzene	0.1
n-Propylbenzene	0.1
n-Pentanal	0.1
Iso-propanol	0.1
2-Butanone	0.1
3-Methyl-3-butanone	0.1
4-Methyle-2-pentanone	0.1
n-Hexane	1
n-Nonane	1
n-Decane	1
1-Decane	1
Ethylbenzene	1
alpha-Pinene	1
n-Hexanal	1
n-Butanol	1
Ethoxyethylacetate	1
1,2-Dichlorethane	1
3-Xylene	10
n-Butylacetate	10

Group-specific TVOC, on the other hand, is calculated on the basis of the response of a single VOC. This single VOC-- most commonly Toluene --acts as the normalizing agent on behalf of the mixture. In other words, group-specific TVOC represents a simple integrated measure of indoor VOCs using a single calibration curve for one specific VOC-- as if all detected compounds were that specific VOC. There are inevitably intrinsic differences in quantification between these two methods. Other methods for reporting TVOCs use some combination of the above two methods while separately reporting the concentration of VOCs of particular health concern such as Benzene.

2.2 VOCs in Indoor Air

Studies have demonstrated that levels of several organic compounds indoors are twice to 100 times those found outdoors, depending on the VOC.[31,32,33] Excluding ETS, there are several hundred VOCs that have been found in non-industrial indoor settings, and numerous sources of such compounds have been reported.[34] There are two major sources of VOCs that contribute to the quality of indoor air, external sources and internal ones. Several IAQ studies reported data for indoor VOCs that have been traced to external sources. Example of reported external sources that contributed to indoor VOCs are emissions by nearby industrial settings, vehicles on nearby roads, parking lots and garages; exhaust from adjacent buildings; leakage from underground fuel tanks/sewers and contaminated sites such as nearby landfills.[35,36,37,38,39,40,41]

Similarly, several IAQ studies reported VOC data that are traced to internal sources. Examples of reported internal sources are HVAC systems (fans, motor oil), building materials, office and household equipment, microbial VOCs (MVOC), cleaning and maintenance products, as well as emission from occupants and their activities.[42,43,44] Emissions from interior finishes and furnishings such as carpets, curtains, painted walls, cabinets and ceiling tiles are considered a source of indoor VOCs.[45] Insecticides, circuitry in electrical equipment (e.g., TVs, computers and printers), and commonly used cleaning products (e.g., household shampoos, dishwashing detergents) as well as normal daily activities such as showering are among other reported sources of indoor VOCs.[46,47,48,49,50,51,52,53] Sources such as personal care products (skin moisturizer, perfumes and deodorants) have been found to increase the daily exposure of occupants to VOCs. It is reported that concentrations of *decamethylcyclotetrasiloxane* and *decamethylcyclopentasiloxane* are higher in buildings with high occupancy rates, more people per floor. It was found that the aforementioned VOCs are major constituents of personal deodorants.[54] Polar VOCs such as alcohols, esters, and aldehydes are major components in the composition of household products such as fabric softeners and air fresheners.[55] It is estimated that more than 3000 chemicals are used to produce fragrances and that synthetic organic chemicals constitute the vast majority of the raw materials used.[56]

Several of the referenced studies employed sophisticated analytical facilities including laboratory emission chambers to trace and find the sources of indoor

VOCs. The use of emission chambers to trace the source of indoor VOCs are necessary, especially when sources of indoor VOC emissions are many and varied. Tracing VOCs from surfaces of interior finishes and furnishings are impossible without the use of laboratory emission chambers since collecting an indoor air sample can only identify the concentration of indoor VOCs but can hardly identify the source of these VOCs. It is commonly acknowledged that indoor finishes and furnishings act as perpetual emitters of trace-level VOCs, which are effectively re-circulated, re-adsorbed and re-emitted by the action of ventilation systems in buildings.[57] This adds yet another dimension to the difficulty of disentangling the sources of VOCS that could have directly contributed to the air concentrations sampled.

The two principal factors affecting the exposure of building occupants to indoor VOCs are 1) time spent indoors and 2) exposure to indoor sources. Several indoor time-activity researchers have extensively evaluated the first factor. Their findings suggest that people spend at least 90% of their time indoors, in offices, schools, residences and other indoor settings. More detailed review on the time spent indoors will follow. However, as it pertains to the second factor, exposure to indoor sources, researchers have used the amount of indoor air inhaled to estimate personal exposure. Adults approximately consume 20 m^3 of air per day. School-age children and older people take in somewhat less, approximately 13 m^3 per day each.[58] These figures vary based on gender, health and age. These figures translate, on average, to 17 kg of indoor air per day per person.

Based on the above two factors, it has been estimated that potential exposure to VOCs from indoor sources is several orders of magnitude higher than exposure to VOCs outdoors.[59,60] Health impact of VOC exposure from inhaled indoor air depends on interrelated determinants. For example, characteristics of individuals such as sensitivity and gender contribute to the magnitude of exposure. Women are found to be more susceptible to environmental changes within their immediate environments than men. Several studies have indicated that women tend to report IAQ problems more often than men.[61,62,63]

2.3 Time Spent Indoors

Studies on time-activity patterns have indicated that the amount of time spent indoors depends on the age of occupants since older people and toddlers tend to spend more time indoors, nature of ones work, occupation, personal habits and climatic conditions. [64,65,66,67,68,69,70]

The term "time budget" is used to represent the systematic record of how time is spent by a person over a specific period of time.[71] An early survey carried out by Bevans in 1913 of the amount of time spend during leisure time is an early scientific application of the time budget method.[72] Large-scale time budget studies were conducted in United States during the 1930s.[73] Time-activity diaries of human behavior have been used since mid-1920s in several European countries. It was during the 1960's that Szalai, a Hungarian researcher, while working for the United Nations Institute for Training and Research, coordinated the first multinational time-activity study.[74]

Szalai tabulated data on approximately 25,000 people from 12 countries in Europe, the Soviet Union and the US to study and compare the time and social-activity patterns across several cultures and boundaries. This multinational study is known as the Multinational Comparative Time Budget Research Project (MCTBRP).

The MCTBRP did not collect data on potential human exposure (e.g., smoking, non-smoking) nor did it explicitly distinguish between time spent indoors and outdoors. Lack of potential exposure data and clearer indoor-outdoor classification system has signaled the need for more detailed and special-purpose activity-pattern studies that are exclusively tailored to estimating activity patterns of indoor occupants and their potential exposure to indoor pollutants. Recently, researchers from Australia, UK and Canada have collaborated to improve the classification used for human time-activity patterns during a 24-hour day.[75]

It was only as recent as 1989 that Ott, one of the pioneers in indoor exposure studies used the codes from the MCTBRP data and estimated the amount of time that people spend indoors, in-transit and outdoors. Ott concluded that employed persons in the US spend 92% of their time indoors, 6% in-transit and only 2% outdoors. His study, and many others that followed have all supported the notion that people are mainly indoor species. "In a modern society", said Ott, "total time outdoors is the most insignificant part of the day, often so small that it barely shows up in the total." [76]

Table 2.3 summarizes results from both the US National Human Activity Pattern Survey (NHAPS)[77] and the Canadian Human Activity Pattern Survey (CHAPS)[78]. The US- NHAPS was conducted as a follow-up to a California Activity Pattern Survey (CAPS).[79,80] The CAPS study was conducted by the California Air Resource Board using a probability based diary study of activity patterns of California adults (n=1762) and children (n=1200) from 1987 to 1988 and from 1989 to 1990 respectively. The NHAPS study was a two-year (1992-1994) national study (n=9386) conducted by the University of Maryland Survey Research Center using probability telephone survey of independent random samples of US households. The CHAPS is a Canadian study conducted by Health Canada and University of Ottawa (nine-month period in 1994/1995) using Computer Assisted Telephone Interviews (CATI) on a random urban population (n= 2381 households) of four cities (Toronto, Vancouver, Edmonton and Saint John, NB).

The survey confirms that people spend almost all of their time indoors. Two-thirds of ones life is in fact being spent inside a home. This fact sheds light on the significance of indoor air, the importance of monitoring its quality and its overall contribution to the health and well being of building occupants.[81, 82]

Table 2.3: Results from the US National Human Activity Pattern Survey (NHAPS – 2001) and the Canadian Human Activity Pattern Survey (CHAPS – 1997). Data Extracted and tabulated by S. Rastan.

Time Activity Pattern (%)	**US-NHAPS (n=9196)**	**Canada-CHAPS (n=2303)**
Indoors	**92.4**	**93.8**
Indoor - Home	68.7	65.7
Indoor - Work/School/Others	16.4	21.0
Indoor - Vehicle	5.5	5.4
Indoor - Bar / Restaurants	1.8	1.8
Outdoors	**7.6**	**6.1**

2.4 Exposure to Indoor VOCs

A series of studies examined associations between health outcomes such as asthma or asthma related symptoms and indoor environmental factors such as indoor VOCs. A small nested case-control study (47 cases with diagnosed asthma, 41 controls) has associated shortness of breath with the presence of carpets and indoor VOCs. Significant VOC odds ratio (OR) ranged from 4.9 (95% CI 1.1-22.8) for toluene to 9.9 (95% CI 1.7-58.8) for total VOCs.[83] A cross-sectional study reported a marginally significant association (OR = 1.5, 95% CI 1.0-2.4) between prevalence of asthma and the presence of newly painted interior surfaces in homes.[84] It has been reported that eosinophil, a type of white blood cell active in allergic diseases, concentration in blood was elevated in subjects from recently painted dwellings.[85] In a cross sectional study of 627 subject (school children age 13-14) within different schools, associations were observed between current asthma and school VOC concentrations.[86]

Although a review of IAQ epidemiology literature is beyond the scope of this research, no study, according to the author, has yet been able to directly associate non-industrial indoor VOCs exposure, other than from ETS, to a significant health outcome. However, it should be mentioned that many IAQ epidemiological studies have acknowledged the fact that non-industrial indoor environmental factors, such as temperature, humidity and ventilation rates along with VOCs could together be associated with health outcomes. Most of the findings reported in the literature make it difficult to attribute any association to VOCs alone. Because of the multiple correlation observed among exposure factors, it is not possible to clearly implicate VOCs as a causative agent for any non-industrial indoor health outcome.

The multitudes of interrelated factors in indoor environments and the complex chemistry of indoor air impede causal interpretations to a health outcome. As an attempt to adjust for some of these factors, several controlled studies have been performed. Two such studies have reported increased nasal inflammation and decreased lung function as the result of acute impacts of high level VOC exposures.[87,88] Both studies used 25,000 ug/m^3 of a VOC mixture and exposed subjects to period of time approaching 4 hours. The relevance of such acute and high exposure levels to normal day-to-day activities of building occupants is no doubt questionable. Despite these limitations, evidence from a number of studies conducted and presented during many recent international indoor air conferences (Indoor Air 1999, Healthy Buildings 2000, Indoor Air 2002 and Healthy Buildings 2003) does place the benefit of doubt to the side of the "alternative hypothesis". That is to say, current IAQ studies hypothesize the potential influence of VOC emissions from interior finishes and furnishings on the perceived air quality in non-industrial microenvironments and ultimately on the overall health and wellbeing of building occupants.[89,90]

One of the earliest health impact studies of indoor exposure to VOCs is attributed to the works of Molhave and his research group.[91,92] According to Molhave, health effects of indoor VOCs can be grouped into two main categories: 1) effects common to VOCs as a group and 2) effects common to a particular VOC.[93,94] Table 2.4 outlines a classification of health effects to indoor chemicals including those from indoor VOCs.

Table 2.4: Indoor VOCs and Health Effect Classification (Molhave et al. 1986).

Acute effects: Surface reactions in skins and tissues exposed to indoor air such as the mucous membrane in the eyes, nose and the skin on the face, neck and hands.
Sub-acute effects: Headache, drowsiness, and weak inflammatory responses.
Chronic effects: Absorption and metabolism of certain VOCs and their by-products at levels unspecified in non-industrial microenvironments.

Based on evidence from Molhave's field and experimental studies, a tentative subjective dose-response range for VOC exposure has been suggested. At total VOC (TVOC) levels below 200 ug/m^3, it has been assumed that there would be no measurable short-term health effects. At concentrations exceeding 3000 ug/m^3 odors are significant and symptoms become prevalent. In between the range of 200 ug/m^3 and 3000 ug/m^3 odor, irritation, and discomfort may cause discomfort.

Molhave refers to this "gray" exposure zone as the multi-factorial exposure range. Within this range, outcome appears as a consequence of VOC exposure if other factors such as temperature, humidity, smoking, sex and age do contribute to the etiology. At exposure levels exceeding 3000 ug/m^3, VOCs almost invariably produce symptoms, and at levels exceeding 25,000 ug/m^3 most VOCs are generally toxic.[95] Table 2.5 presents Molhave's indoor TVOC demarcations.

Table 2.5: Subjective TVOC Target Levels and Health Effects (Molhave, 1990).

Total Concentration ug/m^3	**Irritation and Discomfort**	**Exposure Range**
< 200	No Irritation or discomfort	Comfort range
200 – 3000	Irritation and discomfort possible if other exposures interact	Multi-factorial exposure range
3000 – 25000	Exposure effects and probable outcomes if other exposures interact	Discomfort range
> 25000	Additional neurotoxic effects	Toxic range

2.5 Sampling Indoor VOCs

This study focuses on one specific class of sources, namely *interior finishes and furnishings*. The terminology of "interior finishes and furnishings" is also a classification used by building practitioners in the architectural engineering and construction industry. It constitutes the contents of both, division 9 and 12 of the standard 16 divisions used by the Construction Specification Institute (CSI).* To this end, interior finishes and furnishings represent this study's "indoor VOC source of interest".

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* CSI is a national US-based Organization. The Canadian counterpart is known as Construction Specification Canada (CSC). Both use the standard 16-division format.

Researchers have found that high levels of indoor VOC concentrations could be due to emissions from newly installed interior finishes and furnishings.[96] Indoor temperature, relative humidity, and indoor ozone levels further influence emission characteristics of interior finishes and furnishings.[97,98] Ventilation rate and air exchange rate also impact emissions from interior finishes and furnishings and hence indoor VOC concentrations.[99]

When considering an approach for measuring VOCs in an indoor industrial setting, knowledge of the relevant industrial processes is available. Accordingly, VOCs can be predicted and their sources traced to the processes that generated them. Concentrations of indoor VOCs in industrial microenvironments are also, and mostly, at relatively high concentrations, parts per million (ppm) levels. For such microenvironments, there are recommended and accepted protocols for source sampling and air measurements.[100] The situation, however, in non-industrial indoor microenvironments is not as simple.

The concentration of VOCs in non-industrial indoor microenvironments such as offices and homes are at parts per billon (ppb) levels with a plethora of sources.

> From a chemical perspective, the indoor [non-industrial] environment is a reaction vessel with chemicals continually entering and exiting. Some of these chemicals can react with one another (or themselves) creating reaction products that might otherwise be absent from the indoor setting. Many resulting products are more reactive and/or irritating than their precursors.[101]

In light of the above, any approach for the measurement of VOCs in a non-industrial indoor microenvironment should consider the multi-source, wide range, and low levels of chemicals present indoors.[102,103] The many chemicals present in indoor air, their numerous sources and the varying operating and environmental conditions in non-industrial indoor environments greatly influence the levels, compositions and fluctuations of indoor VOC concentrations. Increasing the specificity and sensitivity of measurement methods by means of analytical techniques requires expensive, involved and time-consuming procedures.[104] Other means of achieving accuracy in measuring low-level, multi-source, and wide-range VOCs are indeed needed for practical measures.

Most indoor air quality investigators use industrial hygiene sampling strategies to sample indoor VOCs. These strategies, as mentioned earlier, are based on the prior knowledge of processes that predict sources. Such a prior predictive knowledge is limited and rarely available in non-industrial indoor settings.

Measurements of VOCs in non-industrial indoor environments are typically performed by using one or several of the following sampling approaches: 1) *area sampling*; 2) *source sampling*; 3) *surrogate sampling* and; 4) *personal sampling*[*]. Each of these sampling approaches requires a relevant sampling strategy and measurement method. Generally speaking, sampling approaches used for the

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[*] Personal sampling in the context of this classification refers to *breathing zone sampling* and/or *biological monitoring such as VOCs in blood samples.*

measurement of VOCs in non-industrial microenvironments are commonly based on *area sampling* using either active or passive methods. Some of these methods will be examined later. A limited number of measurement studies in non-industrial microenvironments have considered *personal sampling* as a measurement approach to trace sources of and exposures to indoor emitted VOCs.[105, 106]

Since many interior finishes and furnishings do emit VOCs, *source* sampling and *surrogate* sampling are considered appropriate approaches to trace VOC emitting sources.[107,108] *Emission sampling* is indeed a type of s*ource sampling*. Emission sampling uses environmental chambers to capture and identify surface emissions. It is a method used to estimate the contribution of an interior finish to the quality of indoor air in terms of its chemical load. Environmental chambers range in size, from small cells to full-size rooms. Due to the expenses and complexities involved in the operation of environmental chambers, Figure 2.1, source sampling is mostly performed in specialized laboratories. The only available source sampling method that is partly appropriate for field and in-situ emission sampling is the Field and Laboratory Emission Cell – FLEC, Fig. 2.2.

The FLEC is an emission sampling cell with a diameter of 150mm. It is used in combination with an active sampling pump and tube. Due to its small size and portability, the FLEC is gaining the approval of IAQ practitioners for in-situ emission sampling of VOCs from surfaces of materials such as vinyl floorings. It is considered a viable alternative to laboratory-based environmental chambers.[109]

Although the FLEC offers a practical approach to in-situ material emission sampling, its application is rather limited to few and select materials. The FLEC operates with few essential accessories such as an air supply unit. The latter partly hinders FLEC's portability. In addition, the FLEC requires a sealed sampling cell. This requirement has limited the types of materials that could be sampled in-situ. Only smooth and even interior surfaces such as vinyl flooring could be sampled with the FLEC. Sampling carpets, however, entails cutting a sample from the carpet and placing it inside a special FLEC adapter. Sampling emissions that require cutting pieces from an interior finish is not an in-situ or field sampling.

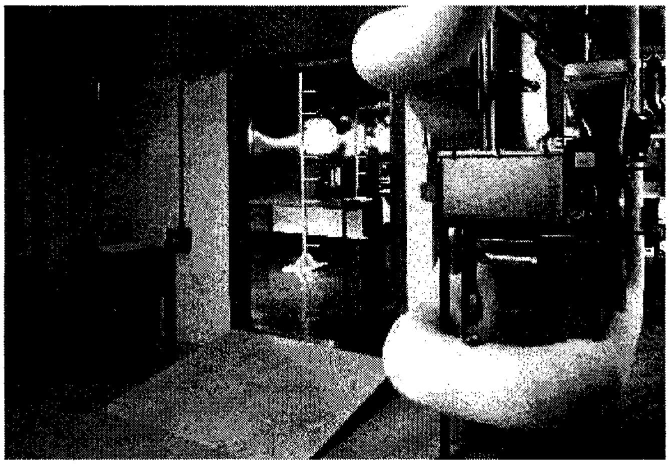

Figure 2.1: The doorway and the ramp to a large scale stainless steel chamber for sampling VOC emissions from finishes and furnishings. National Research Council of Canada
(From: www.mit.edu).

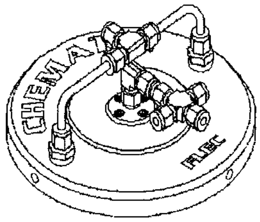

Figure 2.2: Field and Laboratory Emission Cell, FLEC
Ø 150 mm (From: www.flec.com).

Another type of *source sampling* used for the measurement of VOCs is *sensory sampling*. Many IAQ-VOC researchers have extensively studied this approach.[110,111,112,113] A trained panel of people, such as a jury, sniff the air from a specially designed and controlled environmental chamber containing samples of building materials such as carpets or painted gypsum boards and report their sensory response according to the subjective perceptions.

Surrogate sampling is yet another sampling approach to trace and measure VOC emissions from surfaces of interior finishes and furnishings. It uses a surrogate that has traced or influenced the history, the presence, the decay, and the reaction of VOCs in indoor air. Surrogates can be items, pollutants or activities. They can originate either indoors or outdoors. As an example, since it is relatively simple to collect dust in buildings, dust is a common surrogate for some VOCs. Floor dust is an ideal sink for large molecular VOCs. It offers a simple, though limited, approach for the measurement and the tracing of sources of indoor VOCs.[114,115] Dust sampling was initially used for the measurement of pesticide residues in homes. It has been reported that measuring pesticides in household dust is more practical than measuring pesticides in the indoor air.[116] Using a vacuum cleaner, collected dust could be placed inside an empty thermal desorption tube and analyzed by direct desorption.[117] Other potential surrogates such as ozone, formaldehyde, organic acids as well as personal habits, smoking and hobbies have been used as surrogates for measuring and identifying sources of indoor VOCs.[118,119]

The duration of sampling required to obtain sufficient amount of indoor generated VOCs presents a challenge for many in-situ emission sampling strategies. Sampling periods using active sampling are constrained by the type of pumps and sampling mediums used. The humming noise generated by most industrial hygiene personal sampling pumps has been an annoyance to the occupants of homes and office workers. The background noise level in non-industrial indoor settings is far below any industrial indoor environment. This makes the so called "quiet" personal sampling pumps noisy in non-industrial indoor settings such as an office or a home. As a result, passive sampling badges are being advocated for sampling VOCs in homes and offices. Notwithstanding the uncertainties associated with passive diffusive sampling including uptake rate fluctuations, air velocity dependencies, starvation effects and recovery deficiencies, practitioners and researchers alike do favor the use of passive diffusive sampling over any other sampling method due to it ease of use. Passive sampling is becoming the method of choice for the measurement of VOCs and identification of their sources. Due to their operational simplicity, ease of deployment and independence on pumps and related calibration, passive diffusive badges are becoming the standard practice for sampling air in non-industrial indoors. [120]

There are two types of passive diffusive samplers: 1) diffusive badge sampler and; 2) diffusive tube sampler. The badge is chemically desorbed and the tube is thermally desorbed. Diffusive badges tend to have higher uptake rates than the diffusive tubes. In both cases uptake rates are air velocity dependent, although the tube is less affected by air velocity due to the smaller inlet diameter. Analyses of passive diffusive badges require dilution by solvent extraction. As far as laboratory analysis is concerned, the tube is more sensitive than the badge due to the absence of solvent extraction in thermal desorption methods. It has been reported that uptake rates in passive diffusive tubes are more stable than the passive diffusive badges due to the lesser dependency of the former on air velocity.[121]

The 3M-OVM 3500 and the SKC diffusive badges are two commonly used passive badges. The Perkin-Elmer diffusive tube, on the other hand, is a passive tube that is rarely used in North America but widely used in Europe for the measurement of VOCs in non-industrial indoor environments. Diffusive uptake rates are VOC dependent, both in terms of concentration and compound. The uptake rate of the 3M passive badge varies from 21 to 48 cc/min while the uptake rate of the Perkin-Elmer's passive tube varies from 0.2 to 0.6 cc/min.[122,123] Uptake rates are controlled by the size of the sampler, the inlet diameter, the type of the membrane and the quality of the adsorber.

2.6 Measuring Indoor VOCs

The following section presents a review of a few case studies pertaining to different sampling approaches that are commonly used for the sampling of VOCs and the identification of their sources in non-industrial indoor environments. Specific reference is made to passive diffusive sampling methods, including badges and tubes, due to their prevalent use by practitioners. Reference is also made to other sampling methods including active sampling, using a sampling pump with either a chemically desorbed charcoal tube or a thermally desorbed Tenax tube.

The use of direct monitoring methods such as portable analyzers and the application of the newly designed solid-phase micro extraction (SPME) sampling method are also included in this review.

Cohen et al. (1990) investigated the performance of 3M passive badges (OVM 3500) for low levels indoor and outdoor concentrations of VOCs. The investigators used a three week sampling duration and observed deviations between – 41% to + 22% in uptake rates compared with predicted values based on chamber studies. The low and high levels of some specific VOC concentrations used for uptake rate assessment were 10 ug/m^3 and 100 ug/m^3 respectively. Their results indicate that the 3M passive sampler works best under conditions of high concentration with low RH (27%) or low concentration with high RH (73%).[124] Both of these environmental conditions are not the average conditions found in non-industrial indoor environments.

Ullrich and Nagel (1996) performed similar assessment study for the 3M passive badge OVM 3500 sampler, using much lower concentrations ranging between 1 to 20 ug/m^3. Sampling period ranged from two days to three weeks. The authors compared the passive badge with active sampling using standard charcoal tubes. They reported a mean bias ranging from + 2% to – 19% and a mean coefficient of variation ranging from 5% to 17% between passive and the active sampling.[125]

Indoor air velocity in this study was reported at 0.02 m/s. This rises a question on the technique used for measuring air velocity at a level that is almost 50% lower than the lowest detection limit of the most sensitive hot-wire air velocity transducers.[126, 127]

Crump (1999) suggested that air velocities as low as 0.007 m/s do not influence uptake rates in passive sampling if thermally desorbed Perkin-Elmer diffusive tubes were used.[128] There was no mention about the technique used for measuring air velocities at such low levels (10 folds lower than the lowest detection limit of a high quality laboratory air transducer), nor any reference was made to any experimental data. The influence of air velocity in the uptake rate of passive sampling methods has been overlooked in many indoor air VOC investigations.

Wolkoff et al. (1991) used the 3M diffusive badges in their study of two identical new homes in Denmark. One of these homes was occupied while the other was unoccupied. VOC sampling was performed periodically over one year with a sampling duration of one week. Air concentrations of several VOCs were reported, including polar and non-polar VOCs. Passive sampling was compared in parallel with active sampling. Tenax thermal desorption tubes were used during active sampling. Their study raised some of the limitations associated with diffusive badge sampling in low level ppb environments and long term sampling durations. These limitations were the loss of sensitivity due to solvent extraction and the loss of specificity associated with the identification of polar VOCs.[129]

Otson et al. (1994) used 3M passive diffusive badges in a nationwide study of indoor VOCs in 757 Canadian homes. The sampling duration was 24 hours (much shorter compared to other studies). Approximately equal numbers of homes were sampled in each of the four sampling events during the different seasons. Samples were chemically desorbed and analyzed by GC-MS. Seasonal variations were recorded and air exchange rates in some of the homes were measured by using a tracer gas technique (SF_6). The results of this study indicate a mean VOC concentration (based on 26 VOCs) of 8 ug/m^3 ranging from 1 ug/m^3 to 41 ug/m^3. The limit of detection was also reported (1.6 – 5.9 ug/m^3).[130,131] The study also included detailed analytical procedures for sample treatment, transportation, preparation of blanks, recoveries, calibration standards and estimated uptake rates.

It is interesting to note, that IAQ studies rarely report their limits of detection and/or quantitation. Even when they do report a limit of detection, it is not clear which limit the authors are referring to. In fact many studies only report their limit of detection (LOD) in nanograms of some specific VOC. This LOD could be confused with ILOD (Instrument Limit of Detection) or the MLOD (Method Limit of Detection), and neither is of any use in the context of IAQ investigations. To be useful, the limit of detection must take into account the sampling approach selected. Although reporting the performance limit of detection (PLOD reported in ug/m3) is helpful, it is the performance limit of quantitation (PLOQ, which is three to four times that of PLOD) that would best incorporate the actual detection limit of the sampling approach used. If VOC measurements in indoor air quality studies are to be quantitatively compared, a standard reporting procedure needs to be established and followed. Currently there is no standard operating procedure (SOP) for indoor VOC sampling. In Otson's study, the unit used in reporting the limit of detection suggests a PLOD. Upon closer examination of the results of this Canadian study, approximately 50% of the reported VOCs concentrations were below the upper limit of the reported LOD.

Ullrich et al. (1996) used the exact same type of badges in a study of indoor VOC concentrations in 59 homes in Germany with a sampling duration of two weeks. Field sampling in two different residential neighborhoods using diffusive badges (3M-OVM 3500) for personal breathing zone and area sampling was performed. Biological monitoring for blood and urine was also performed but not reported. Personal breathing zone sampling and biological monitoring are uncommon in non-industrial indoor environmental sampling. This is one of the few studies that used several parallel sampling approaches for the measurement of VOCs in a non-industrial environment. This parallel sampling were likely performed to relate VOC exposure to indoor sources and emissions. One of the residential neighborhoods in the study was in a close proximity to chemical industries while the other was a reference site. All together, 156 subjects (60 at the case site and 96 at the control site) representing a population of non-smoking, non-employed women between the ages of 50 to 60 years were selected. Subjects at each site agreed to wear the passive badges 12 days before the official 2-day sampling period planned for all participants. The 2-day sampling was planned to correlate personal with biological sampling. Indoor living room air and outdoor air were sampled using the same type of badges for area sampling. Area sampling coincided with personal sampling. Living conditions as well as all activities during the 14-day sampling campaign were collected using self-administered questionnaires. Based on the results, the study reported a mean deviation of 5% to 50% depending on the type of VOC and its concentration (the lower the concentration, the higher the deviation reported). Detection limits were reported for two VOCs. Detection limit for limonene was reported at 1 ug/m3 and that for chloroform at 0.1 ug/m3. Results for chloroform were not reported because 80% did not exceed the detection limit. Correlation coefficient between personal and indoor area VOC samples ranged from 0.69 to 0.87. Correlation coefficient for short term (2 days) and long term (14 days) personal samples ranged from 0.26 and 0.71 depending on the VOC. The study suggests that the broad range in the latter reflects the inherent variability in indoor VOC source strengths and the time/activity pattern of building occupants.[132] It may be of interest to note that Ullrich's and Otson's studies have shown a remarkable agreement in the relative ratio of two VOCs that are commonly encountered in non-industrial indoor environments, Toluene and Limonene.

Brown et al. (1992) measured the concentration of a mixture of VOCs in the air of 100 UK homes using the Perkin-Elmer passive diffusive tube (Tenax) with varying sampling durations. Their findings suggest that exposure time and volatility of VOCs greatly influence diffusive uptake rates of each individual VOC.[133] In two experimental studies, Brown (1993) and Brown and Crump (1993) used diffusive sampling tubes with a sampling period of up to seven months. A significant decline in the effective sampling rate with sampling time was reported during the first month of sampling, while no further decline was reported after 5 months of sampling.[134] Furthermore, their studies highlighted a significant decline in the uptake rate with sampling time for the more volatile compounds such as Benzene and Toluene. The authors could not find any significant change for compounds less volatile than Xylenes.[135]

The largest case study for the measurement of VOCs in UK homes is a study by the British Research Establishment (BRE). This was a study of 174 homes in Avon, England, carried out by the University of Bristol. For 12 months, diffusive tubes were deployed on a monthly basis in selected homes to measure the concentration and find the sources of indoor VOCs. Sampling duration was 30 days. Details of building characteristics and occupant activities were recorded. Full building characterization and time-activity reporting were performed to detect possible links between indoor VOC concentrations and their sources. For example, it was found that painting activity strongly influenced the mean VOC concentration; VOCs were higher in newer homes; benzene was higher in homes of smokers and those with attached garage.[136,137]

Two other UK studies involved 40 asthmatic homes in Southampton and 36 homes of occupants who complained about poor indoor air quality. In both studies building materials including specific finishes and furnishings such as coal tar roofing membrane and chipboard flooring used by the builders were linked to the levels of VOCs measured.[138, 139] The identification of these sources was only possible after difficult and painstaking "forensic-type" investigation.

Lynch and Kipen (1998) reported the effect building materials have on indoor VOC loading and occupants' complaint. Area based active sampling using charcoal tubes in an office building during and following a renovation revealed very low-level exposure to organic compounds. Building occupants complained of eye and upper respiratory tract irritation. Despite low VOC concentrations, and lack of consistent medical findings among employees who were evaluated by an occupational physician, IAQ complaints by building occupants continued. After numerous investigations and intensive sampling campaigns, the source of occupants' complaint was traced to VOC emissions from the roofing material that was recently installed.[140]

Weschler et al. (1990) attempted to find an association between sources of indoor VOCs and sick building syndrome. On separate occasions over a one-year period, moderate levels of TVOC concentrations were measured in an office building with a history of occupant complaints. The reported symptoms were characteristic of sick building syndrome. The objective of the study was to determine if VOC levels were higher than those measured in "complaint-free" buildings and, if so, to identify sources and other factors that might have contributed to the observed and elevated VOC concentrations. VOCs were sampled with passive diffusive badges. Sampling periods ranged from 3 to 4 weeks. Following collection, the badges were chemically extracted, and the compounds in the extract were separated and identified using a GC-MS. Over 40 different organic compounds with concentrations in excess of 1 ug/m^3 were identified; several compounds had values greater than 100 ug/m^3. The total concentration of VOCs detected was in excess of 3000 ug/m^3. Sources of the identified compounds where suspected at first to be from cleaning products, floor waxes, latex paints, and vehicle exhausts from the underground garages. However, following a more extensive investigation the main source of VOC emission was linked to be the oil that was used in the hydraulic system of the elevators. It was found that organic chemicals were being volatilized from the hydraulic fluid of the elevator system while the elevator shafts transported these chemicals to the different floors. Neither the elevator shafts nor the mechanical room that stored the fluid reservoirs were vented to the outside. The problem was compounded by the relatively small amount of outside air used for ventilation of the building (< 6 L/s or about 12 CFM per occupant translating into ¼ air change per hour). At such low ventilation rates, compounds with a strong source can achieve high concentrations in a short period of time.[141] This is an example where a sensory sampling approach, if used, would have found the source of the problem at the outset.

Cavallo et al. (1994), studied VOC concentrations in an Italian office building. The study was carried out during winter and summer by collecting indoor and outdoor air samples. The samples were actively collected on a Carbotrap tubes for 240 minutes. Sampling tubes were thermally desorbed and analysis was performed by gas chromatography (GC). TVOC values were computed by adding the concentrations of all VOCs obtained. Indoor concentrations of TVOCs were between 137 ug/m^3 to 423 ug/m^3 and 105 ug/m^3 to 283 ug/m^3 for winter and summer respectively. In one specific office room, the TVOC concentration was

5000 ug/m^3 in winter day and 3500 ug/m^3 in summer day. This room was the data processing center of the office building where computers, printers, plotters and specialized graphic facilities were present. The study reported 12 different categories of VOCs and concluded that the most abundant indoor VOCs were the aromatics and alkenes. Together the aromatics and alkenes contributed more than 40% to all VOCs collected. Outdoor TVOC concentrations were higher in winter than summer (mean 215 ug/m^3 and 18 ug/m^3 for winter and summer respectively). Air exchange rates were reported between two and three air changes per hour.[142]

Identification of sources of indoor VOCs in non-industrial indoor environments is difficult. In very few cases, sources could be identified. The aforementioned Italian case study is an example of source predictability. It should be emphasized, however, that printing rooms with specialized printing equipments, even if located in an office building, should be treated as an "industrial" indoor environment with its own ventilation and extraction system.

Toshie et al. (1994) reported the results of an IAQ investigation for ten large office buildings in Tokyo, Japan. The study was part of an international survey of indoor air quality in office buildings with sites in France, New Zealand, Korea, US and Japan. The buildings were chosen according to standard criteria for age, usage and total floor area. Self administered questionnaires and air measurements were performed. Temperature, RH, air velocity, CO_2, CO and suspended particulate matters were measured. However, only the Japanese study sampled for indoor chemicals such as TVOC and formaldehyde. Measurements were performed during spring, summer and winter. TVOC and formaldehyde were measured three times a day during working hours. Both outdoor and indoor samples were collected. Mean outdoor TVOC concentration was reported to be 660 ug/m^3 (270-1510 ug/m^3) and mean indoor TVOC concentration was reported to be 1190 ug/m^3 (450-4310 ug/m^3).[143] Although indoor concentrations of VOCs were almost twice that of outdoors, the investigators were not able to explain with any certainty the differences observed or to attribute the results to any indoor emitting source. What is then the merit behind sampling indoor VOCs if one is unable to associate the results obtained with the sources that emitted them?

Wolkoff et al. (1996) used a laboratory-based chamber to study VOC emissions from interior finishes and the effects of indoor environmental parameter on material emissions. The researchers placed different pieces of nylon carpets and PVC floorings inside a small-scale environmental chamber (a European chamber called CLIMPAQ) for several weeks. They reported that chamber air velocity did influence emission from carpets and tiles even though emissions from such materials are known to be diffusion-controlled. In theory, a diffusion-controlled emission is air-velocity independent. Such an observed dependency suggests that some interior finishes with plasticizer might be unstable against oxidation (the higher the air velocity the higher the rate of oxygen supply to the surface and micro-pores of the material). Hence some interior finishes and furnishings such as carpets might well play a major role in indoor VOC loading through their increased emissions releasing secondary and reactive by-products.[144] Based on the results obtained, the researchers recommended a maximum chamber air velocity of 0.1m/s to limit the oxidation process during material emission sampling. Controlling such a low-level air velocity inside any dynamic emission chamber requires great effort and complex settings that are beyond practical and applied means.

Wargocki et al. (1999) studied the perceived indoor air quality and VOC concentration inside a full scale office setting using a simulated pollution load represented by the presence and absence of a 15 years old carpet hidden from the subjects behind a partition wall. The sensory responses and mental performance aptitudes of the subjects were measured simultaneously with the concentration of 25 different VOCs. VOCs were sampled by area based sampling using active Tenax tubes. Sampling duration was fivehours. Indoor formaldehyde and CO_2 concentrations were also measured. Ozone was sampled both inside and outside. Sensory responses as well as performance measures of the subjects could not be associated with total indoor VOC concentrations (TVOC). However, once the TVOC was resolved into its individual components, differences between the absence and the presence of the pollution load, that is the hidden carpet, became apparent. The most abundant of these VOCs were organic acids, aldehydes and ketones.[145] This suggests that sensory and performance responses based on VOCs are more influenced by lower boiling point VOCs than others. As mentioned earlier, it has been argued that the present definition of VOCs according to their boiling point as per WHO[146] is limiting because other physicochemical properties are as important as the vapor pressure of VOCs. Current studies on indoor VOC measurements are indeed considering wider definitions for indoor VOCs.[147] Some of these definitions have taken into consideration the secondary emissions by interior finishes such as the reactive by products of a carpet during its life cycle, operation and maintenance.

Anderson et al. (1996) studied the effect of indoor VOC concentrations on VOC emission rates from five commonly used interior finishes. Both source sampling and sensory sampling approaches were used. Samples of different interior finishes were sequentially placed inside three identical environmental chambers with different ventilation rates. By changing ventilation rate inside the chambers, concentrations were changed and, by measuring concentrations, emission rates were calculated. VOCs were collected using active Tenax tubes, and analysis was performed using thermal desorption and injection into a GC with both flame ionization and mass spectrometry detectors. Quantification of individual VOCs, sum of "not-well-separated-clustered-peaks" (Σ VOC clustered peaks) and the Total VOC (TVOC) were calculated from retention times between hexane and hexadecane using toluene as a response factor. Effect of VOC concentration on VOC emission varied for different materials and different VOCs. PVC flooring exhibited the least observable effect while carpet exhibited a moderate inverse effect. This sheds light on the sink effect exhibited by a fleecy material such as indoor carpets. According to Anderson and his group, there seems to be no direct agreement between chemical and sensory measurements. They suggested that low concentrations of some specific compounds not detected by GC are responsible for the sensory effect. Due to the observed independence of source emission rate and indoor VOC concentration for both flooring materials[*] the study concluded that sensory measurement as well as direct source measurement are both essential for any proper identification of sources of indoor VOCs in non-industrial settings.[148]

Wessen, et al. (1995) reported a simple source and area sampling approach for the measurement and identification of sources of indoor VOCs. Both source specific and area specific samples were collected using a standard IH personal sampling pump. Air samples are collected on two parallel fitted charcoal tubes. One tube was used for area sampling and the other for sampling of the trapped air inside a desiccator's cover placed on top of a flooring material (Figure 2.3). Despite limitations associated with static sampling and emission perturbation, sources of VOCs inside a few problem buildings were partially identified using such as a technique.[149]

Koziel and Pawliszyn (2001) studied the application of a novel sampling technology SPME (solid phase micro extraction) to the measurement and identification of VOCs in non-industrial indoor environments. SPME presents many advantages over other sampling and analytical methods. It combines sampling and direct transfer of the analytes into a GC.

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[*] Flooring materials are the most perturbed of all building materials. Although walls occupy more surface area per volume than floors, walls do not get perturbed by daily activities, as do floors.

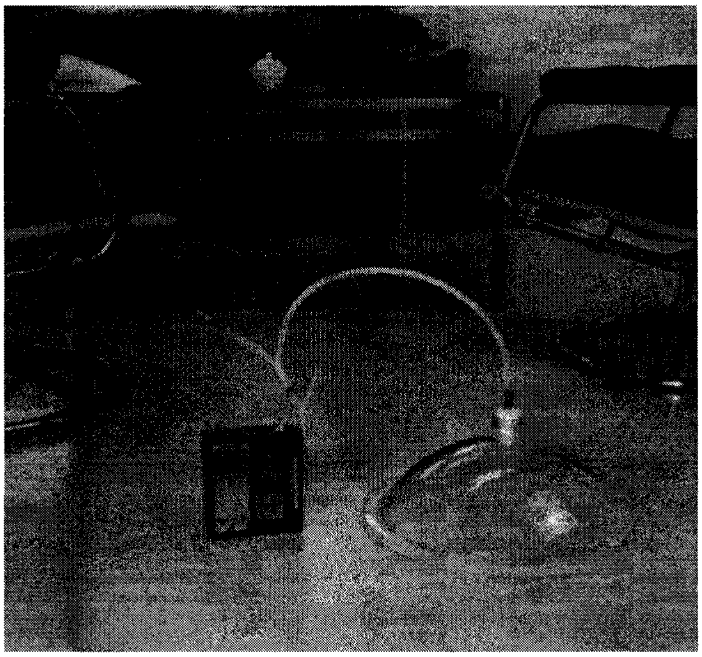

Figure 2.3: VOC sampling from room air and flooring material -area and source sampling approaches (From: Wessen et al. 1995).

The collected analytes are directly desorbed by the high temperature of the GC's injector port. No organic solvent is needed during analysis. The principal sampling method in SPME is based on diffusion of air into a needle holding a micro-fiber coated with an adsorbent or an absorber. Not only the polarity of the micro-fiber coating can be chosen to match the polarity of the analytes of interest but also different coated micro-fibers can be chosen for different families of VOCs including formaldehyde, organic acids, VVOC, SVOCs and MVOCs. The micro-fiber consists of a fused silica fiber coated with a polymer that is fitted in a syringe-like holder, Figure 2.4.

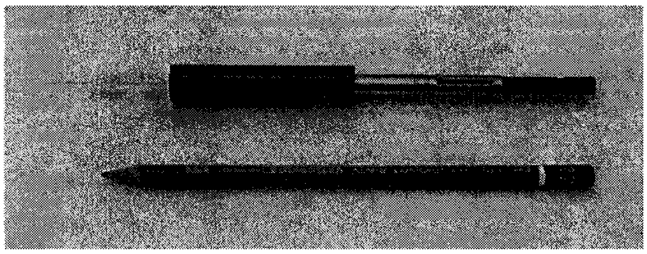

Figure 2.4: The SPME holder with the fiber exposed (left). The size can be compared with the pencil (From: Ryhl-Svendsen, M & Glastrup, J 2001).

Indoor VOC concentrations were reported using SPME. Sampling was performed inside two homes. Active charcoal tube sampling was also performed for comparison. Sampling time for SPME and charcoal tubes were 120 min and 150 min respectively. Measured concentrations of TVOC were typical by 500 ug/m^3 to 3000 ug/m^3. According to SPME method of operation, an equilibrium VOC concentration is needed for a steady uptake rate of VOCs from the air into the micro-fiber of the SPME. For example, if the air concentration was high in the first 30 min of sampling and then dropped, the analytes would start to re-equilibrate to the new ambient concentration. The time needed to re-equilibrate depends on the physicochemical parameters of the analyte. The study reported that while it takes less that 1 min for pentane to re-equilibrate, it took 2 hours for dodecane. [150]

Despite the above shortcoming, Svendsen and Glastrup (2000) have used SPME for sampling VOCs inside a museum environment. Air samples were taken from inside cabinets and displays that housed historic items. They reported that many VOCs and several reactive volatile organic compounds could be detected in the low ppb range (± 5 ppb).[151] Since its commercial introduction in the early 1990s, SPME has been successfully applied in the food and pharmaceutical industries; however its use in non-industrial indoor VOC source and emission sampling remains to be tested.

2.7 Sources of Indoor VOC Emissions

Multiplicity, unpredictability and lack of identity of indoor sources are the challenges that need to be addressed during indoor VOC sampling. In light of industrial hygiene sampling strategies, the AIHA manual on exposure assessment discusses the concept of homogenous exposure group (HEG) and outlines methods for their identification.[152] The manual reviews the following approaches: task based approach, job description approach, and chemical based approach. The evaluation of the HEG is related to potential exposure to contaminants (or any other agents). This exposure potential is based on sources that are process implicit. In non-industrial indoor environments there are no such things as process implicit sources, except for few activities such as office printing, home cooking and cigarette smoking. Other limitations that are unique to non-industrial microenvironments are: wide ranges of VOCs present; sporadic inter-zonal airflows; presence of reactive compounds; complicated source-sink dynamics; varying activity patterns; and the presence of contaminants at very low concentrations.

Indoor air quality investigators measure the concentrations of indoor VOCs in non-industrial environments and use the data to trace potential sources including those emissions from interior finishes and furnishings. However, the concern in using industrial hygiene sampling methods in non-industrial microenvironments raises the question of representative sampling. In this brief review, different sampling approaches and measurement methods were presented. The choice of whether to use one sampling approach over another, or one sampling method over another depends on the objective, that is to say, the purpose of measuring VOCs in a non-industrial microenvironment. If screening of microenvironments for TVOC is the aim, then standard industrial hygiene sampling methods may suffice provided that a sufficient volume of air is sampled. If resolving occupant complaints is the aim, then a comprehensive measurement approach with sampling, analysis and interpretation methods that provide accurate and reliable source identification and satisfy the criterion of in situ and temporal sampling is indeed necessary.

Two important criteria need to be addressed during an indoor VOC source investigation. First, one needs to determine the relationship between indoor sources and indoor VOC concentrations. Second, one needs to resolve the association between VOC concentrations and the complaints. How can this be done when there is neither a standard indoor air VOC measurement method nor a consensus on what to measure?

Even when measurements are performed and indoor VOC concentrations are obtained, the challenge yet remains in how to identify the sources and where the numbers behind these concentrations actually came? An elimination of a "wrongly implicated" source by a false positive identification due to poor sensitivity of the approach used has broad consequences both in terms of financial and capital resources.[153]

2.7.1 Environmental Chamber Sampling

The use of environmental chambers to identify sources of indoor VOCs can be traced back to the early 1960's when NASA was conducting spacecraft material emission and out-gassing studies.[154] NASA's material out-gassing research could be considered as one of the earliest example of material emission testing to evaluate products and materials that are being considered for "construction and building" applications including those materials used for the interior of spacecrafts and cabins. NASA's material emission testing has been used to screen materials based on their emission characteristics for the construction of spacecraft exteriors, interior finishes and furnishings as well as the supplies used by astronauts.[155]

The application of environmental chambers in building construction and indoor air research gained momentum after the widespread release of formaldehyde from disintegrating insulation materials used inside homes. During the 1970's, the presence of formaldehyde was confirmed in thousands of homes in North America and Europe. [156] It was through the use of environmental chambers that the foam insulation (UFFI: Urea Formaldehyde Foam Insulation) in those buildings was identified as the source of formaldehyde emission. Household items made from wood and press wood products, textiles, plastics and vinyl materials were also tested using environmental chambers and all were identified as potential sources of formaldehyde.[157] Chemical emissions from these interior finishes and furnishings and their association with formaldehyde have raised public concern over the safety of homes, construction and building materials, household products and the quality of the indoor air breathed by the population at large. One may thus trace the outset of emission testing of building materials in non-industrial indoor environments to the UFFI episode of the early 1970's. An ever-increasing public interest in, and demand for healthy and environmentally friendly building materials have further advanced the field of material emission testing.[158]

Material emission chambers are almost similar to the chambers used in animal toxicology studies. Chambers in the context of IAQ are designed to permit the testing of samples from building materials including interior finishes and furnishings. Environmental chambers can range in size from a few liters to room size. The American Standard for Testing of Materials ASTM E1333-96, suggests a chamber size of $22m^3$ to qualify as a large scale chamber while ASTM D5116-90 qualifies any size less than $5m^3$ as small scale chamber.[159,160,161] The European standard, ENV 717-1 proposes three different chamber sizes, $\geq 12m^3$, $1m^3$ and $0.225m^3$ respectively.[162]

2.7.1.1 Design Considerations

Emission chambers are designed to sample sources of emissions such as VOCs from a carpet under simulated and controlled climatic conditions. Interior surfaces of chambers are usually glass, stainless steel, and a few are even electroplated with nickel, to reduce baseline contamination and surface adsorption.[163,164,165] Synthetic materials used in the construction of emission chambers are carefully selected, in part, for their emissions of and reactivity with ozone and volatile organic compounds.[166] Inlet air to the chamber is either supplied from ultra clean pressurized air cylinders or supplied through a fan that passes air through a set of filters for purification and baseline control. Filters include High Efficiency Particulate Air "HEPA" filters, molecular sieve filters and activated charcoal filters. Ventilation rate, air temperature, relative humidity, and interior pressure are all carefully monitored.[167] The steady state and equilibrium requirements for these thermodynamic properties are of critical importance during material emission chamber testing.[168] Achieving a steady state emission and maintaining an equilibrium chamber concentration are the two most crucial and involved tasks during chamber emission testing.[169]

Although glass or stainless steel are the two commonly used materials for the interior surfaces of emission chambers, research indicates that regardless of the material used, sorption of chemicals to and from the interior surfaces of emission chambers needs to be carefully addressed, and corrected for, regardless. Studies indicate that loss of VOCs from the test materials to the surfaces of chambers is specific for each VOC and the type of surfaces.[170] Absorption or chemical reaction inside chambers may cause significant variations to actual material emission.[171]

Studies have suggested that emission chambers need to be conditioned along with the test material under investigation for weeks until the system reaches a steady state condition.[172] A steady state condition is the condition when VOCs are being emitted from the material into the chamber at a definite rate while all local thermodynamic properties within the chamber remain unchanged. This condition is difficult to achieve and the term quasi-steady state can better describe emission chambers in terms of their thermodynamic state.

Environmental chambers should be conditioned before each test. Each of the conditioning activity needs to be performed for several days if not weeks depending on the size of the chamber, the area of sample and the physical configurations of the chamber and the sample. A single material emission test may take up to several days for conditioning let alone the time that it may take the system to reach its equilibrium state. An environmental chamber and the sampling material within it is indeed a thermodynamic system. This system is said to be in equilibrium when none of its thermodynamic properties are changing with time at a measurable rate. The latter takes any where from several weeks for fast emitting materials to months and even years for slow emitting ones.[173]

Building materials such as interior finishes and furnishings, once installed in an indoor environment, are mostly slow emitting ones. It may be of interest to note that the cost of maintaining and running an emission chamber is in the hundreds of dollars per day based on chamber usage and type of analysis. Some large scale environmental chambers such as the one at the National Research Council of Canada has cost over $1M just to build, let alone operate.

An environmental chamber must provide an access to its interior volume either by a direct door or through an intermediary chamber with airtight, non-emitting, non-adsorbing seal. Every time the door of a chamber is opened, the entire system becomes contaminated and it should go through the aforementioned time consuming conditioning cycle. Ports for temperature, humidity, air velocity and pressure probes are required in the design of emission chambers, while more ports for sample collection are needed. These ports present further challenge for designers in terms of airtight and sealing of the chamber.

Environmental chambers should be designed to ensure adequate mixing of the air within its interior. Low speed mixing fans or multi-port inlet and outlet diffusers are two techniques that can be used to achieve adequate mixing. In some cases, specially designed fans with interior blades and exterior drives are attached to environmental chambers to achieve cleaner mixing, since blade/drive integrated electrical fans tend to emit chemicals that could add to the chamber's baseline contamination.[174,175] Locations of air inlets and air outlets ought to be carefully designed and engineered to achieve the desired mixing, limit short-circuiting, and establish a uniform air velocity distribution inside the chamber. Determining the level of air mixing in the chamber is also critical because it, along with other parameters mentioned above, play a fundamental role in the calculation of source emissions.[176]

The use of a tracer gas is one approach used for the determination of the degrees of air mixing through established mixing factors.[177] A tracer gas such as SF_6, N_2O or CH_4 could be blended with chamber's inlet air at some constant rate. The concentration of the tracer gas at the outlet is measured over time until steady state and equilibrium is achieved. Chamber concentrations versus time are then compared to a theoretically driven diminishing growth curve to calculate the air change rate.

2.7.1.2 Practical Considerations

According to ASTM D-5116, tests to determine the adequacy of mixing and hence steady state should be conducted not only in an empty chamber, but also with inert substances of the type, shape and size of materials to be tested to ensure that the placement of materials do not perturb mixing.[178] This entails inserting a non-emitting "blank-material" that mimics the material to be tested including its surface characteristic, size, shape and volume. The latter, though important, is rarely practiced.

Material emission chamber studies require samples from interior materials that are recently collected from within a building. In practice, removing and collecting samples from interior finishes for emission sampling is not a simple task. The problem lies not only with the inherent disturbance and damaging nature of such a task—especially when it comes to wall-to-wall carpets --but on identifying and limiting the number of interior materials to remove at the outset. Ideally, an IAQ practitioner prefers to sample emissions in-situ. However, there is no simple or practical device or method per se that can sample VOC emissions in-situ.

Several studies have outlined some of the problems associated with the use of laboratory emission chambers and their limitations in representative emission sampling.[179,180,181,182,183]

In summary, comparability, reproducibility and relevance are the main problems and limitations that are associated with the application of laboratory emission chambers in accessing VOC emissions from interior finishes and furnishings. There are unique parameters that are exclusive to each building. Each building is unique in its location, design and age of its finishes and furnishings. Indoor VOC emission profiles of interior finishes and furnishings become specific to each building.

VOC emissions profiles could change according to environmental parameters that may well vary between each floor, each room and even each site within a room inside buildings. During the construction of a building, materials are delivered, stored and used in sequences that are specific to each building and site. During the implementation of these sequences, materials are shuffled and subsequently exposed to many environmental and operational conditions that are themselves specific to each building, location and site. As a result, a material that is delivered from a manufacturer or supplier no longer possesses its original emission profile.

Thus, emissions from building materials become specific to each building and each room. Although a wall-to-wall carpet may be moved to a large-scale chamber, removing sections of walls, floors and ceilings along with the carpet is no doubt beyond most practical means. Although sampling interior finishes and furnishings using full scale model replicas and placing them inside full scale emission chambers can support some of the unique and varying environmental parameters mentioned above, such full scale emission chambers entail the use of sophisticated control and ventilation system.[184]

Adding yet to the complexity of emission sampling, if one takes a carpet as an example, emission of its top fabric might have been indeed influenced by the emissions of the under pad and adhesive used. The fabric of the carpet may have also acted as a sink for the emissions generated by the once freshly painted walls of the room in question.

The multitudes of spatial and temporal environmental parameters present in a non-industrial indoor environment such as an office workstation or a living room are far from being qualitatively identified, let alone being quantitatively determined. Given the unique set of parameters and variables present in an indoor setting, sampling emission from samples of interior finishes or furnishings by using laboratory chambers that are set in pre-defined and controlled conditions is not representative of the true and actual conditions, in-situ. Laboratory-based emission testing does in fact oversimplify the dynamics of in-situ emissions present in real indoor environments. Some of the issues and oversimplifying assumptions that have been so far used in practice and which have been raising the concern over the unrepresentative nature of laboratory-based material emission sampling are:[185,186,187,188,189]

1. Laboratory chambers are normally calibrated using evaporation as opposed to using some representative planar surface diffusive emission that is similar to interior finishes and furnishings;
2. Even if a calibration gas is used instead of a liquid evaporation, such standards are normally introduced via a chamber's inlet as opposed to it being introduced from within the chamber;
3. The assumption that air inside an environmental chamber is completely mixed with a velocity similar to that encountered indoor is normally not applicable;
4. The absence of sink effects during a laboratory-based emission sampling is not representative of the true dynamics of indoor emissions.

Various laboratory emission sampling techniques have been developed and many have bypassed some of the above limitations. Some of the techniques developed have resulted in the development of general guidelines for material emission sampling.[190] These assumptions and their underlying principals warrant some critical review to better understand the practical limitations of laboratory-based emission sampling and the applicability of emission data generated by such a sampling approach to actual indoor emissions.

2.7.1.3 Calibration Considerations

Emission chambers, being small or large are normally calibrated using certified evaporation rates of liquid solvents. Such a calibration technique uses liquid to gas phase transfer mechanism based on the convective flux from a liquid solvent, including water, into the surrounding air. The convective coefficients whether free convection or forced convection, are derived by using a simplified mass balance equation. The convective coefficients are functions of temperature and air velocity. To mimic actual indoor conditions, calibration of emission chambers should be carried out under similar indoor air velocities. Average indoor air velocities hover around 0.05 to 0.1 m/s. Since there is a fan that is being used inside most laboratory emission chambers to satisfy the "perfect mixing" assumption, air velocity inside such chambers will be several times higher than the typical range mentioned above.

The evaporation rate of a liquid VOC is generally proportional to its vapor pressure and dependent on air velocity, temperature, and relative humidity. Many of the VOC evaporation rate data have been established using a device called Thin Film Evaporometer. ASTM D-3539 is the relevant standard for using the Evaporometer. The Evaporometer consists of two chambers: an outer chamber, which serves as a constant temperature environment, and an inner chamber where evaporation takes place. The temperature, humidity and airflow within the inner chamber are controlled. The actual site of evaporation of the test material is a filter paper disc suspended from an optical Electro-balance weight-sensing device. The output signal from the Electro-balance is fed to a digital meter. As per the ASTM standard, the temperature of the inner chamber needs to be maintained at 25C with a RH at 0-5% and an airflow rate of 21 L/min. There is no direct reference as to the actual value of air velocity at the surface of the test material.[191]

Many VOCs do exhibit linear relationships between their evaporation rates (mass per unit area per time) and surface air velocities. Exceptions include the VOCs that possess high heat of vaporization. A fast evaporating VOC exhibits a temperature depression of the emitting surface, which in turn depresses the evaporation rate. There is an empirical relationship (independent to the above ASTM standard) that is normally used to adjust for the proportionality between air velocity and the measured VOC evaporation rate:

$$E \ \alpha \ 1.86 + \{v / (0.0155v + 0.0706)\}$$

where (E) is the VOC evaporation rate; and (v) is air velocity. The above relationship is only valid to surface air velocities between 20 and 170 cm per second.[192]

2.7.2 In-Situ Emission Sampling

The Danish National Institute of Occupational Health has proposed an alternative approach to laboratory-based emission sampling by developing a portable micro-cell named the FLEC (Field and Laboratory Emission Cell).[193] The design of the FLEC addresses the problem of adsorption of VOCs by the large interior surfaces of laboratory chambers.[194] The FLEC is made from a stainless steel cell shaped like a parabolic cone. The mouth of the cone is placed against flat surfaces of interior finishes from which emissions are sampled.

Due to its relatively small size (35 cc volume; 177 cm^2 sampling area), the ventilation rate as represented by number of air changes per hour (ACH) and the loading factor, the ratio of material surface area per room volume, are significantly greater than what is normally encountered in actual indoor environments. A typical ACH air changes per hour (h^{-1}) in an indoor non-industrial environment such as a typical office room ranges from 0.5 h^{-1} to 6 h^{-1} The average loading factor of a typical room is 0.4 m^2/m^3 for floors, and 1.2 m^2/m^3 for walls. The typical ACH and loading factor in the FLEC is ~350h^{-1} and ~500m^2/m^3 respectively.

Emission back-pressure is a phenomenon that is normally encountered during surface emission sampling. It occurs when the rate of emission exceeds that of the rate of removal. Due to the large surface area of the FLEC compared to its cell volume, some surface emission perturbation may occur. Surface air velocity inside the FLEC is very low as compared to the average 5-10cm/sec found indoors. Inside the FLEC the surface air velocity has been estimated to be very low, in the range of 0.003–0.017 m/s depending on the inlet flow rate.[195] Inlet flow rates are recommended to be in the range of 100–500 cc/min. There are few studies that compared the FLEC with other laboratory-based emission chambers. Emission rates using the FLEC were generally reported to be lower than those found using the other chambers. The observed differences may have also been due to the different models and parameters used to estimate the emission rates including different curve fitting regression coefficients and exponential rate constants.[196,197]

The reason behind selecting a parabolic conic shape for the FLEC has not been widely published and its effect on emission perturbation remains partly unknown.[198] However, a section through the conic profile of a Pseudosphere may seem an appropriate match to the FLEC. Such a sectional profile generates a surface of revolution of constant negative curvature. The curve generated is called the tractrix, a curve with the property that the length of the segment of the tangent line from any point on the curve to the y axis is constant. The property of the tractrix was used in the design of the novel sampling cell, described later, to control air velocity over the surface of an emitting material.

2.7.3 Sampling Emissions Indoors

There are many sources that contribute to indoor VOCs in non-industrial environments. Indoor air sampling is generally based on area sampling. Sampling indoor air of a building provides indoor VOC concentrations without reference to any suspect sources. Area based sampling cannot identify the source of indoor emissions. As briefly descried above, there are two basic types of indoor air sampling that are generally used in-situ; active sampling, and passive sampling. The question yet remains whether these two in-situ area based sampling methods could be used to identify sources of indoor VOCs.

2.7.3.1 Active Pump Sampling

Active sampling involves the passage of known volume of air by means of forced movement through an adsorbing medium. Examples of adsorbing mediums applicable for VOCs are granular charcoal, activated carbon, carbon molecular sieve and other polymerized porous mediums such as 2,6-diphenylene oxide polymer known as Tenax. During active sampling, VOCs are collected over a period of time, usually less than 24 hrs, to obtain an average concentration over the sampling period. Active sampling could be used to sample emission sources and estimate emission rates. In one example mentioned above, Figure 2.3, a Pyrex Desiccator's lid was placed over a flooring material and connected to a sampling train using a charcoal tube and a sampling pump.[199] Such a system, although simple, has had limited success in sampling VOC emissions from interior finishes and furnishings since it does perturb surface emissions. With a pump sampling at a rate of 100cc/min, a normal sampling rate in charcoal tube sampling, the enclosed volume under the lid would rapidly be under vacuum. This rarefied atmosphere perturbs the in-situ dynamic of emission at the surface of the flooring material. Such a rarefied atmosphere would activate the release of VOCs from the flooring material that otherwise would have not been released under normal in-situ conditions.

2.7.3.2 Passive Diffusive Sampling

Passive sampling offers a simpler alternative to active sampling. Most commercially available passive samplers operate on the principal of diffusion.[200] Diffusive sampling has been available since the 1930's and has been in commercial use since the early 1950's. It was not until the early 1970's that mathematical treatments were published.[201] The mathematics of diffusion codifies the factors that control diffusive uptake rates. The application of Fick's first and second laws in diffusive sampling is one example of a mathematical treatment that has been generally used in the design of diffusive samplers.[202] During diffusive sampling, VOC molecules diffuse from regions of high concentration to regions of low concentration. Fick's laws of diffusion describe the movement of VOC molecules within this concentration gradient. One setback with passive diffusive sampling is its reliance on an air velocity (>0.15m/s) that is above the normal air velocities encountered in non-industrial indoor settings (<0.1m/s).

2.7.3.3 Hybrid Sampling: The Canister

The use of very low air flow sampling system consisting of an evacuated canister connected to a limiting orifice is another method that could be used for sampling emissions from interior finishes and furnishings. Canister sampling could be considered a hybrid sampling method since it involves an active pump for its preparation, vacuuming, while during sampling it uses a pressure difference mechanism to sample air in a passive way, per se. The use of this method in material emission sampling was first attempted by the author at the Environmental Research Laboratory of McGill University.[203] There are many challenges that are associated with Canister sampling including leaks and diminishing flow rates in sampling rates. Although several modifications have been made to address some of those challenges, more validation studies are needed to justify the application of canisters in material emission sampling.

2.8 Concluding Remarks

Whether adapting active, passive or hybrid sampling to in-situ surface emission sampling, it should be understood that surface emissions do not only vary based on time and location of sampling but also on physiochemical properties of the emitted VOC such as its vapor pressure, boiling point, and diffusion coefficient. Surface emissions also depend on the emitting material such as its porosity, density, and partitioning coefficient. Other factors that also influence surface emissions are the treatments applied on interior finishes and furnishings during their fabrication, installation and use. These treatments contribute to the so-called secondary emissions.[204] The presence of other indoor sources and changes in indoor and ambient environmental conditions also perturb emissions from the surface of interior finishes and furnishings.[205, 206]

Developing an appropriate, representative and practical sampling method for in-situ VOC emission sampling from surfaces of interior finishes and furnishings is indeed a challenge. The next chapter outlines the framework of this research, its protocol and its question statement addressing the challenges ahead.

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Chapter Three

Research Protocol

The main objective of this research is to develop a practical sampling approach for the identification of sources of indoor emissions from interior finishes and furnishings, in-situ. This research limited its scope to interior materials that are: 1) in common use, 2) take up the bulk of indoor surfaces and, 3) in direct contact with indoor air. These are thus interior finishes that cover floors, walls and ceilings. Most of such surfaces are solids including flooring materials, ceiling tiles and walls. From this generic list of interior finishes, carpet as a flooring material, tends to emit VOCs in low quantities and for a long duration. Carpet also acts as a source and a sink and it is associated with secondary emissions from daily use and cleaning. In fact carpet is considered to be one of the most challenging materials to sample VOC emissions from, especially when it is in-situ. For the purpose of this research, carpet is selected as the interior finish to challenge the outcome of this research and development study.

3.1 The Question

A practical indoor air quality sampling strategy entails using simple, available and affordable sampling methods. A practical sampling method should be able to at least pinpoint and reveal sources of indoor pollutants such as VOC emissions from interior finishes and furnishings. In indoor air quality investigations, once an emitting source is identified, remedies such as source removal or dilution by ventilation could be applied to reduce exposure of building occupants to indoor pollution.[1,2,3] Currently, there is no method available to sample surface emissions from fleecy interior finishes and furnishing in-situ. Sampling VOC emissions from an indoor office-carpet, for example, entails removing and cutting few pieces from the carpet and shipping them to a laboratory for chamber emission sampling. Sampling emissions by cutting and removing pieces of an interior carpet is not a practical or a representative sampling approach. Cost wise, the cost of a single 24-hr integrated laboratory-based VOC emission sampling from a single piece of a carpet using a laboratory-based emission chamber is approximately $2000.[4]

This research considers the following question: *Could VOC emissions from surfaces of interior finishes such as carpets be sampled in-situ?*

In situ sampling entails that the sampling method should be noninvasive, non-perturbing, representative and simple. The term "in-situ" makes reference to the sampling of an interior finish as it is originally installed indoors. Non-invasive makes reference to keeping interior finishes as-is in their original indoor setting. "Representative" makes reference to sampling while keeping the indoor environmental parameters such as air velocity, temperature and relative humidity, each of which does influence surface emissions, as present indoors. In fact, representative sampling is sampling while including the influence of parameters such as temperature, relative humidity, air velocity and their variations during the sampling process. Representative sampling also should include the exposure history of an indoor finish to those external determinants such as storage, installation, usage and those sink effects that are associated with secondary emissions. "Simple" makes reference to the viability of the sampling method to building practitioners who are in the forefront of receiving indoor air quality complaints from the building occupants and who are entrusted to making appropriate decisions in terms of material selections and remedial actions. The health and safety budget allocated for indoor air quality investigations in most office buildings can hardly be stretched to pay for laboratory-based material emission sampling. In fact sending few samples of an interior finish such as a carpet to a laboratory for VOC emission sampling could consume the entire health and safety budget of the building manager for a year.

3.2 The Definition

From the definitions of VOCs and their groupings, as presented in the previous chapter, a definition for indoor VOCs that is most appropriate for this investigation is now proposed. Due to the comparative and empirical nature of this investigation, and in line with the provisions of sampling and analytical tools available for this study, VOCs in this thesis are defined as those compounds of carbon that are:

1. Captured by activated carbon.
2. Extracted by carbon disulfide.
3. Analyzed by gas chromatography.
4. Separated by a non-polar capillary column.
5. Detected by Flame Ionization Detector.

In other words, and according to the above limiting parameters, VOCs in this investigation are those non-polar compounds with a boiling point above Benzene (~80°C) and less than Naphthalene (~180°C). The lower boiling point limit is based on the fact that Benzene is a common impurity (1%-5%) that is found even in the best quality commercially available carbon disulfides, CS_2. The latter is the extracting solvent used during sample analysis. The chromatographic retention time of Benzene is close to that of the solvent peak. This makes qualification of compounds eluting prior to benzene a laborious task. The higher boiling point limit of 180°C is based on the limitation of the capillary column used in this research; a standard non-polar capillary gas chromatography (GC) columns. The polarity limitation mentioned above, is also intrinsic in both the capturing medium (activated charcoal granular / carbon felt) and the type of capillary columns being used. Thus, regardless of theoretical definitions or groupings of indoor VOCs, this "study-specific" VOC definition is based on the available analytical tools for this investigation.

3.3 The Challenge

The main challenge that faces indoor air quality investigators is how to locate the source of indoor emissions. Even if an in-situ material emission sampler becomes available, the challenge that remains is emission assertion. To help explain the above, the following question needs to be examined: How could it be ascertained that what is being sampled from a surface of a material is truly what is being emitted?

This question raises the issue of standard reference materials (SRMs). These are materials used to compare and validate results for quality control and assurance purposes in the field of analytical chemistry. However, in material emission sampling, there is not a single reference emitting material per se that could be used as a standard reference material to make sure, both qualitatively and quantitatively, that what is being sampled is indeed what is being emitted.

3.3.1 A Novel Reference Emitting Material (REM)

Currently VOC emissions from surfaces of interior finishes are sampled using emission chambers. Sampling emissions within these chambers are usually referenced to the evaporation rate of a liquid phase solvent such as toluene. The mechanism of evaporative-based emission differs substantially from the diffusive-based emission. The emission mechanism from surfaces of interior finishes and furnishings is mostly based on diffusion and not on evaporation. The evaporative-based references that are currently used in laboratory emission chambers do not represent the actual diffusive-based emission from surfaces of interior finishes and furnishings. For calibration purposes a representative reference, a diffusive surface with a known VOC emission rate, is no doubt required. Such a reference material needs to mimic, as close as possible, the actual emission mechanism present in interior finishes and furnishings. Ideally, such a standard reference emitting material (REM) should meet the following criteria:

1. The REM must be planar.
2. The REM must occupy the same volume and space in the chamber as the sampling material with a similar loading factor; the ratio of the surface area of the sampling material to the volume of the sampling chamber.
3. The REM must emit a known VOC at known rate with pre acquired data on the influence of temperature, pressure, air velocity and humidity on its emission rate.
4. The REM must emit its VOC from within the chamber.
5. The REM must emit its VOC according to the diffusion transport mechanism.

The closest standard that will meet the above criteria is the permeation tube. However, permeation tubes do not occupy the same volume as sampling materials do once placed in a chamber/cell for emission testing. Unlike a planar flat surface such as a carpet, a permeation tube is tubular in form. To emit at a constant rate, permeation tubes require a constant flow of air that is most commonly set at 60°C. VOC emission and reactivity at such a temperature range may not behave similarly to those indoor VOCs being emitted from interior finishes and furnishings at normal indoor air temperatures. In additions, permeation tubes require accurate temperature control. A mere fluctuation of 1°C in the temperature of the airflow would change the emission rate from a permeation tube by 10%.[5]

In the absence of a representative reference emitting material, the current available sampling methods used for surface emission sampling are prone to quality control and quality assurance issues. To support the primary objective of this research in developing an in-situ material emission sampler for a fleecy interior surface such as a carpet, it became evident that designing and developing a REM would indeed be a prerequisite. The first phase of this research is thus allocated towards investigating the possibility of developing and validating a novel reference emitting material, a REM.

Developing and validating a novel REM entails the use of a primary calibration standard. A calibration standard should ideally be based on established physical laws. One of the most accurate reference standards is the gravimetric method in weight measurement. Permeation tubes, for example are calibrated using gravimetric methods.

Although there are many published methods for producing standard VOC atmospheres, for the purpose of this research the permeation method seemed to be the preferred method for generating standard VOC concentrations. The lessons learned from the industry that produces permeation tubes were used towards achieving the objective of developing the REM.[6] Permeation tubes use the inherent microstructure of special membranes such as fluorinated ethylene propylene (FEP), tetrafluoroethylene (TFE), or polyethylene as mediums to regulate the permeation rate and the diffusion of particular VOCs. Each membrane has it own specific pore size distribution. These pores permit selective permeation of VOCs based on their molecular size, vapor pressure and solubility. The rate of permeation and compound selectivity are functions of the matrix and the thickness of the membrane, its type, its surface area and the temperature of the surroundings. The concept of permeation, which is the cumulative action of diffusion and sorption, of a VOC molecule through the pores of a membrane is comparable to the emission of a VOC from the matrix of a building material such as a carpet. This inherent similarity is exploited in this research for the development of a REM, a reference for surface emission sampling. Surface VOC emission sampling using standard sampling methods to compare the response of the REM in two laboratory emission chambers, an ASTM-based and the FLEC, will be conducted. The development of the REM is an important milestone towards achieving the objective of this research. Without a REM it would be practically impossible to ascertain that what is being sampled by a novel material emission sampler is truly what is being emitted from the sampling material.

3.3.2 A Novel Material Emission Sampler

As mentioned earlier, the primary objective of this research is to develop means of obtaining source specific VOC emissions from surfaces of interior finishes and furnishings, in-situ. The mandate of this research is to achieve the above objective by using an appropriate, reliable and representative sampling method.

A sampling head that would rest on top of a fleecy material such as a carpet will be developed and tested. Unlike the FLEC, the design of such a sampling head would take into consideration the following criteria:

1. It should be a dynamic emission sampler, c.f. static head space sampler.
2. It should be appropriate for in-situ emission sampling of fleecy surfaces.
3. It should not perturb surface emissions.
4. It should maintain a constant sampling flow rate.
5. It should have little reliance on air supply and flow controlling devices.
6. It should support the application of both passive and active sampling.
7. It should rest onto interior planar surfaces horizontally, vertically, and even onto ceiling surfaces upside down.

Based on the above criteria, several sampling configurations including various sampling heads will be designed and tested. From the lessons learned from each set of tests and configuration, the most appropriate sampling head will be selected to further carry on the mandate of this research. Results obtained using the newly developed sampler will be used to assess its ability to sample in-situ VOC emissions from a fleecy interior finish such as a carpet.

3.4 Experimental Setups

Several REM-based comparative tests using an ASTM-based laboratory chamber, henceforth called the ASTM, the Danish Field and Laboratory Emission Cells, henceforth called the FLEC, and the newly developed emission sampler, henceforth called the Kappa, will be performed. VOC emissions from a set of five carpet samples will also be conducted using the ASTM, the FLEC and the Kappa. Results obtained will be compared and analyzed using the coefficient of variations in chromatographic retention times (qualitative) and the normalized peak area (quantitative) of the most abundant VOCs captured.

Due to inherent limitations associated with passive badge sampling, all sampling campaigns in this investigation are based on active tube sampling. The limitations observed during preliminary tests using passive badges are presented later. It suffices to mention that background impurities detected in passive badges were the main shortcomings observed in passive badge sampling. Based on data generated by the preliminary passive badge experiments an improvement to the passive badge system is proposed.[7]

The ASTM, a 50-liter stainless steel emission chamber, will be used as a de facto gold standard during this study. The chamber is designed in accordance with the American Society for Testing and Materials guide. A sampling and analysis system for the ASTM, the FLEC and the Kappa will be developed. Over 50 values and 12 airflow meters will be assembled together to control and monitor the different sampling scenarios required to achieve the objective of this research. Appendix A presents the schematic of the proposed sampling and analysis system.

Due to the generally low levels of VOC emissions from surfaces of interior finishes and furnishing, carpets in particular, developing a sensitive sampling and detection methodology is critical in this study. A dual cryogenic condenser and focusing system is incorporated for trace ppb (parts per billion) analysis.

Different sampling, analysis and detection methods are tested for optimization. The sampling methods include loop injection, charcoal tube, thermal desorption tube, and passive badge sampling. The analysis methods include cryogenic focusing, direct injection and solvent extraction. The detection methods include FID (Flame Ionization Detection), PID (Photo Ionization Detection) and PAD (Photo Acoustic Detection).

For gas chromatography (GC) analysis, two separate GCs are used. A Varian GC systems, located at McGill University's Environmental Laboratory, is used for the analysis of samples based on solvent extraction and an HP GC systems, located at Concordia University's IAQ Laboratory, is used for the analysis of samples based on thermal desorption for cryogenic focusing. Two sets of capillary columns, 105 meters 3um film, and 30 meters 3um film are used. Different temperature programs from –10°C to +180°Cs are tested for GC separation of VOCs.

The newly developed REM will be tested using the above two GCs, with its own FID. Separate GC PID and infra red PAD systems are also used. REM sampling includes the use of charcoal tubes for solvent extraction, Tenax tubes for thermal desorption/cryogenic focusing, and a sampling loop for cryogenic focusing/direct injection.

ASTM and FLEC sampling will be tested using the same two GCs with own FIDs. Separate GC PID (FLEC only) and infra red PAD (ASTM and FLEC) systems are also used. ASTM and FLEC sampling include the use of charcoal tubes for solvent extraction, Tenax tubes for thermal desorption/cryogenic focusing, and a sampling loop for cryogenic focusing/direct injection.

The newly developed Kappa will be tested using the same two GCs with own FIDs. Kappa sampling includes the use of charcoal tubes for solvent extraction and Tenax tubes for thermal desorption/cryogenic focusing.

3.5 Milestones and Activities

The following are the key milestones/activities of this research:

1. Develop an integrated laboratory based material emission sampling system to incorporate the ASTM and the FLEC.
2. Develop a REM for surface emission referencing.
3. Select the most appropriate sampling approach from a list of active and passive sampling methods including charcoal tubes, thermal desorption tubes and passive badges.
4. Compare the ASTM with the FLEC using the newly developed REM.
5. Develop a new surface emission sampler, the Kappa, for in-situ applications.
6. Compare the newly developed Kappa with the FLEC using the REM
7. Compare the newly developed Kappa with both the ASTM and the FLEC using a real commercial office-based carpet.

3.6 Expected Contributions

Developing a new methodology involves a choice between adapting existing ones to the research at hand or, creating a new one for adoption. For the purpose of this research the former choice seemed more appropriate. The approach selected for answering the question statement of this research is basically an adaptation and modification to existing and standardized methods and tools used in industrial hygiene sampling. Environmental chambers are already used in toxicological research laboratories. Emission chambers are but an adaptation of those environmental chambers to the field of surface emission sampling. Active and passive sampling using tubes or badges are standard industrial hygiene sampling methods widely used to capture VOCs. These sampling methods are adapted for in-situ surface emission sampling of VOCs from interior finishes and furnishing in non–industrial settings. Permeation tubes have long been used to generate standard atmospheres in laboratories for calibration of analytical systems.[8]

The REM is only a modification to the permeation tube to mimic surface emissions from interior finishes and furnishings. The ASTM and the FLEC are two standard environmental laboratory emission chambers used for building material emission sampling.[9] The Kappa sampler is developed to facilitate in-situ VOC emission sampling from surfaces of interior finishes and furnishings since both the ASTM and the FLEC are practically non in-situ samplers. The contribution of this research to the field of indoor air quality is mainly on its novel and simplified approach to in-situ surface emission sampling. The latter provides the answer to the current limitation present in identifying sources of indoor VOC emissions, in-situ.

In addition to the novel in-situ emission sampler, the Kappa, a novel reference emitting material, the REM, is another contribution to the field of quality control and assurance (QC/QA) in material emission sampling. There are also other latent and secondary contributions that result from the course of this research. These include the limitation of capillary-canister sampling and passive diffusive badge sampling. Reference to these secondary contributions will be mentioned in the upcoming chapters and the associated appendices.

Endnotes

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Chapter Four

A Reference Emitting Material (REM)

Emission chambers are used to estimate VOC emission rates from samples of interior finishes or furnishings. Bulk samples are usually cut and taken from building interiors and brought into a laboratory for VOC emission testing. Toluene is normally used to generate a reference atmosphere inside the chambers. The reference concentration is then compared with the emitted VOCs from finishes and furnishing for emission rate calculation. Typically, reference VOC generation procedures include either the use of calibration gas cylinders, syringe infusion pumps, capillary diffusion vials or permeation tubes.

4.1 A Novel Reference

Emissions from planar, dry, and solid building materials are diffusion controlled and are generated from within the emission chamber from a dry, solid and planar surface. The application of some of the aforementioned VOC generating procedures as a standard reference material (SRM) for diffusive-based emissions from planar building materials is indeed limited.

A novel reference emitting material (REM) is developed to represent surface emissions from planar surfaces. Several REM prototypes were designed and tested. Different container cells such as glass, aluminum and stainless-steel were tested. Different thicknesses of permeating Fluorinated Ethylene Propylene (FEP) Teflon-based DuPont polymer films were tested. Different methods for sealing the membranes were evaluated. Different sizes of REMs with different membrane surface areas were also examined.

Weight loss was used as the basis for calculating permeation rates. Due to the sensitivity of the laboratory microbalance system used, the maximum allowable sampling weight of the REM, including its configuration, composition and VOC source, could not weigh more than four grams. This presented a major design and fabrication challenge. However, once a number of such "micro" REMs were built, each with different surface permeation areas including $1 \mathrm{cm}^2$ and $0.5 \mathrm{cm}^2$, extrapolation to larger surface areas was to be performed. Results could be partially verified by comparing both the larger REMs and the micro ones with standard VOC generated atmospheres. The standard atmospheres were to be generated by using certified permeation tubes. Although permeation tubes are not the ideal method to generate standard atmospheres, they are the most representative from among the other standard generating techniques available. Trace VOC analyses were also performed using two emission chambers, the ASTM and the FLEC. Inline sampling using Photo Acoustic Detection technique, Photo Ionization Detection technique and Gas Chromatography Flame Ionization Detection technique with cryogenic focusing were used. Details of each one of these experimental setups are presented.

As it pertains to permeation rate calculation of the primary mini-REMs, the weight loss of VOC source within each mini-REM, that is the permeation of a VOC through a membrane, were monitored by a microbalance over an extended period of time. Special data acquisition software (TAL Technologies, Philadelphia PA, with an in-house modification) was used to monitor and record the time average weight loss along with room temperature and relative humidity.

The microbalance used was located in a conditioned room representing a normal office room conditions, with a fluctuating temperature range of 23°C to 29°C. This range is representative of most non-industrial indoor environments. To control for the influence of asymmetrical radiant temperature fluctuations, effect of sun light, a black curtain was placed permanently on the windows of the room in which the microbalance is located. The acquired data was analyzed to calculate the permeation rate of the mini-REMs.

The effects of environmental conditions on permeation rates were also monitored. Pure chromatography grade liquid Toluene was used as the emitting source. The selection of Toluene as the VOC for the mini-REMs was based on parameters that are explained below. Once emission rate, weight loss from the mini-REMs was monitored, larger REM replicas with different sizes, shapes and volumes were built for emission rate extrapolation. Extrapolations of emission rates were aimed, at the outset, to be based on results from the initial mini-REM experiments. However, due to analytical limitations, as explained below, several modifications to the experimental setup were made. In short, three full-scale REMs were finally built to mimic a surface emission in terms of VOC diffusive transport, by a dry and solid planar material occupying the same size, shape, and volume within an emission chamber or cell.

4.2 Methods

Different methods were used to quantify the emission rate of a REM. The first method was based on the physical property of weight loss using a microbalance. The second method was based on the response of a photo ionization detector. The third method was based on the response of a photo acoustic detector. The fourth method was based on the response of a flame ionization detector. The following present the different methods and the related experimental setups.

4.2.1 The Microbalance Method

Figure 4.1 presents the experimental setup used to estimate the emission rate of a mini-REM. The mini-REM was machined and custom-made using a high purity aluminum (petri-dish like design: 20mm∅, 4mm thick) designed with a sealable cover that accommodates a permeation membrane with a net surface area of 1 cm^2. The mini-REM weighs 2.273 grams (Sartorius 2S electronic ultra-microbalance ± 0.002 mg accuracy). Different permeation membranes were used in the mini-REM experiments. A specially selected O-ring provided a seal between the aluminum petri-dish, the membrane and mini-REM's cover. 0.2 ml of liquid Toluene was transferred into the min-REM. Figure 4.2 illustrates the design of a mini-REM with a sealing O-ring to prevent toluene from escaping from the threaded edges of the mini-REM and only allowing permeation through the membrane.

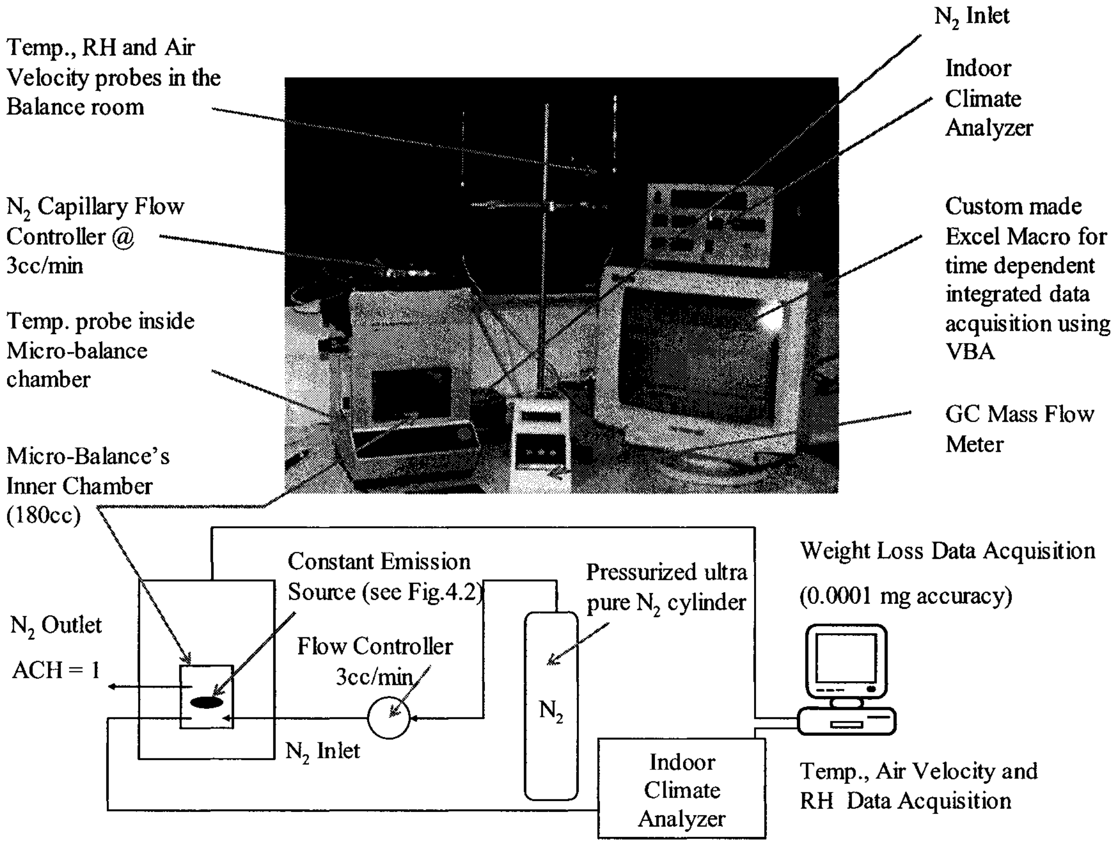


Figure 4.1: A micro-balance to estimate weight loss of a mini-REM.

The mini-REM was placed inside the housing of the electronic microbalance, a small glass chamber having a volume of 180cc (cubic centimeter). The mini-REM was left inside the balance for the duration of the experiment (~33 days). A Teflon tube was gently inserted into the housing of the electronic microbalance to supply a flow of nitrogen at a constant rate of 3cc/min. A capillary column of 0.1 um diameter was used to maintain and control the flow.

Based on the above flow rate and chamber volume, air exchange rate inside the weighing chamber is estimated at one unit per hour (ACH = 1).

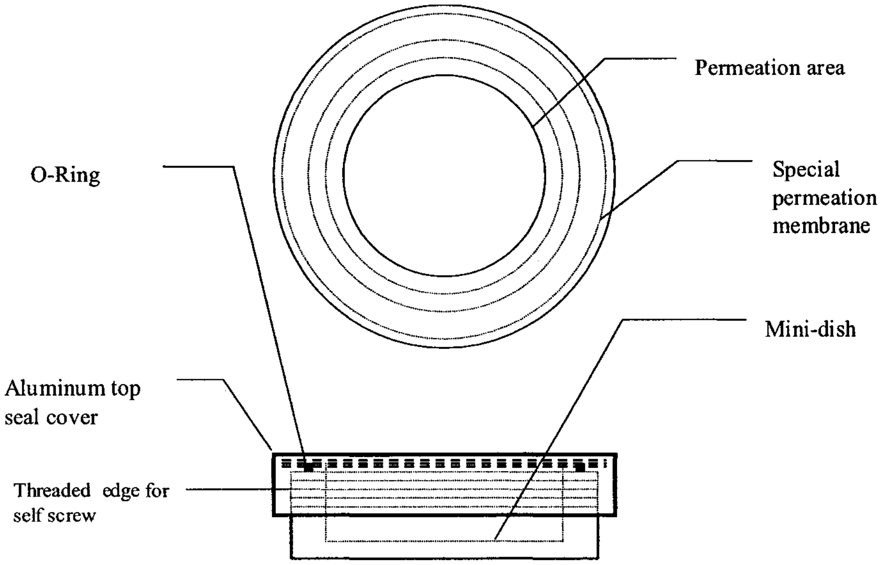


Figure 4.2: Mini-REM (2.273 grams, 20mm ∅, 4mm thick, 1cm^2 permeating surface).

The weight loss of Toluene permeating from the mini-REM was recorded. Data was acquired once every minute for approximately 33 days. A data acquisition program with a dedicated computer was used. The average rate of the mini-REM's weight loss was estimated at 2ug per min. The weight loss followed a linear regression with an R^2 of 0.99, Figure 4.3.

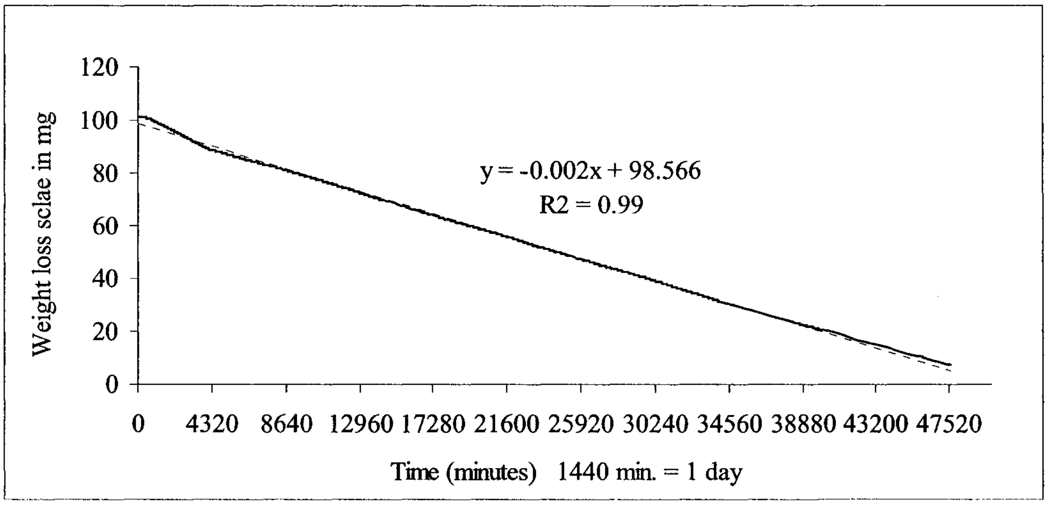


Figure 4.3: Mini-REM emission rate at 2ug/min.

Room temperature during the experiment was recorded, tagged and matched with sampling points as represented by each weight loss records. Figure 4.4 presents temperature records matched with the time of weight loss record data during the experiment.

The software used provided a tag for each record allowing respective time synchronization between all the measuring instruments including the microbalance, two temperature sensors and room air velocity sensor. Average room air velocity was recorded to be < 0.8 cm/sec. Although only matched records are presented, the trend can be observed. The objective is to present matched temp-weight loss profile to indicate the constancy of emission rate by the mini-REM during normal indoor temperature fluctuations (24°C-29°C). Humidity was measured using a hair hygrometer with a strip chart recorder. RH ranged from 30% to 60% (± 5%).

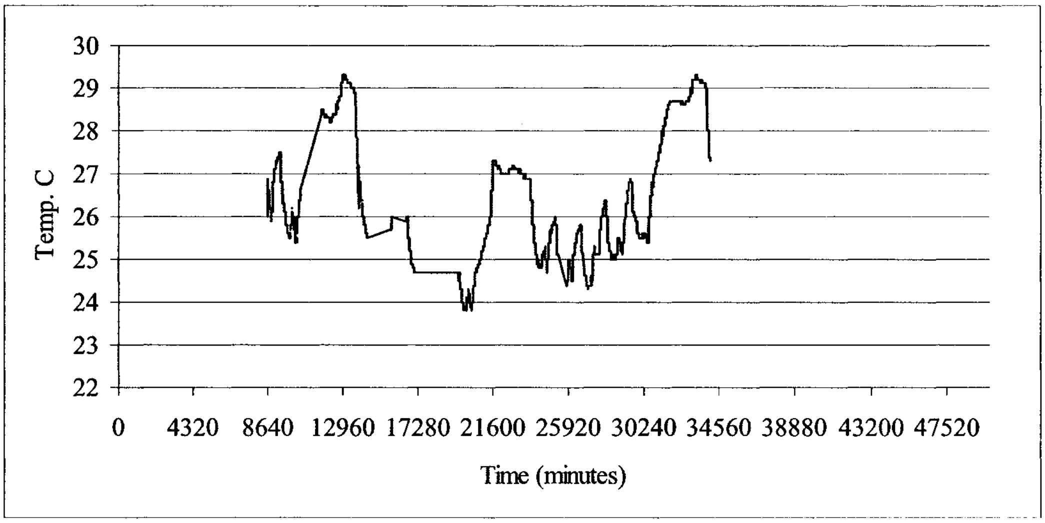


Figure 4.4: A sample of temperature profile during mini-REM's weight loss experiment matched with the time line (x-axis) of Figure 4.3 above.

4.2.1.1 Membrane Thickness

Scaling the above mini-REM into a realistic size that can be used in environmental chambers and that mimics the size of building material samples for example, 30cm by 30cm carpets, ceiling tiles, etc. produces a REM that generates a large amount of toluene that is not applicable to low emission profiles from interior finishes and furnishings. For example, using the FLEC (Field and Laboratory Emission Cell) as a surface emission sampler, a FLEC-based REM with a surface emitting area of ~177cm^2 would emit in excess of 350 micrograms of toluene per minute-- using the same permeation membrane used in the original mini-REM. With a recommended FLEC inlet flow rate of ~250cc/min, an equivalent in-cell VOC concentration of some 1416 mg per m^3 would be generated *(Concentration = Emission rate / Flow rate)*. This is at least 1000 times the average amount of VOC concentrations found in indoor non-industrial environments. The membrane used would thus need to be replaced by a thicker one to reduce emission rate of the mini-REM to at most 2 nanograms per minute (ng/min.). With such an emission rate, a FLEC-based REM would emit its VOC at a rate comparable to those found indoors.

4.2.1.2 Microbalance's Detection Limit

A thicker permeation membrane was selected to replace the thinner membrane. A similar test was performed under the same setup and operating conditions. Weight loss data was again recorded. Figure 4.5 summarizes the weight loss data of the mini-REM with the modified thicker membrane. It is observed that the recorded weight data is at the level of the background noise of the microbalance. An interesting observation can also be observed from the recorded data. Background noise diminishes during nighttime data acquisition. This is supported by the fact that the room where the microbalance is located, McGill University's environmental research laboratory, is adjacent to a city wide underground transportation network, the underground subway. The subway train operating times matches that of the start and end of the observed excess background noise.

The slope of the straight line shown in Figure 4.5 represents the weight loss during the "quiet/vibration-free" nighttime period. From this slope an emission rate of some 10ng per minute is estimated. As a result, a time protocol restricting sampling record to nighttimes was used. However, upon closer evaluation of the results it was realized that a 10ng weight-loss record is well below the operational limit of the microbalance. The reliable repeatability of the microbalance is at 2ug (micro-gram). The experimental setup used was deemed inappropriate to test any low emitting REM below the 2ug/min rate. The use of a microbalance as a mean to record the weight-loss of low emitting reference surfaces is beyond the instrument's capability. Other means need to be investigated.

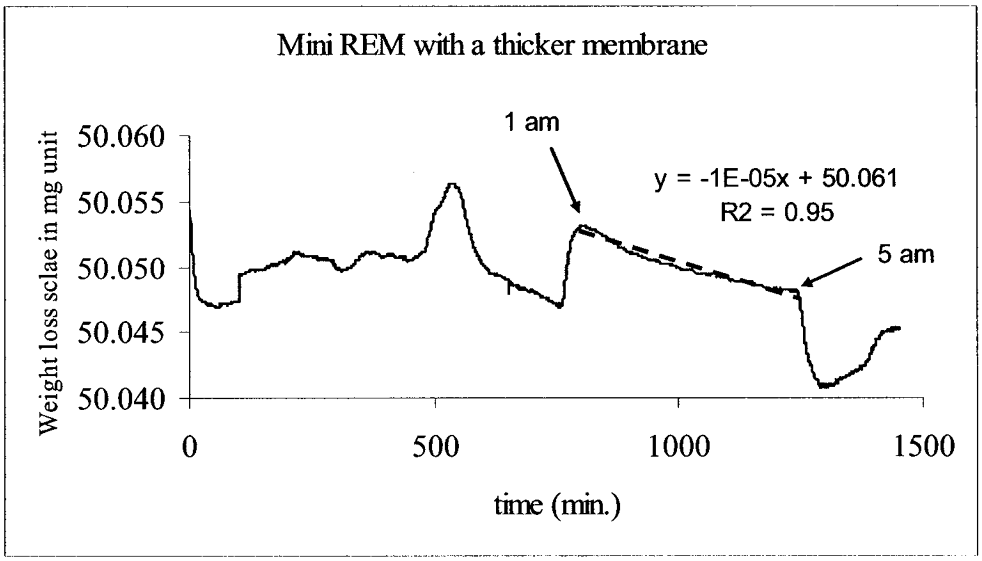


Figure 4.5: Weight loss profile of a mini-REM with a thicker permeation membrane. REM's weight loss during nighttime "quiet" period estimated at 10 nanogram per min. (Microbalance's Detection Limit is 2 micrograms)

4.2.1.3 O-Ring's Solvent Reaction

The quality of the O-ring used to seal the mini-REM was also found to be a source of contamination. During all tests it was observed that the color of liquid toluene inside each mini-REM gradually changed from a normal colorless liquid to dark yellow. On closer investigation, it was found that the O-ring reacted with the saturated vapor of toluene inside the mini-REMs. The O-ring used was a common Buna-N (Nitrile) O-ring. The Buna-N O-ring was replaced by a

Polytetrafluoroethylene (PTFE) Teflon-based O-ring. Subsequently, the reaction that led to the color change of Toluene inside the REMs was eliminated.

4.2.2 Gas Chromatography Photo Ionization Detection Method

Having observed some limitations for the application of a microbalance to estimating weight loss data for a constant emitting source, a more sensitive setup was developed. The new setup replaces the balance with a chemical detector. A GC-PID system (Gas Chromatography - Photo Ionization Detector) was used to measure the toluene concentration inside a specially designed dynamic chamber. Figure 4.6 is a schematic of the chamber used. A mini-REM used previously was placed inside the chamber. An automated injection valve with a sampling loop was used to inject samples at every five minutes interval. The high emitting mini-REM, the one with the thin permeation film, generated consistent chromatographic responses with peak height variations of less than 5%.

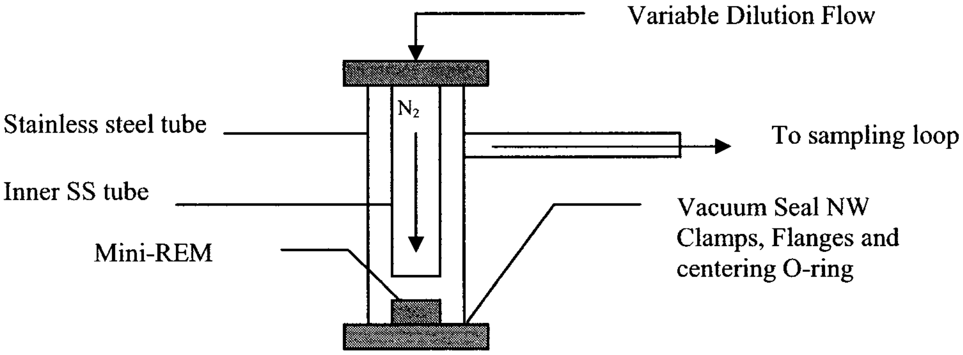


Figure 4.6: Mini-REM permeation chamber at room temperature.

However, the low emitting mini-REM, the one with the thick permeation film, generated chromatographic responses that were at the noise level of the PID. The PID was found inappropriate for measuring the low emitting mini-REMs. The following are the reasons leading to this conclusion.

4.2.2.1 Standard Atmosphere

Generating a ppb (parts per billion) of toluene standard atmosphere is no doubt a challenging task. Measuring it is yet more challenging. Surface adsorption of toluene onto the inner walls of the stainless-steel chambers is a factor that has contributed to the loss of gas-phase concentrations generated by the mini-REMs. To reduce surface adsorption, the supply air flow was humidified. Water moisture tends to occupy any potential sink site and hence repelling VOCs from adsorbing on to surfaces.

4.2.2.2 PID and Humidity

RH (relative humidity) of the inlet flow (dilution flow) greatly influences surface adsorption. In the case of toluene, higher RH reduces surface adsorption. RH may need to be high enough (>50%) to limit toluene adsorption onto surfaces of tubes and chamber walls. This raised the issue of the applicability of the PID in measuring humidified environments. Photo ionizations detectors are sensitive to humidity.[1] Detection will lead to measurement errors.[2] A different detection system that is able to compensate the effect of humidity is required. Hence, a photo-acoustic infrared detector with humidity compensating and toluene-sensitive optical filters was used as an alternative to the GC-PID.

4.2.3 Gas Chromatography Photo Acoustic Detection Method

A REM with a surface area matching that of the surface of the FLEC was designed and machined using the same design principles as those used in the designing of the mini-REMs. The surface area of the scaled-up REM was 177cm^2. The permeation membrane used for this FLEC-based REM is the thick membrane used for the mini-REM. This scaled-up REM was used for an initial proof of concept. The periphery rim of the REM was machined smooth so that the FLEC rests on it and establishes a seal. However, due to an inherent limitation in the design of the inner white silicone O-ring of the FLEC, the edges of the FLEC and the rim of the REM did not make a proper seal.

Addressing the issue of leaks in the FLEC-REM assembly, a new REM was machined in such a way that it can be inserted and flush-fitted directly into the FLEC's standard test plate (Fig. 4.7). The anodized rim surface of the test plate (manufactured by FLEC) provides the smooth surface needed for the FLEC to provide the appropriate seal needed. This however, reduced the REM's net emitting surface area form 177 cm^2 to 95 cm^2.

Two other REMs were similarly machined with net emitting planar surface areas of 38 cm^2 and 7 cm^2 respectively. These three REMs (95 cm^2, 38 cm^2, and 7 cm^2) are referred to as REM-L, REM-M & REM-S (large, medium and small). Details of emission rates obtained using these three REMs are presented in upcoming sections.

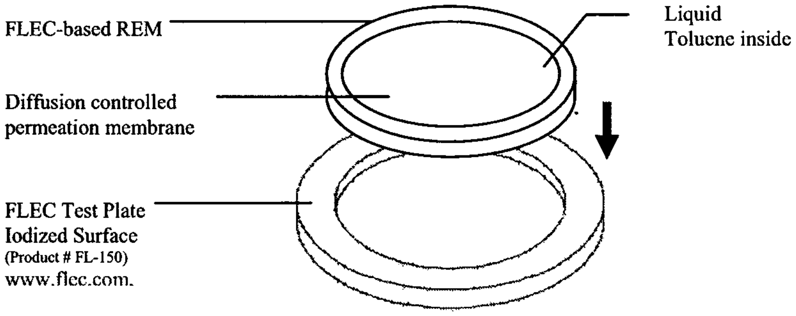


Figure 4.7: FLEC-based REM.

Because of the results of the microbalance and the PID tests, a new experimental setup was designed. In this setup the GC-PID was replaced with an infrared photo acoustic detector (IR-PAD). The IR-PAD can compensate for different moisture contents hence reducing the error in detection. Details of the configuration of the system are outlined in Figure 4.9. The system was calibrated using standard and certified permeation tubes at 60°C. To maintain and control permeation cell temperature, a water bath was used. The mini-REM permeation chamber, Figure 4.6 above, was used as the permeation cell. A stainless-steel inlet tube, five meters long, was looped around the cell before air enters the cell to assure temperature stability of the sampling gas, N_2, prior to dilution.

The entire cell assembly, including the looped tube, was immersed into the water bath. Air temperature was measured inside the cell using a mercury thermometer.

Results of temperature measurements have indicated that the bath temperature needs to be set at 61.8°C to maintain the N_2-stream temperature at 60°C inside the permeation cell. Maintaining this temperature at an exact level is critical for permeation rate stability and hence calibration purposes. Maintaining precise temperature for toluene permeation tubes requires sophisticated temperature control ovens. Such ovens can only be found as GC ovens. Standard laboratory ovens can only control and maintain temperature to within ±2.5°C. It was due to this reason that a water bath was used instead of an oven. Using low rate (<2000ng/min) toluene permeation tubes at a temperature greater than 30°C needs an accurate temperature control and recording system.

Volatility of toluene at normal indoor air temperature ranges, 20°C to <30°C, is almost similar to the volatility of water. Table 4.1 presents the saturated vapor pressures of both water and toluene at indoor air temperatures. This relative low volatility is realized when it is compared with benzene's saturated vapor pressure of 95 mmHg at 25°C. Hence, the influence of indoor temperature fluctuations may not greatly affect toluene permeation rates to an extent more than that of water evaporation at room temperature. At temperatures greater than 30°C any minor change in temperature would greatly influence the evaporation of toluene and subsequently the toluene permeation rate (Fig. 4.8). This fact has been considered to justify the selection of toluene as an appropriate solvent for the REM and its application as a standard reference emitting material for surface emissions at normal indoor conditions.

Table 4.1: Toluene versus water - comparison of saturated vapor pressure at indoor air temperature limits.

Temperature	Water	Toluene
20C	18 mmHg	22 mmHg
25C	24 mmHg	28 mmHg
30C	32 mmHg	37 mmHg

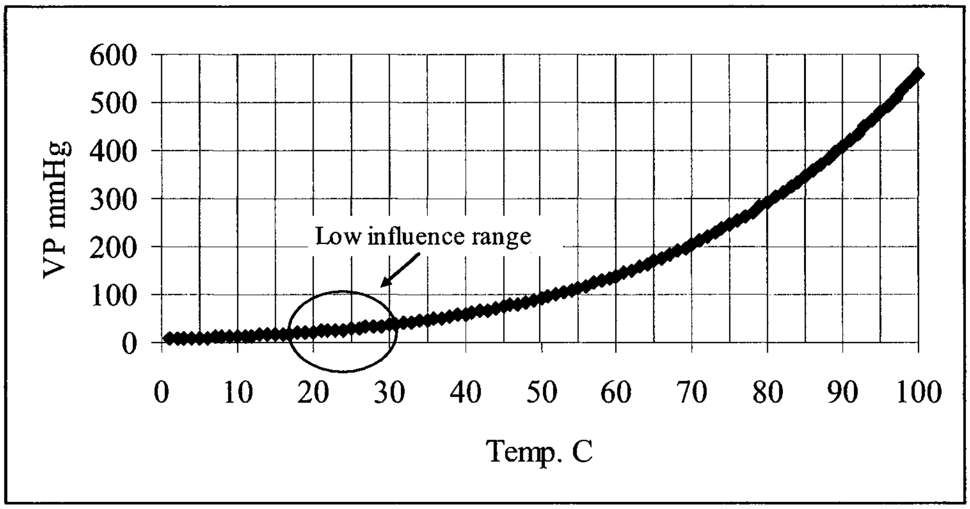


Figure 4.8: Relative influence of temperature on vapor pressure of toluene. The vapor pressure of toluene is estimated by the empirical relation:

$ln\ P_{sat} = 13.9987 - (3096.52 / (219.48 + t))$

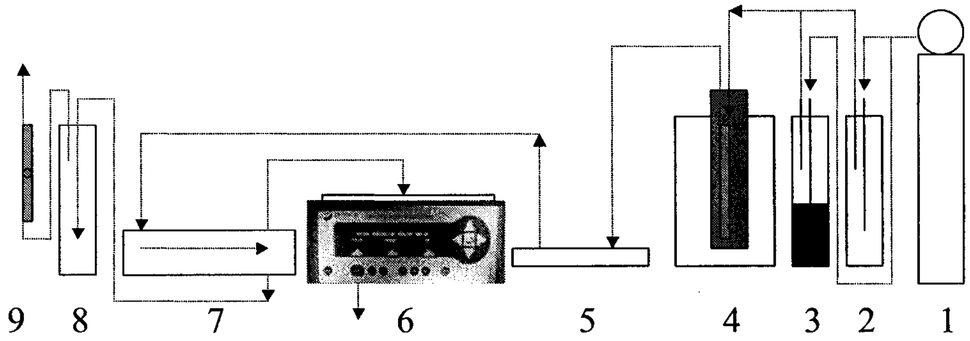
t is in degree C and P_{sat} in kPa (1 mmHg = 0.133 kPa).

In this setup, the medium size REM (REM-M) was used to test the overall performance of the system and to estimate the REM's emission rate. The emission rate was estimated using a 5-point calibration curve (4 standard certified toluene permeation tubes and a system baseline). Emission rates of permeation tubes used were 497 ng/min, 766 ng/min, 1078 ng/min, and 1665 ng/min. All permeation tubes were used at its recommended certified flow temperature of 60°C. Each tube was placed inside the permeation cell/chamber and submerged in a temperature controlled water bath as descried earlier.

A micro-flow controller maintained a constant N_2 flow rate to the permeation chamber at 262 cc/min. A humidification chamber with Nafion tubing was used to control the moisture content of the standard generated atmosphere. An on-line infrared photo-acoustic detector (IR-PAD Bruel and Kjaer photoacoustic analyzer; B&K Model 1312) was used to measure the concentrations of the standard generated toluene atmospheres at different moisture contents.

Having established the response of the systems to the different permeation tubes at different moisture contents, the REM-M was placed in a Field and Laboratory Emission Cell (FLEC). The concentration in the FLEC was detected by the IR-PAD using the same dilution flow and conditions used during permeation tubes and baseline experiments. Figure 4.10 summarizes the results.

The top four regression lines as shown in Figure 4.10 are the responses of each permeation tube. Regression equations are also listed for each tube in respective order. The first equation is for the top line representing the 1665 ng/min permeation tube. The second equation is for the following line representing 1078 ng/min permeation tube. The fifth line however is the response of the REM-M used. The last line, dotted, is the baseline response of the system with pure N_2.



1. Pure Nitrogen Supply Cylinder (80psi) with a GC-quality micro flow controller (0-500cc/min. ± 1cc/min).
2. Dry glass mixing buffer chamber (Dry).
3. Humidified glass mixing buffer chamber (partially filled with purified water) with a Nafion tube placed above the surface of the water.
4. Permeation Tube Cell 5m mixing loop embedded in temperature controlled water bath (± 0.1C).
5. FLEC (Field and laboratory Emission Cell) with FLEC's own test plate. To further improve the seal between the FLEC and its test plate three small carpenter clamps were used to apply pressure on both the FLEC and the Test Plate. The REM was placed inside the test plate.
6. Infra-Red Photo Acoustic Detector (IR-PAD) with Moisture (H2O) compensation and VOC (Toluene) sensitive optical filters.
7. Stainless Steel Mixing Buffer Chamber (1 Liter)
8. Glass Mixing Buffer Chamber
9. Floating ball (stainless steel) flow meter to seal any air backflow during IR-PAD sampling run (IR-PAD sampling pump at ~250CC/min).

Figure 4.9: IR-PAD emission rate detection system for REMs.

From the regression equations, one can observe the stability of the values of the slope. This is an indication of the precision of IR-PAD response and its repeatable and consistent compensation for humidity at different toluene concentrations and humidity levels. Y-intercepts are concentration factors. Taking the value of each y-intercept and plotting it against corresponding permeation rate of each tube generates the calibration curve outlined in Figure 4.11.

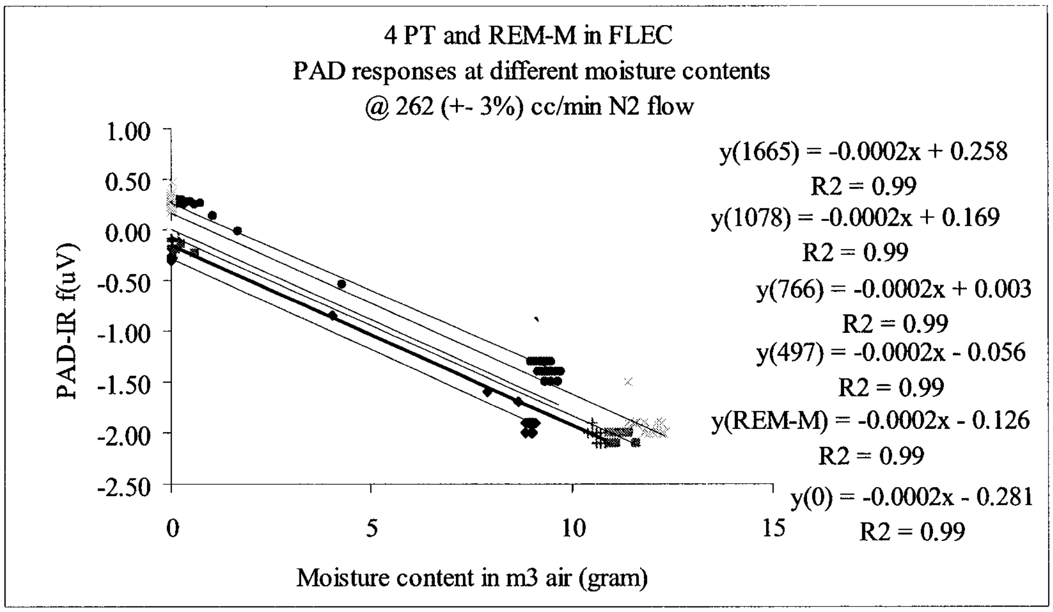


Figure 4.10: Emission rate from the FLEC-based REM-M.

Using the calibration equation, Figure 4.11, the emission rate for the FLEC-based REM, that is the REM-M, is estimated at 419 ng/min, or 11.0 ng/min.cm^2 (based on REM-M surface area of 38 cm^2).

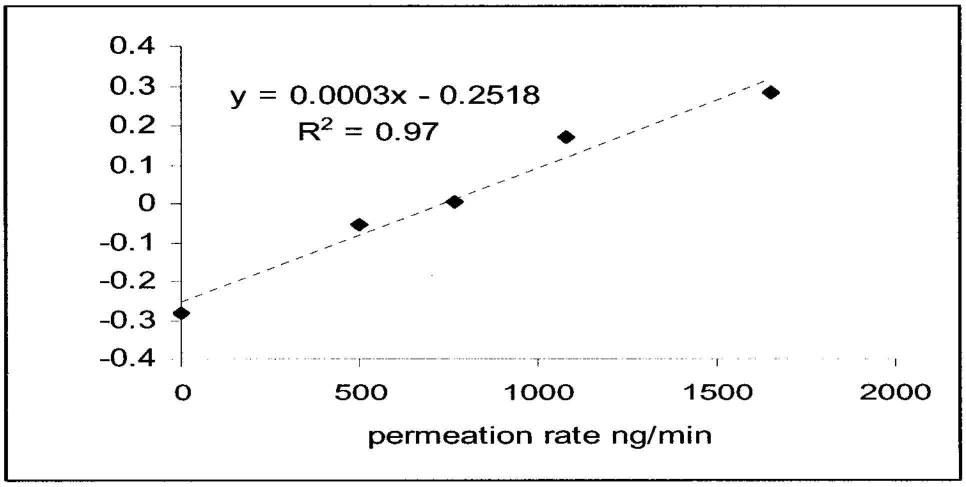


Figure 4.11: Five point PT calibration (Y-Axis = PAD-IR response scale).

4.2.4 Gas Chromatography Flame Ionization Detection Method

REM-L, REM-M, and REM-S were tested using an FID method. The aforementioned permeation tubes were used to calibrate the FID system. IR-PADs are rarely used to sample surface emissions since the PAD, although extremely sensitive and compensating, are not specific. Although the issue of detection specificity is not important for the REMs, it would become important when the scope of this research moves towards field sampling of surface emissions from interior finishes and furnishings with unknown VOCs. The objective, at this stage, is to develop a reference emitting material that emits a very low but constant amount of a VOC from a planar surface at room temperature.

Each REM tested, REM-S, REM-M, and REM-L, had an emitting membrane with a surface area of 7, 38, and 95 cm^2 respectively. The following presents the experimental set-up used and the experiments conducted to test the application of the novel Reference Emitting Materials using two industry-accepted VOC emission samplers commonly used for building material VOC emission sampling, the ASTM-based 50-liter environmental chamber and the FLEC.

Based on conditions of, and results obtained from, the above two-industry accepted emission samplers, additional tests were carried out to evaluate, as a proof of concept, the response of both the FLEC and the newly developed material emission sampler, the Kappa, to the REM. Details on the FLEC and the Kappa REM sampling are presented in a later chapter. In this chapter however, emission rates of the three REMs and the extent of the observed variations between the ASTM and the FLEC are reported.

4.2.4.1 The ASTM, the FLEC and the REMs: Setup

An ASTM-based 50-Liter chamber and the Danish FLEC were both used in this study as two accepted standards for material emission sampling. The ASTM-based chamber used was equipped with a specially designed equilibrium preservation mechanism, chamber gate that conserved the loss of equilibrium conditions achieved within the chamber during insertion and extraction of the REMs in and out of the chamber. The new insertion/extraction technique minimized perturbation effects during specimen insertion/extraction and conserved the quasi-equilibrium state achieved inside the 50L chamber. The mechanism is similar to a drawer with each end acting as a door. The chamber became sealed at either drawer positions (open-pulled and closed-pushed). The insertion/extraction of each REM was performed in less than few seconds. Previously, and without this new drawer-like chamber door, insertion of any sampling material into the ASTM-based chamber took at least several minutes due to the numerous screws (>25) that had to be unscrewed each time for material insertion and removal.

Toluene concentrations generated by the reference emitting materials (REMs) inside each of the two chambers (50L ASTM-based & FLEC) were compared and referenced to concentrations generated by the certified permeation tubes (PT) used in the previously presented setup, IR-PAD, with the exception of two PTs. One

PT with an emission rate of 1665 ng/min was replaced with a newly certified PT with an emission rate of 1413 ng/min. The 1665 ng/min permeation tube had reached its expiration date during the experiment and hence it was replaced. Under normal conditions, permeation tubes come with a one-year expiration date from the date of certification. Although each PT could be returned to the manufacture for a re-certification, a decision was made to purchase a newly certified and ready-for-use one since re-certification of an older PT takes 6-8 weeks of testing and re-calibration. A second PT with a very low emission rate of 48 ng/min was added to the set of PTs as an extra point to include a low concentration into the calibration curve.

Both the ASTM-based chamber and the FLEC were connected to a cryogenically concentrating and focusing gas chromatography system equipped with a Flame Ionization Detector (FID). Liquid nitrogen was used as a VOC condensing medium. Helium gas was used as the carrier gas and clean air was used as the sampling gas.

As a measure of humidity control, sampling air was branched into a two-way stream. One stream passed through a humidification chamber (Restek cat. # 24282). The other stream bypassed the humidification chamber and to be mixed later with the former humidified stream inside a stainless steel mixing chamber. A programmable temperature controlled oven (Fisher Scientific Isotemp Model 818F, temperature range 35C to 325C, temperature range uniformity ± 2.75°C) was used for the generation of standard VOC atmospheres generated by the PTs for calibration purposes.

Several simultaneous methods of generating standard VOC atmospheres can be used in the above sampling system. These methods include: 1) a calibration Gas (Scotty TO-14 Calibration Mix 1 @ 100 ppb) with a regulator (Scotty 512AS180SG @ 15 L/min) for flow control; 2) a syringe infusion pump (Fisher Scientific Model KDS100), and 3) permeation tubes (Kin-Tek) in a micro-chamber equipped with 5 meters coiled stainless steel tube (1/8" Ø) placed inside the Isotemp programmable oven. In line with the earlier experimental setups used, permeation tubes were selected to generate low-concentrations of Toluene atmospheres in this experiment. The selection was based on the fact that it allowed relative comparison of results with those obtained with the previous experimental setup used, the IR-PAD, and the diffusive emission mechanism that could be only achieved by using PTs.

The five certified trace-source permeation tubes (KIN-TEK type HRT) with permeation rates of 48 ng/min @ 30°C, 497 ng/min @ 60°C, 766 ng/min @ 60°C, 1078 ng/min @ 60°C, and 1413 ng/min @ 60°C were used to generate standard Toluene atmospheres. Temperature uniformity inside the center core of the oven, where the permeation tube (PT) chamber is placed, was within 2% at 60°C; c.f. ±5% for the entire inner volume of the oven as per manufacturer's specification.

Airflow through the PT chamber (as presented in Fig. 4.6 above but with some minor modification for oven connection) was maintained at 388 cc/min.

Flow rate during the duration of all tests varied by 12%. Average toluene concentrations generated by the PTs using the system parameters mentioned above were calculated by the quotients of PT emission rates (emission rates) by the flow rate of N_2 entering the PT chamber.

$$C = \text{Emission Rate} / F \qquad [\text{eq. } 1]$$

where, C is volumetric concentration in ng/cc; emission rate is the emission rate of each permeation tube in ng/min; and F is the flow rate in cc/min. The average expected concentrations using the above equation were 0.19, 1.28, 1.97, 2.78 and 3.64 mg/m3 respectively for the 48 ng/min @ 30°C, 497 ng/min @ 60°C, 766 ng/min @ 60°C, 1078 ng/min @ 60°C, and 1413 ng/min @ 60°C permeation tubes respectively. Due to temperature range limitation of the oven (Min. at 35°C), the emission rate (emission rate) of the first permeation tube (i.e., the 48ng/min @ 30°C) was extrapolated to 35°C using the following empirical rate correction equation:

$$\text{Log emission rate}_{T1} = \text{Log emission rate}_{T0} + \psi (T_1 - T_0) \qquad [\text{eq. } 2]$$

where emission rate $_{T1}$ is emission rate at the new temperature in °C and emission rate$_{T0}$ is the emission rate at the original temperature which the tube was certified at, and ψ is an empirical temperature coefficient estimated at 0.034 for the permeation tubes used .[3]

Under normal laboratory conditions, the above equation translates to a 10% variation per 1°C change. In other words, for each 1°C increase/decrease in temperature, emission rate increases and decreases by 10%. The oven used in this experiment maintains its core temperature within 2% of the set temperature. Since a 2% increase/decrease from the 60°C oven set point temperature is approximately 1°C, variations in permeation rates due to oven conditions were estimated to be ±10%.

According to manufacturer's specifications, expected accuracy of concentrations generated by permeations tubes were to be within 4% if flow rate and oven temperature were controlled at ±1% and ±0.1°C respectively.[4] Achieving such a level of control in flow rate and temperature was practically beyond the capabilities of the "normal laboratory" flow controllers and the oven used in this setup. It will be thus necessary to take into consideration these variations in emission rates and concentrations generated during the calculations.

In addition, it may also be necessary to correct for the flow rate to a reference condition due to changes in temperature (T) and pressure (P). Many types of flow measuring devices are used to determine flow rate, and each specific type should be considered independently before applying any corrections. For example, in case of bubble flow meters one can apply the following equation to correct for STP (Standard Temperature and Pressure):

$$F_Y = F_X\,(P_X/760) * \{298 / (T_X + 273)\} \qquad [eq.\ 3]$$

where F is the flow rate, $_Y$ annotates a reference condition and $_X$ annotates a measured condition.

However, in case of floating ball flow meters, a different flow principal is involved. The scale of such flow meters is a function of gas density, viscosity and momentum.

In the latter case, the following equation is recommended for STP correction:

$$F_Y = 0.626\,F_1\,(P_X/T_X)^{1/2} \qquad [eq.\ 4]$$

where F is the flow rate, $_Y$ annotates a reference condition (at 25°C and 760 mm Hg) and $_X$ annotates a measured condition.

This experimental setup, as described above, uses floating ball flow meters to control and measure the flow rates in a system. Each floating ball flow meter was checked and referenced by a bubble flow meter. Neither the temperature nor the pressure at the laboratory, where PT and REM tests were preformed, was significantly different from the STP. Hence, it is assumed that room P&T is not a significant factor to influence the readings of the flow measuring devices used.

Laboratory room temperature was 24°C ±3°C and room RH was 45% ±10%. Moisture content in the sampling systems was measured using an infrared photo-acoustic spectroscopy equipped with an optical narrow band filter for moisture detection (Bruel & Kjaer type 1302 optical filter # EB 6009). A water bubbler was used to generate moisturized air at ~17 g/m^3. Based on the temperature of the room, this translated into a mean RH inside the sampling system of ~70% with an observed variation of ± 18%. This high level of RH was used to reduce the adsorption effect of toluene onto the inner surfaces of tubes and chambers. A baseline toluene concentration of the system before and after each run was performed for baseline monitoring. An equilibrium period of 24-hr was used for each set of PT tests.

A portion of each standard generated atmosphere was diverted into a 2cc stainless steel sampling loop (1/8" Ø) while the rest of the flow was vented. The loop was connected into a two-position six-way injection valve (VICI – GC Valco). Sample flow to the loop was maintained at 50cc/min. A single needle valve was used to control the flow rate into the loop and consequently diverting the remaining flow to a restrict-free vent. This configuration was deemed necessary to limit/reduce flow rate fluctuation as the result of the backpressure generated by the six-way injection valve.

The flow rate to the vent was periodically measured to check and balance the system. As mentioned earlier, the flow rate of the system varied by as much as 12% during the course of the tests. Along with the aforementioned backpressure, variation in flow rate could be attributed to the overall plumbing of the system that includes multiple connections in series and in parallel of flow meters and valves. Other contributing factors to the flow rate variation may be attributed to inherent leaks in both the ASTM and the FLEC chamber/cell.

Once a sample was collected in a 2cc loop, the content of the loop was carried by Helium gas (at 40 cc/min) to a cryogenic condenser (Tekmar 14-6000 modified for on line injection). A glass bead column was used as the condensing medium that was cooled with liquid nitrogen to (negative) -100°C. At this temperature any sampled Toluene would be condensed. During sample condensation, a pre-programmed moisture removal cycle (Moisture Control System – MCS within the Tekmar 6000 system) expunged the condensed H_2O from the cryogenic process. The resulting dry sample was desorbed at 250°C and transferred through a heated nickel tubing to a cryogenically cooled focuser for a second stage sample concentration at (negative) –100°C (Tekmar Cryofocusing Module 14-2530). At this stage, all the toluene sampled is focused at the tip of a deactivated thin-wall silicon-treated stainless steel pre-column (Restek MXT-Guard ID 0.53 cat. 70046). The tip was heated to 250°C and the sample was injected by a spilt-less injection port into the GC-FID equipped with a 105m fused silica capillary column for separation (Supelco - VOLCOL 105m x 0.53 mm x 3um film).

Separation of Toluene was achieved within 10 minutes (retention time 8.73 with FID) of the GC run. GC's (HP 5890 series II) oven program was set at 60°C ramping to 160°C at a rate of 10°C/min. Detector temperature was set at 250°C and flow rate to the column (He) was set at 8 cc/min, H2 (to the FID) at 30 cc/min, Air (to the FID) at 330 cc/min and N2 (auxiliary gas to the FID) at 27 cc/min.

4.2.4.2 The ASTM, the FLEC and the REMs: Analysis

The time required to establish equilibrium for toluene concentration in the system as represented by FID responses for each set of PT injections was estimated to be between the 12-hr and 24-hr range. Figure 4.12 illustrates the time-till-equilibrium of one dozen repeated air samples from one specific PT, 1078 ng/min at 60°C. Based on experience gained using the sampling system, a minimum of 12 hours in-between PT sampling and a minimum of 30 minutes in between loop injection were established as the equilibrium-time protocol for the remaining of the tests. The 30 minutes in-between loop injection was to allow sufficient time for flushing-off toluene from the 2cc sampling loop between each injection.

Figure 4.13 presents the results of the five point system calibration attained using the five certified permeation tubes. Each data point is the mean value of FID responses of a set of direct on-line injections. Twenty two separate injections were conducted. Experimental coefficient of variation (Standard Deviation / Mean) of mean FID responses to each PT standard generated atmosphere ranged from 5% (for the high emission rate PT) to 17% (for the low emission rate PT). Table 4.1 presents the FID responses of the five permeation tubes. Based on results obtained, an empirical detection limit for the setup was estimated at 100 ug/m^3 or >25 ppb at FID response of 750.

Variation of concentrations that could have been generated by the same permeation tubes used in this test is highly dependent on the stability of the oven temperature and system flow rate.

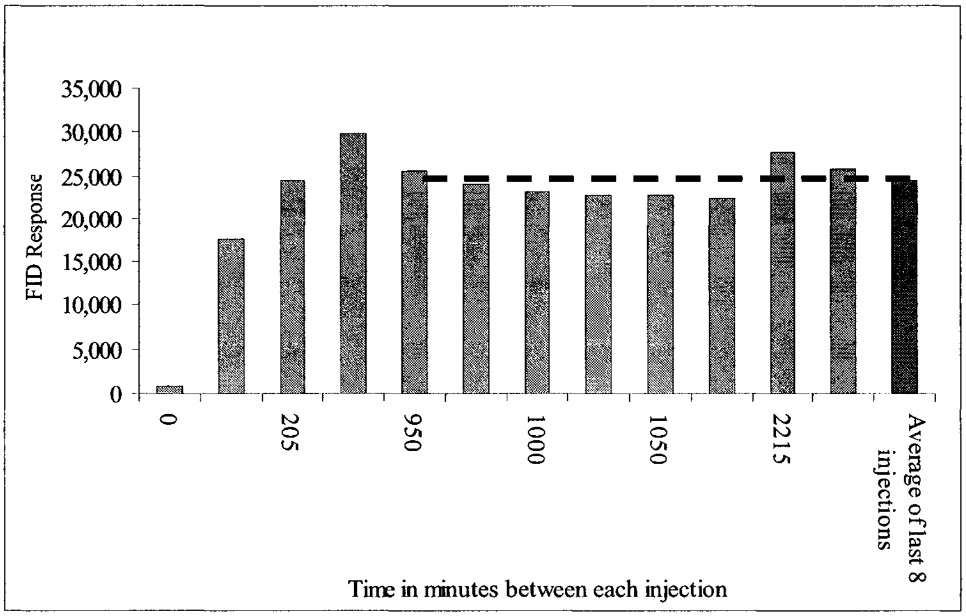


Figure 4.12: FID response of 12 time-interval on-line GCFID sampling of a Toluene standard atmosphere generated by a permeation tube using a 2cc-sampling loop.

As mentioned earlier, incorporating oven temperature and flow-rate variations need to be included in the calibration curve of the system. To estimate the effect of oven temperature and flow rate variations, the average values used in the calculations presented in Table 4.2 were replaced by respective distributions estimated by the means and the standard deviations of the input parameters, oven temperature and flow rate.

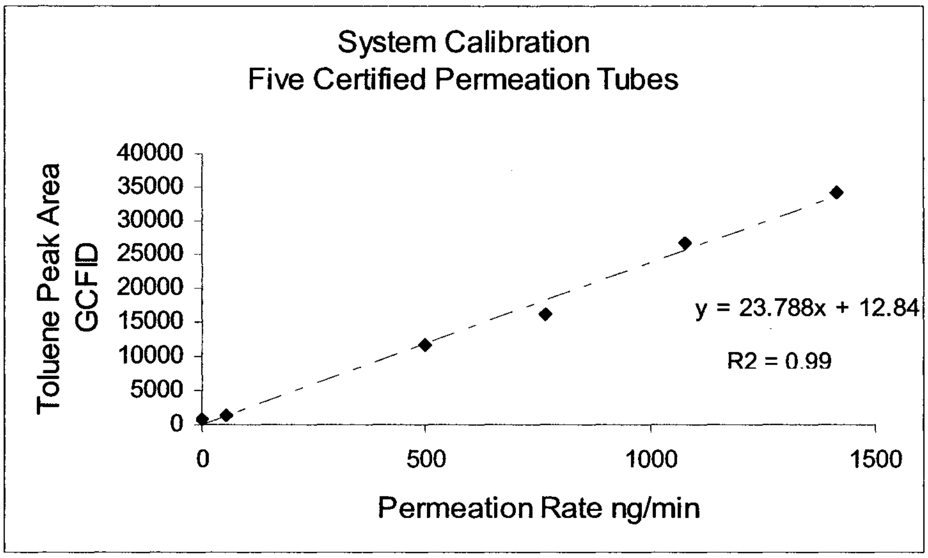


Figure 4.13: Responses of the FID cryogenic system to low-level Toluene emissions by five certified permeation tubes – The first point in the Figure (close to the y-intercept) is the baseline response of the system.

Table 4.2: Mean FID cryogenic system response to the five permeation tubes.

Permation Tubes (ng/min)	**1413**	**1078**	**766**	**497**	**48**
Number of Loop Injections	*5*	*8*	*4*	*2*	*2*
Mean (FID* Response)	*34225*	*24286*	*16122*	*11187*	*1258*
SD* (FID Response)	*1701*	*1879*	*1241*	*907*	*209*
CV* % (FID Response)	*5.0*	*7.7*	*7.7*	*8.1*	*16.6*

*FID (Flame Ionization Detector); SD (Standard Deviation); CV (Coefficient of Variation).

A Monte-Carlo (MC) simulation with 5000 sample iteration was used to incorporate these variations (mean 60°C; SD 1°C for oven temperature; mean 388cc/min; ±12% for chamber flow rate). The potential variation in PT generated concentrations due to the influence of these two input parameters is presented in Table 4.3 below. These variations will be taken into consideration during the calculation of emission rates by the REMs in a later section.

Table 4.3: A 5000 sample iteration using a Monte-Carlo simulation program by @Risk, Palisade Inc.

Permation Tube (ng/min)	**1413**	**1078**	**766**	**497**	**48**
Minimum (ng/cc)	2.94	2.24	1.60	1.03	0.11
Mean (ng/cc)	3.66	2.79	1.98	1.29	0.14
Maximum (ng/cc)	4.51	3.42	2.47	1.60	0.18
Standard Deviation (ng/cc)	0.28	0.22	0.16	0.10	0.01
CV %	7.7	8.1	8.2	8.2	8.3

Having established the system calibration curve, a REM-S (small size), a REM-M (medium size) and a REM-L (large size) with respective planar permeating surfaces of 7, 38, and 95 cm^2 was each alternately and separately placed inside the ASTM-based chamber and the FLEC. As explained, the design of the REMs with its circular and planar shape was made such that each REM precisely fitted inside FLEC's Test Plate chamber (Chematec # FL 150).

All conditions of the system including flow rate, temperature, RH, sampling and analysis procedure, were kept similar to that of the conditions used during the sampling and analysis of the standard atmospheres generated by the permeation tubes. The only modification was to allow the flow of air to bypass the permeation tube chamber and directly flow either into the FLEC or into the ASTM-based chamber.

Baseline toluene background samples of the system, the empty FLEC and the empty ASTM-based chamber before and after each REM test were performed. In line with the equilibrium time protocol established earlier, each REM was allowed to equilibrate inside each chamber for a minimum of 24-hr before sampling. An in-between loop injection period of 30 minutes between each repeated sample injection was also used.

Table 4.4, Figure 4.14, and Figure 4.15 present emission results of the three REMs placed separately inside both the FLEC and the ASTM-based chamber. The two chambers produced comparable results and the three REMs exhibited steady and matching emission rates per unit area.

Results indicate that the REMs generated toluene emission with a coefficient of variation (based on average FID responses) ranged from 3% for REM-L, 6% for REM-M, and 9% for REM-S despite fluctuation in the indoor temperature of the laboratory in which the tests were performed (24°C ± 3°C).

Table 4.4: Mean emission rates by the there REMs based on average FID responses of the five permeation tubes.

REM (Surface Area)	50L ASTM ng/min; ng/cm^2.min [± 1 SD]	FLEC ng/min; ng/cm^2.min [± 1 SD]
n	5	5
REM Small (7 cm^2)	79; 11.3 [91– 67]; [13.0-9.5]	87; 12.4 [100 - 74]; [14.3-9.6]
REM Medium (38 cm^2)	449; 11.8 [494 – 404]; [13.0-10.6]	435; 11.4 [479 - 391]; [12.6-10.3]
REM Large (95 cm^2)	996; 10.5 [1051 - 971]; [10.6-10.2]	964; 10.1 [1012 - 916]; [10.7-9.6]

Mean estimated emission rates of the REMs based on the above experiments in both the ASTM and the FLEC are 83, 442 and 980 ng/min (or 11.9, 11.6 and 10.3 ng/min.cm^2) for REM-S, REM-M, and REM-L respectively. REM-M has been used in a different experimental setup using a different detection method (see the Photo Acoustic Detector setup above).

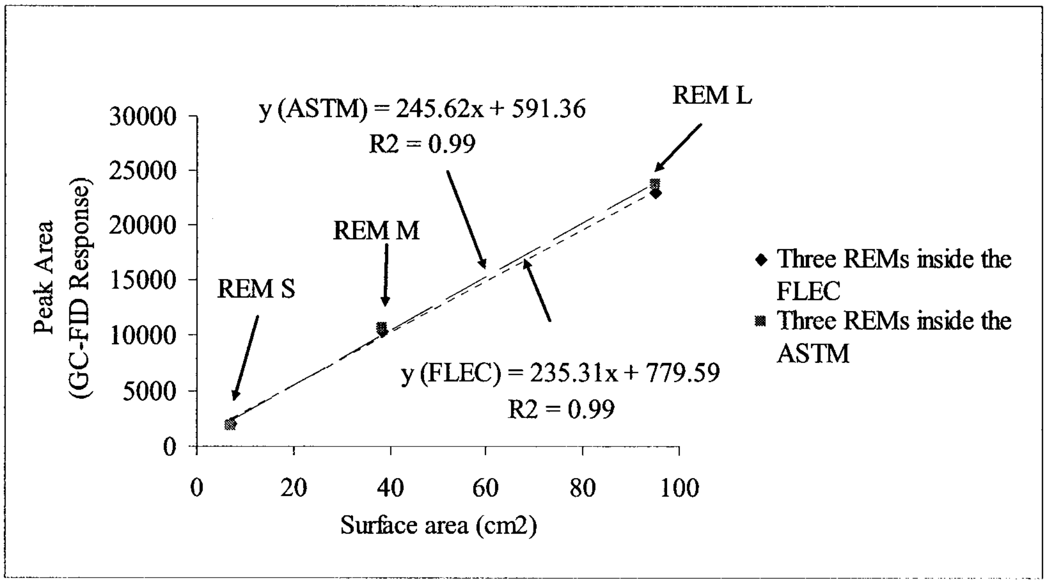


Figure 4.14: Sampling results of three REMs placed inside the FLEC and the ASTM under similar conditions.

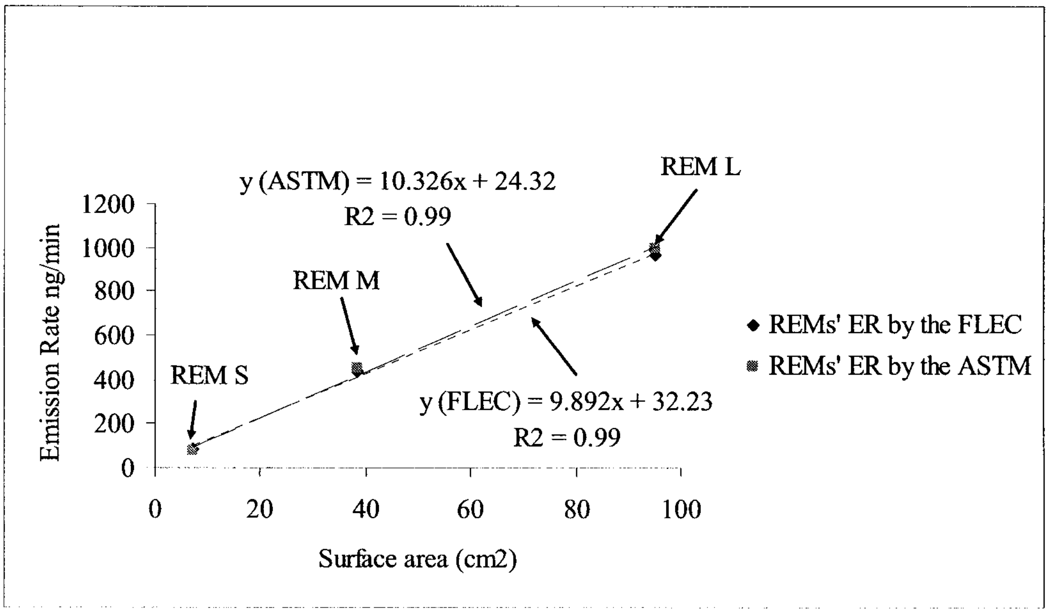


Figure 4.15: Calculated emission rates of the three REMs placed inside the FLEC and the ASTM. Emission rate values are referenced on certified permeation tubes under similar conditions.

The estimated emission rate for REM-M with the FLEC using the PAD was 419 ng/min or 11.0 ng/min.cm^2. According to Table 4.4, the calculated emission rate for REM-M with the FLEC using the FID was 435 ng/min or 11.4 ng/min.cm^2. This translates into a difference of less than 5% using two entirely different settings as well as sampling and analytical methods.

4.2.4.3 The ASTM, the FLEC and the REMs: Simulation

The predicted variation in the 5-point calibration curve as estimated by the Monte Carlo simulation (Table 4.3 above) was incorporated in the calculation of REM's emission rate per unit area. The Monte Carlo simulation was used to replace the mean values of the three input parameters: 1) the slope of the calibration curve, 2) the y-intercept of the calibration curve, and 3) FID responses of REMs' emission rates per unit area, with their respective distribution. Each distribution was assumed to be normal with a corresponding standard deviation that was either estimated by a previous Monte Carlo simulation as in the case of the slope and the Y-intercept of the calibration curve, or empirically calculated using test results as in the case of REM-M's repeated tests and FID responses. Table 4.5 presents the input parameters used in the MC model.

Table 4.5: Input parameters for a Monte Carlo simulation estimating the distribution function of emission rate by REMs per unit area.

Input Parameters	**Mean**	**SD**	**CV%**
Slope of the Calibration Curve (FID response per unit ER)	**23.8**	**2.0**	**8.3***
Y-Intercept of the Calibration Curve (FID response)	**12.8**	**1.0**	**8.3***
REMs' FID Responses per unit REM area by FLEC	**269**	**27**	**10**
REMs' FID Responses per unit REM area by ASTM	**266**	**16**	**6**

(simulated results)*

With the above input parameter, emission rate of the REMs per unit area are calculated in both the FLEC and the ASTM based on 5000-point iteration using a Monte Carlo simulation. The results of this iteration are presented in Table 4.6.

Table 4.6: REM emission rate per unit area based on Monte Carlo Simulation.

REM ER	**FLEC**	**ASTM**
Mean (ng/min.cm2)	10.9	10.7
SD (ng/min.cm2)	1.5	1.1
CV %	13.8	10.3

Results indicate that the mean emission rate for the REM per unit area in both the FLEC and the ASTM were in close agreement, 10.9 ng/min.cm^2 for the FLEC, and 10.7 ng/min.cm^2 for the ASTM. Although there exist several studies that compared material emission results using small environmental chambers and the FLEC, conflicting reports regarding their similarity have been found.[5,6] The present investigation have indicated that the FLEC and the ASTM-based chamber compared well for the three different sizes of REMs. It also indicated that both samplers compared well even after incorporating potential and possible variations in flow rates, oven temperature, and FID responses and calibration. Figures 4.16 and 4.17 are the results of the MC simulation.

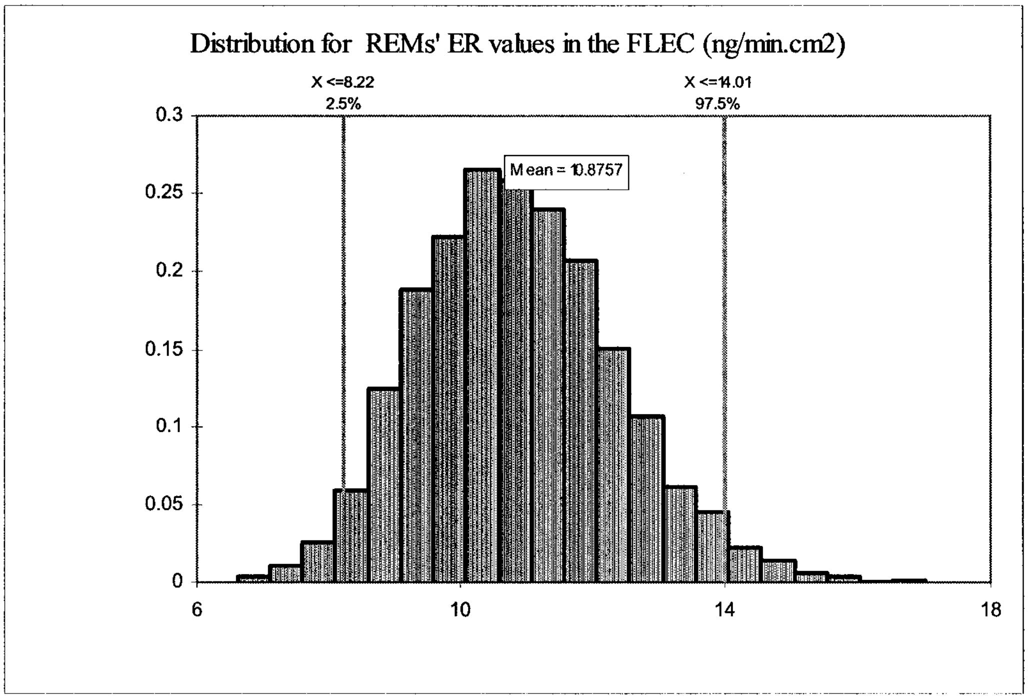


Figure 4.16: Results based on Monte Carlo simulation for possible emission rate values of the REM by the FLEC (per unit area).

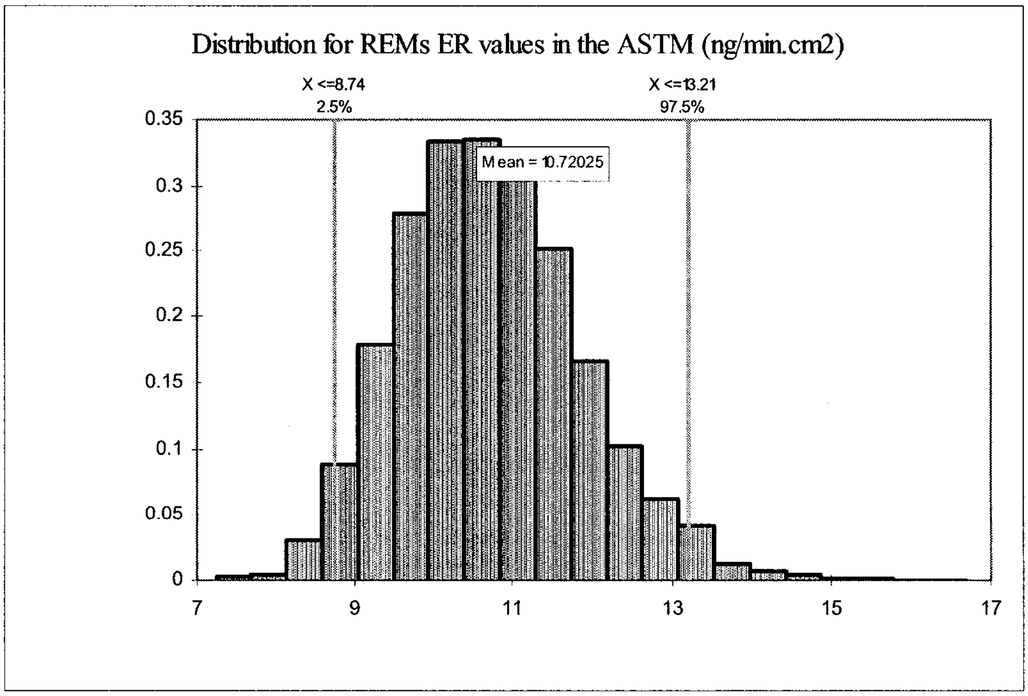


Figure 4.17: Results based on Monte Carlo Simulation for possible emission rate values of the REM by the ASTM (per unit area).

4.3 Concluding Remarks

Three different sizes of REMs (REM-S, REM-M, REM-L) with the same membrane were tested for toluene emission. Their permeation rates compared with rates generated by five certified permeation tubes with different permeation rates. The REMs were tested using two different emission samplers (ASTM and the FLEC) and three alternative detection methods (PID, PAD and FID).

According to Table 4.4 above, the average observed, non-simulated, ER value of REM-M per unit area using the FLEC with the GC-FID cryogenic analysis method at a flow rate of 366 cc/min and a sampling volume of 2cc, was 11.4 ng/min.cm^2. The observed emission rate of the same REM, REM-M, per unit area using the FLEC with the PAD method, at a flow rate of 262 cc/min and a sampling volume of 140cc, was 11.0 ng/min.cm^2, a good agreement considering the different settings, sampling and analytical methods used. Despite the different samplers, the ASTM and the FLEC, the different detection systems and injection methods used, the differing flow rates and the different sampling volumes, the difference in the ER values per unit area are indeed marginal and could well be due to sampling and analytical errors. The mean observed emission rate values for all the three REMs per unit area, Table 4.4, was 11.3 ng/min.cm^2 and 11.2 ng/min.cm^2 for the FLEC and the ASTM respectively. According to the results of a Monte Carlo simulation, the estimated value of REM emission rate per unit area was 10.9 ng/min.cm^2 and 10.7 ng/min.cm^2 for the FLEC and the ASTM respectively.

Regardless of type of the volume of the chamber used, the variations in flow rates, the different calibration methods, the different analytical instruments, the different sampling volumes, and the various intrinsic factors that may have contributed to the sampling and analysis errors such as permeation tube temperate variation and indoor temperature fluctuations, the REM has proved to be a promising and a novel reference emitting material for surface emission sampling.

This chapter presented the design, development and demonstration of a new VOC reference emitting material (REM) with a planar, dry, and solid surface mimicking toluene emission by interior finishes and furnishings. Emission rate by the REMs were estimated using two different material emission samplers, an ASTM-based small scale chamber and the European Field and Laboratory Emission Cell (FLEC).

In the next chapter, the design and development of the new in-situ emission sampler, the Kappa, will be revealed. Several tests will be conducted to compare the Kappa with the FLEC using a new ultra-low emitting REM to further mimic the low emission profile of an interior finish such as a carpet. Finally, a set of tests will be conducted to capture VOC emissions from a newly installed carpet using all the three samplers, the ASTM, the FLEC and the newly developed Kappa, for comparative analysis.

Endnotes

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Chapter Five

A Novel Surface Emission Sampler: The Kappa

To identify sources of indoor air pollution, practitioners tend to conduct air sampling close to the suspected source, hoping to associate the source-emission contribution to the indoor air pollution. This practice presents a lack of selectivity, which is inherent in total air sampling. If for example, indoor air sampling close to a carpet was preformed to identify its VOC emissions, the capturing medium, be it a passive badge, a charcoal tube or a canister, could well capture emissions from a nearby furnishing or from an occupant wearing deodorant. In this case, volatile components of these other indoor sources will also be captured. That is why most IAQ practitioners recommend cutting and removing pieces of carpet and sending them for emission testing to laboratories equipped with special environmental/emission chambers. Hence, off-site sampling rather than in-situ sampling is the norm in IAQ source investigations. However, most building managers resist the practice of cutting and removing samples of interior finishes and furnishings from their buildings for emission sampling. Removing samples from interior finishes and furnishings disturbs the interior decor and the daily activities of building occupants. It also requires costly refinishing to match any removed and damaged interior surface. Regardless of the costs involved in redecorating and refinishing, the cost of emission sampling at the lab is one major deterrent to most building managers. It costs over $2000 for a single indoor carpet sample to be sent and tested at the lab by chamber emission testing.[1]

This chapter presents a material emission sampler that is designed and developed for sampling VOC emissions from indoor finishes and furnishings, in-situ. During the course of developing such a sampler, numerous experiments and design adjustments have been conducted. Various versions of the sampler were built and tested. Based on knowledge gained from a number of empirical studies performed and the experiences gained using the different versions of the proposed sampler, a functioning prototype was finally developed. This prototype sampler is called the Kappa. In this chapter, the design detail of the Kappa will be revealed and results from two sets of experiments will be presented.

The first sets of experiments compare the Kappa with the only sampler which has been widely used in Europe as a field emission sampler, the FLEC. A new REM is used to compare both the Kappa with the FLEC. This new REM was developed to emit toluene at a much lower rate per unit area compared with the three REMs used in the previous set of tests outlined in the preceding chapter. The surface area of the new REM has been designed to be as large and as planar as practically possible mimicking and representing samples of planar interior finishes. Due to practical limits imposed by the FLEC, the maximum surface area of an emitting surface may not exceed 180cm^2. The surface area of the new REM (henceforth called REM-X) was thus 177cm^2. This is almost 90% larger than the largest REM (REM-L at 95cm^2) used previously.

The permeating membrane used in REM-X was also modified to allow toluene emission at a much lower rate than any previous REM developed. This was intended to further mimic the low emission profile of dry and planar interior finishes and furnishings, a characteristic of an indoor surface such as a carpet. The thickness of the permeating membrane used in all the previous three REMs (REM-S, REM-M, and REM-L) was a gauge 200 film (50 um) while the permeating membrane used for the REM-X is a gauge 2000 film (500 um). A 10-fold increase in membrane thickness was also intended to reduce emission rate to a minimum. This new REM-X was adapted to accommodate the sampling requirements of both the FLEC and the Kappa.

The second sets of experiments that will be presented in this chapter are those tests conducted to compare the sampling performance of the three emission samplers, the ASTM-based, the FLEC and the Kappa, in parallel. In this set of experiments, samples from an interior carpet coming from the same batch, type and age, are used as VOC emitting sources. Repeated tests were performed with each sampler and results compared.

From a practical comparative analysis point of view, as it pertains to this chapter, definition of three terms/concepts needs to be outlined at the outset. These terms are repeatability, reproducibility and uncertainty.

Repeatability, a measure of precision, in general is the ability of a measuring system to provide closely similar results for repeated sampling of the same "measurand" under the same conditions of measurement.[2] However, in indoor air quality sampling, especially in emission sampling of interior finishes and furnishings, it is not possible to repeat a measurement in exactly the same way since the emission profile of a measurand is always changing. A more practical/applied definition is needed. According to the European Standard EN 45020, the term repeatability is referred to as the internal variability.[3] In this research, such variability is presented as the difference between the results of emission sampling using the same sampler, although with different but "same-batch-same-type" carpet samples. This internal variability (or repeatability) is presented in terms of a sampler's coefficient of variations.

Reproducibility, a measure to identify the real value hence accuracy, is the closeness of agreement between the results of measurements of the same "measurand" carried out under changed conditions of measurement.[4] As mentioned above, in indoor air quality sampling, especially in emission sampling of interior finishes and furnishings, it is not possible to repeat a measurement of the same "measurand". The emission profile of a measurand changes with each successive measurement. A more practical/applied definition is also needed. According to the same European Standard mentioned above (EN 45020), the term reproducibility is referred to as the external variability.[5] For the purpose of this research, such variability is presented as the difference between the results of emission sampling between the three different samplers, using different but "same-batch-same-type" carpet samples. This external variability (or reproducibility) is presented in terms of matching chromatographic peaks between the three samplers and the coefficient of variations of their estimated concentrations and calculated emission rates.

As for the uncertainty of measurement, this is the parameter associated with the result of a measurement that characterizes the dispersion of the values that could be "reasonably" attributed to the measurand.[6] In this research, although carpet samples are from the "same-batch-same-type" carpet, there are yet numerous parameters that could characterize the dispersion of values such as the inherent lack of homogeneity in carpet matrices. This raises the question of the conditions under which "reasonable" characteristics could be practically assessed.

These three quality control terms and their definitions are outlined at the outset of this chapter so that the results of the following experiments are viewed from a practical and applied context.

5.1 Background

Identifying sources of indoor VOCs in non-industrial settings presents a major challenge to building practitioners. Associating indoor VOCs to their emitting sources require emission sampling. Emission sampling requires extensive preparation using expensive laboratory-based emission chambers. Such a requirement has so far limited the widespread use of material emission testing in home and office environments. Emission testing of interior finishes and furnishings remains an academic exercise in IAQ circles.

Lack of a simple, affordable and in-situ material emission sampler is one reason that has so far limited the widespread use of emission testing from indoor interiors such as finishes and furnishings. Based on literature reviews and information gathered from several international indoor air quality conferences, one could declare with confidence that in-situ emission sampling is so far limited to an emission sampler called FLEC. The latter however, is material dependent. The FLEC cannot sample emissions from a fleecy material such as a carpet or a workstation partition. The FLEC is also surface dependent. Surfaces of materials need to be solid, flush and smooth for the FLEC to sample properly. The FLEC, similar to other laboratory-based environmental/emission chambers, requires an independent and continuous supply of clean air. This renders the FLEC reliant on source such as a zero-air cylinder or a supply air pump with multistage filtration.

These sampling limitations and dependence on external sources for air has limited the use of the FLEC in many field applications. It is acknowledged, nevertheless, that the FLEC is much more practical for in-lab material emission testing than for field, in-situ emission sampling.

The Kappa was developed in response to the limitations of the FLEC and the needs of building practitioners for a practical field/in-situ sampling tool that would be able to screen and identify indoor emitting sources from among other sources. The design criteria for the Kappa are based on the several prerequisites. These are deemed essential for in-situ emission sampling of interior finishes and furnishings in homes and office settings:

1. The sampler should be able to perform dynamic emission sampling rather than be a mere static head sampler;
2. The sampler should be able to sample emissions from all sorts of finishes and furnishings, fleecy, solid, smooth, rough, flush or jagged;
3. The sampler should be able to sample VOC emissions from interior finishes and furnishings in-situ with limited perturbation.
4. The sampler should incorporate limited reliance on external provisions such as clean air cylinders and pumps.

In addition to the above, a versatile sampler needs to accommodate both passive and active sampling methods. Although active sampling mediums such as charcoal tubes or thermal desorption tubes require a sampling pump, passive badges are pump independent, hence a more logical choice. Although there are inherent limitations associated with the concept of passive badge sampling in general, as will be explained later in appendix D, the Kappa sampler was designed and developed to accommodate both active and passive sampling methods, regardless.

Figure 5.1 presents the design principal of the Kappa. The name Kappa was borrowed from a mathematical profile known as the kappa curve. The curve is also known as Gutschoven's curve, which was studied by G. van Gutschoven in the 17th century and was later investigated by Newton and Bernoulli.[7]

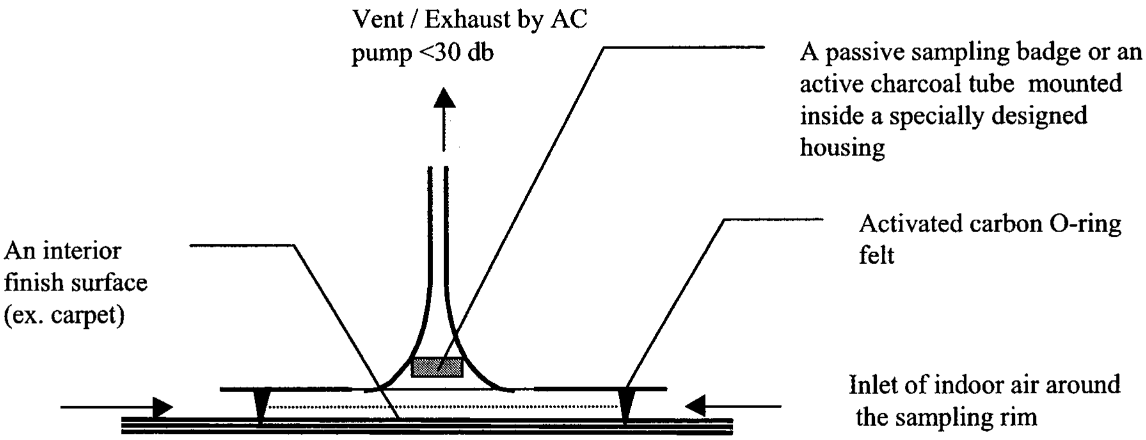


Figure 5.1: Schematic of the Kappa sampler.

In the development of the new sampler, a Kappa curve profile was considered an appropriate profile for converging emissions from planar surfaces to a sampling medium. Such a Kappa profile also forms part of the Converging-Diverging Nozzle (CDN) used in controlling gas flows.

The CDN was invented by Carl de Laval towards the end of the 19th century and is often referred to as the "de Laval" nozzle. The ultimate profile of any CDN is based on factors related to the efficiency by which gas flows through a region of high pressure to one of lower pressure. In a CDN, low velocity air enters into a converging section to gain momentum and exists from a diverging outlet. In the design of the Kappa the converging part of a CDN was profiled as an inlet to the sampler. Velocity of air entering the periphery of the sampler only increases as air approaches the apex of the Kappa. The Kappa provides the necessary sectional profile allowing air to gain momentum and increase in velocity as it ascends away from the surface of the material into the apex of the Kappa without perturbing the natural velocity profile present at the surface of the interior finish or furnishing under investigation.

5.2 Method of Operation

The Kappa sampler consists of three integrated regions, an upper, a middle and a lower part. The upper part consists of a ventilation cell that is connected to an AC driven micro-pump. The lower part is a sampling mouth with a Kappa sampling cell profile. The middle part is a connection-adapter cell providing the necessary connections to most commercially available sampling mediums such as passive diffusive badges, active charcoal tubes, thermal desorption tubes and inlets to evacuated canisters.

During sampling, the micro-pump pulls indoor air into the mouth of the Kappa through a peripheral O-ring rim made from commercially available activated carbon felt (ACF). The ACF is an O-ring that encircles the peripheral rim of the mouth of the Kappa. This ACF O-ring filters and traps VOCs present in air that is being pulled from the surrounding indoor into the sampling cell. Hence, it provides a filtered supply of sampling air to the sampling cell of the Kappa. It is this ACF O-ring concept that forms the fundamental design element of the Kappa, and makes the Kappa a novel in-situ material emission sampler. It is the ACF O-ring that provides the Kappa with a clean sampling air without reliance on an external source such as a zero-air cylinder.

The filtered air passes over the planar surface of the material being sampled and carries with it any emitted VOCs to the sampling medium located at the upper chamber. Due to the large inlet to outlet ratio of the Kappa profile, velocity of inlet air is kept unperturbed and within the range of normal air velocities encountered indoors, <15 cm/s. This ensures that the surface of the emitting material is unperturbed during the duration of the in-situ emission sampling, a key feature of the Kappa sampler. The velocity of sampling air, however, increases as air moves away from the surface towards the apex of the Kappa. Sampling-air velocity increases inversely with the radial profile of the Kappa sampler. This concept was borrowed from the design principle of the FLEC.

5.3 The Kappa: A Hybrid Sampler

The Kappa is designed to support both active and passive sampling methods. During active sampling, using either standard activated charcoal tube or thermal desorption Tenax-based tube, a pre-calibrated needle valve is attached to the ventilating cell of Kappa's upper part to regulate the flow rate in the ventilating cell generated by an AC driven micro-pump. The Kappa assembly comes with its own micro-pump. The pump is supplied and manufactured by a French company (RENA Air Model 200). The pump was selected after a rigorous search-and-test operation for a pump that is small, low noise operations (db<30), sturdy, regular in its flow rate and that is commercially available.[8]

The issue of the humming noise generated by most sampling pumps has been an issue during indoor air quality sampling. Occupants of homes and office building are not used to the same level of noise and sound found in industrial settings; hence they find the noise generated by the standard industrial hygiene personal sampling pumps unacceptable. In fact operating a standard industrial hygiene battery operated personal sampling pump in an indoor non-industrial setting has always been a challenge. Based on experience, the noise generated by such pumps has raised complaints by building occupants both in office and home environments. This was one of the reasons that IAQ investigators preferred the use of passive diffusive badges during their indoor air quality sampling campaigns.

However, the use of passive diffusive badges in indoor air quality investigations has not yet been validated; let alone its use for in-situ material emission sampling. This lack of validation is likely due to a phenomenon called the "starvation effect". Starvation effect in diffusive sampling is a phenomenon that deals with concentration and air velocity in a setting. For a steady diffusive transfer of a certain contaminant to occur from a zone of high concentration to a zone of lower concentration both the concentration profile and the air velocity profile in a setting should at least be at a certain minimum value for the diffusive transport to occur constantly. In non-industrial indoor settings, air velocities are below the minimum required for any constant diffusive transport to occur. Most commercially available passive diffusive badges are validated for industrial settings with average air velocities exceeding 20cm/sec. Normal indoor air velocities in non-industrial settings are in the range of 10cm/sec or lower.

Taking into consideration the aforementioned effect, the Kappa sampler was designed to perform in-situ material emission sampling using commercially available passive diffusive badges. The Kappa sampler is profiled in such a way that it would provide the minimum recommended air velocity needed for a passive diffusive transport to take place. The location of a passive badge inside the ventilating cell of the Kappa was a strategy to this end. Supplemented by the micro-pump, the profile of the Kappa causes sampling air to increase in velocity as it approaches the apex of the ventilating cell, in which the passive badge is housed. Air velocity in that region of the Kappa reaches 40cm/sec. This is the range of face velocity that OSHA maintains inside its exposure chambers used to test and validate the uptake rate of passive diffusive badges.[9]

5.4 The Kappa and the FLEC

This section presents the experimental design and the results of a set of tests conducted to compare the surface emission sampling capability of the both the Kappa and the FLEC.

Since the FLEC is the only available field emission sampler, further tests comparing the Kappa should only be conducted with a similar counterpart (c.f. the ASTM chamber). There is a similarity between both the Kappa and the FLEC. They both are small emission cells, inverted cup look-alike, as opposed to a large cubical chamber such as the ASTM-based 50L chamber. It should be mentioned that the exact volume of the ASTM chamber used in this investigation is ~53L. However the 50L connotation was used for reference only. The cell volumes of the FLEC and the Kappa are 35cc and 13cc respectively.

Loading factor, the ratio of the surface area to chamber or cell volume, is almost similar for the FLEC and the Kappa; ~500 m^{-1} for the FLEC; ~450 m^{-1} for the Kappa. The loading factor for the ASTM chamber is ~1.5 m^{-1} depending on the area of the sampling material. Loading factor has a potential to influence emission rate factors since a different loading factor means a different surface ventilation rate and a different sink effect. A high loading factor signifies a high surface ventilation rate and a low sink effect.

Based on these parameters, it would be more realistic to compare the Kappa with the FLEC using a standard reference emitting material. The absence of a commercially available and certified reference emitting material that could be placed beneath the mouths of both the Kappa and the FLEC and used under normal indoor air conditions, presented major challenges to this research project. Comparing two or more surface-based diffusive emission samplers against each other is not possible without a reference emitting material that could be used to compare emissions with.

5.4.1 The Kappa, the FLEC and the REM

In the previous chapter, a method to develop a REM has been established. Different REMs were built and were tested. Three REMs were compared using both an ASTM-based chamber and the FLEC. Emission rates of the three REMs were sampled and an average surface emission rate of approximately 11ng/min.cm^2 has been estimated using both the FLEC and the ASTM-based chamber. From the lessons learned during the design, development and testing of all the REMs presented in the previous chapter, a thicker membrane REM could reduce the ER and more closely mimic surface emissions of interior finishes and furnishings.

Hence a new REM, which was designed and developed earlier with a thicker membrane, was selected as the reference emitting material for use for the Kappa versus FLEC tests. The reason to select a new REM rather than using one of the three REMs which were previously tested was due to the fact that emission rate from each of the three REMs was higher than desired for the tests. A much lower ER value would be more appropriate. Such a low emitting REM would approximate more closely emissions from solid and planar interior finishes and furnishings commonly used in non-industrial indoor environments. Generally speaking, a TVOC emission rate from a building material such as an OSB (Oriented Strand Board) would be in the range of 10 ng/cm^2.min. However, for a single VOC, emission rates are in the order of 1 to 0.001 ng/cm^2.min.[10]

Developing a low emitting REM is a trial-and-error exercise. One approach is to use a much ticker permeating membrane. However, developing a thick membrane REM requires several months for the REM to equilibrate. A REM would be deemed in equilibrium only when its membrane surface convexes (bubbles up). This is not membrane elongation but rather an indication that enough inner pressure has been built up inside the REM to render it ready for a steady emission. This pressure is caused by the reverse diffusion of some gases such as O_2 and N_2 from indoor air into the inner assembly of the REM. In addition to having a REM with a low and continuous emission rate, the surface area of the new REM should be as large and planar as practically possible. A large surface REM would also more closely mimic the larger samples of planar interior finishes.

Due to design limits imposed by the FLEC, the maximum surface area of an emitting surface that could be placed under the mouth of the FLEC can not exceed 180cm^2. The surface area of the new REM (henceforth called REM-X) was designed at 177cm^2 (a 15cm radius). This is almost 90% larger than the largest REM (REM-L at 95cm^2) used previously. The permeating membrane used in REM-X is modified to allow toluene emission at a much lower rate than those established for the three previous REMs. The thickness of the permeating membrane used in the previous three REMs (REM-S, REM-M, and REM-L) was a gauge 200 film (50um).

The permeating membrane used for the REM-X is a gauge 2000 film (500um). This 10-fold increase in membrane thickness is intended to greatly reduce emission rate. The time required to achieve membrane equilibrium using such a thick film was approximately six months. Having reached its equilibrium, the new low REM (REM-X) was adapted to accommodate the sampling requirements and the sizes of the sampling mouths of both the FLEC (180cm^2) and the Kappa (80cm^2), respectively.

5.4.2 Kappa/FLEC/REM-X: Sampling Setup

The main objective of this set of tests is to compare the Kappa with the FLEC using a standard reference emitting material. Although the actual emission rate of the newly developed REM (REM-X) is not known, but it is anticipated, based on experiences gained from previous REM experiments, that the emission rate of the new REM-X would be much lower than the previous REMs (REM-S, REM-M, REM-L) used. The design experiment of these tests would also reveal two latent objectives. One would be to find out if the REM-X emits at a constant rate under normal indoor conditions, and the other would be to calculate the actual emission rate of REM-X. The three objectives of the Kappa/FLEC/REM-X tests are outlined below.

The first objective is to compare both the FLEC and the Kappa by using each to sample independently, but in a per-defined sequence, toluene emission from the surface of REM-X. This would provide information on the newly developed REM-X and whether it does emit toluene at a constant rate under normal indoor conditions. This would be investigated by monitoring the gas chromatographic responses of all samples obtained allowing a semi-qualitative comparison between the Kappa with the FLEC in their relative performance during sampling from an emitting source like REM. Only if the REM-X has successfully emitted toluene at a constant rate, the next objective of the tests would be to calculate the area specific emission rate of the REM-X. The last objective of the tests would be to use all the data obtained from 1 and 2 to perform a quantitative comparison between the Kappa and the FLEC.

To be able to perform these three objectives, an experimental setup was carefully planned. Sampling was conducted using 7" x ¼" Tekmar stainless-steel multi-sorbent tubes (Part No. 14-1677-203, Tekmar Company, USA) packed with Tenax TA and Carbosieve S-III. The latter adsorbent bed was not required to perform emission sampling of toluene from REM-X, only Tenax was required.

Twenty one such tubes were reserved for the tests. Each tube was tagged with an identifier number and traced throughout its chain of sampling and analysis. Each tube followed a four or five stage process of pre to post sampling and analysis campaign. The first stage was to ensure that each tube has been properly conditioned and cleaned with no background or trace levels of VOCs. This involved conditioning each tube by passing 40cc/min of an inert gas through the tube and heating it for at least 3 hours at 300°C.

Initially the inert gas selected was a high purity N_2. But baseline results indicated that N_2 was not appropriate for the purpose of cleaning such tubes. Hence N_2 was replaced with He for the purpose of conditioning the tubes. The latter proved satisfactory, but at least 4 hrs of conditioning was needed to guarantee a clean baseline. The second stage was to run a chromatographic analysis for each tube before the actual sampling. This stage was deemed essential, since cleaning and conditioning each tube did not guarantee an absolute clean baseline unless proven by a chromatogram. This stage was named “the clean tube certification” stage. The third stage was the sampling stage, which will be described later. The fourth stage was the first run of sampling analysis stage. This stage was the sampling extraction stage by thermal desorption using a cryogenic thermal desorption system (Tekmar 6000 AeroTrap, Tekmar Company, USA) coupled to a second phase cryogenic focuser/injector (Tekmar Cryofocusing Module 14-2530) attached to a Hewlett-Packard gas Chromatograph with a Flame Ionization Detector (HP 5890 GC/FID). This stage is directly followed by a second run sampling, the fourth stage, to make sure that all the toluene captured in the tube during sampling was indeed desorbed and analyzed. This stage was deemed important since few of the second runs had small amounts of toluene as a residual, either in the tube or in the system. Due to this fact, a final conditioning stage, stage five, was also conducted as a third run, only if residuals were found at the preceding stage, to guarantee that there were no more toluene residuals in the tube or in the system. This final stage also served as the tube certification stage to prepare the tube for its next round of sampling and analysis.

Having prepared the protocol for tube preparation, an inspection of the REM-X is performed. This REM, as explained above, was stored and left for several months to equilibrate under normal room conditions.

Both the Kappa and the FLEC were prepared ready to be placed on top of the equilibrated REM-X as per the sampling requirements of both the Kappa and the FLEC respectively. The same AC micro-pump (RONA Model 200, France) used during Kappa sampling is also used during FLEC sampling. Sampling flow rates were maintained during the entire sampling campaign with a mean value of 51cc/min (SD of 2 cc/min; CV 4%; n=32). Sampling time was divided into two sets of durations: a two-hour sampling set and a one-hour sampling set. For each sampling duration set, at least duplicate samples were obtained for the Kappa and the FLEC respectively.

A few extra tests with some variations to the above protocol were added during the sampling campaign. One of the added set consisted of three repeated one-hour sampling by the FLEC using a supply of humidified air rather than the dry (RH<5%) zero-air. The humidification of the supply zero-air was achieved by placing an 8' Nafion tube to the supply line. This allowed the zero-air supplied by the cylinder to equilibrate with the indoor air humidity level at the time of sampling. Indoor RH at the time of sampling using the Nafion tube was measured.

The average RH value was 47% (SD 3%; CV 6%). One more added test was a three hour sampling duration for the FLEC. An additional set of tests was conducted with the Kappa with three repeated samples of three-hour duration for each. In total, 16 REM-X samples were collected of which eight samples were collected by the Kappa and eight by the FLEC.

The FLEC and the Kappa each require a different arrangement in their sampling train assembly. The sampling train for the FLEC requires a supply of a clean sampling air using either a supply pump equipped with a set of filters or using a pressurized zero-air cylinder. The extraction of the sampling air from within the FLEC into the sampling tube requires the use of a sampling pump operating under negative pressure. Such simultaneous arrangement of positive air supply and negative sample air extraction entails a careful balance between the flow of air supplied to the FLEC and the flow of air extracted from the FLEC. During normal sampling operation the air supply rate to the FLEC is recommended to be at least twice that of the sampling air. The balance is diverted to escape through a vent.

However, in this Kappa/FLEC comparative experiment, the supply air and the extracting air needed to be similar in both the FLEC and the Kappa, since the air supply rate influences the concentration generated by the REM. The higher the supply air the lower the concentration, provided that the ER is constant. In the case of the Kappa, there is only one system --a single micro-pump-- that provides both the supply air to Kappa's cell and the sampling air to the sampling tube. There is no venting in a Kappa's sampling train.

To generate a similar REM-X toluene concentration in the Kappa and the FLEC, the supply air to the FLEC was set slightly higher than the sampling air. The mean value of FLEC's supply air was 61 cc/min (SD 1 cc/min; CV 2%, n= 16). This allowed the sampling pump to extract air at its pre-set rate of 51 cc/min (SD of 2 cc/min; CV 4%; n=32) while keeping the FLEC slightly under positive pressure. The extra 10cc/min balance was sent to vent. There is a 10cc/min difference between the supply air to the Kappa and the supply air to the FLEC. Sampling air pulled into the sampling tubes was kept the same in both the Kappa and the FLEC at its mean rate of 51 cc/min. This air supply and extraction rates protocol was necessary to keep the Kappa tests and the FLEC tests comparable. The influence of the extra 10 cc/min on the FLEC's sampling results will be calculated during the analysis.

Supply and sampling flow rates were measured with a newly purchased high resolution digital mass flow meter certified and calibrated by the manufacturer (Digital Flow Check High Resolution Flowmeter Type 5700, 0.01–500cc/min, Alltech GC Equipment). Room temperature and room relative humidity were measured continuously during the entire duration of the sampling campaign with a recoded average of 22.7°C (SD 0.4°C; CV 1.5%) and 41% (SD 3%; CV 8%) respectively.

Table 5.1 presents the FLEC/REM-X sampling campaign and Table 5.2 presents the Kappa/REM-X sampling campaign.

Table 5.1: FLEC sampling campaign for toluene emission by REM-X.

FLEC Test	Cell Flow Rate	Sample Flow Rate	Sample Time	Sample Time	Sample Vol	Room Temp	Sample RH
#	cc/min	cc/min	hr	min	cc	Degree C	%
1	60	51	3h03'	183	9415	23	<5
2	61	53	2h02'	122	6423	23	<5
3	60	50	2h07'	127	6325	22	<5
4	63	50	1h11'	71	3532	23	<5
5	61	49	1h00'	60	2928	23	<5
6	59	48	0h59'	59	2838	23	49
7	60	50	1h07'	67	3353	23	48
8	61	50	1h03'	63	3178	23	44

Table 5.2: Kappa sampling campaign for toluene emission by REM-X.

Kappa Test	Cell Flow Rate	Sample Flow Rate	Sample Time	Sample Time	Sample Vol	Room Temp	Sample RH
#	cc/min	cc/min	hr	min	cc	Degree C	%
1	54	54	3h00	180	9720	23	45
2	50	50	3h00	180	9027	23	37
3	51	51	3h00	180	9099	23	43
4	55	55	2h04'	124	6758	23	42
5	54	54	2h00	120	6420	23	35
6	54	54	2h07'	127	6852	23	39
7	50	50	0h59'	59	2935	23	40
8	52	52	1h01'	61	3196	23	41

Before the start of analysis, the GC-FID and the cryogenic thermal desorption system were tested each day for baseline responses and drifts. The latter involved conducting at least two consecutive empty runs per day before the start of any sample analysis. The first run was to make sure that the GC-FID system by itself was baseline clean. The second run was to make sure that the GC-FID plus the Thermal Desorption systems were both baseline clean. Based on the positive results of these two baseline runs, sample analysis are then conducted from the sample tubes.

5.4.3 Kappa/FLEC/REM-X: Analyses and Results

After conducting REM-X sampling, each sampling tube was immediately placed in the thermal desorption system (Tekmar 6000 AeroTrap, Tekmar Company, USA) for respective toluene analysis. The EPA method TO-17 was used as a best practice guide during the analysis.[11] Helium gas (sample gas) was flushed into each tube for two minutes at room temperature. This was conducted to remove any moisture that may have accumulated inside each tube during sampling. Desorption of each tube was performed at 250°C for 10 minutes.

At 40cc/min., sample gas transferred the desorbed toluene into a cryogenically cooled glass bead tube. The temperature of this tube was pre-set at -150°C. Transferred toluene was condensed and ready for its second stage thermal desorption. During this time, the tip of a deactivated capillary column, located at the injector port to the GC, was cryogenically cooled to -150°C. Toluene was re-desorbed at 250°C and transferred from the glass beads tube through a heated nickel-based line into a cryogenically cooled deactivated capillary tip (Tekmar Cryofocusing Module 14-2530). The temperature of the transfer line was pre-set to 250°C. The duration of the transfer was 2 minutes. This allowed sufficient time for any transferred toluene to be re-condensed and focused at the tip of the capillary injector (Restek MXT-Guard ID 0.53 cat. 70046). The tip of the capillary is then instantaneously heated, third-stage thermal desorption, to +250°C and injected into the GC (HP 5890 GC/FID) column.

The sample is injected into a split-less injection port directly into a 105m fused silica capillary column for GC separation (Supelco - VOLCOL 105m x 0.53 mm x 3um film). Separation of toluene is achieved within 12 minutes (GC-FID retention time of 10.78 min; SD 0.04 min. CV <0.4%) of the each GC run. GC's oven program was set at 50°C ramping to 180°C at a rate of 10°C/min. Detector temperature was set at 250°C and carrier gas flow rate into the column (He) was pre-set at 5cc/min. H_2 flow to the FID was set at 30 cc/min, air flow to the FID was at 350 cc/min and N2 (auxiliary gas to the FID) at 31 cc/min.

A clean tube was used to establish the response magnitude for a net mass of toluene using the same analytical system and sampling procedure described above. A certified calibration gas, 99 ppm by volume, of toluene gas in N_2 (supplied by Matheson Tri-Gas) was used to establish the response magnitude. A 400cc/min flow of this calibration gas was injected into a clean certified sampling tube for eleven seconds. The tube was immediately analyzed using the above analytical procedure. The response of the FID to this calibration with a peak area of 60624114 is used as a quantitative reference for REM-X ER quantification. Based on the result obtained, FID responses of all samples collected are multiplied by a response conversion factor of $5x10^{-4}$ to convert peak areas into net mass of nanogram toluene.[12] Table 5.3 and Table 5.4 present the results of sample analyses for the FLEC and the Kappa, respectively.

Table 5.3: Results of the FLEC/REM-X samples.

FLEC Test	GC-FID Response	Net toluene	Cell Concentration	ACH	Emission Rate	Loading	Emission Factor
#	area count	ng per tube	ng/cc	1/mim	ng/min	cm2	ng/min.cm2
1	132858105	60982	6.5	1.73	391.2	176.6	2.2
2	85042128	39034	6.1	1.74	370.7	176.6	2.1
3	105046363	48216	7.6	1.73	460.5	176.6	2.6
4	46605518	21392	6.1	1.79	379.7	176.6	2.2
5	41684845	19133	6.5	1.75	401.2	176.6	2.3
6	51779700	23767	8.4	1.69	495.8	176.6	2.8
7	59849255	27471	8.2	1.71	489.9	176.6	2.8
8	46148359	21182	6.7	1.75	407.2	176.6	2.3

Table 5.4: Results of the Kappa/REM-X samples.

Kappa Test	GC-FID Response	Net toluene	Cell Concentration	ACM	Emission Rate	Loading	Emission Factor
#	area count	ng per tube	ng/cc	1/min	ng/min	cm2	ng/min.cm2
1	63395657	29099	3.0	4.2	161.7	78.5	2.1
2	59013982	27087	3.0	3.9	150.5	78.5	1.9
3	61717738	28328	3.1	3.9	157.4	78.5	2.0
4	64020544	29385	4.3	4.2	237.0	78.5	3.0
5	49393581	22672	3.5	4.1	188.9	78.5	2.4
6	49387593	22669	3.3	4.2	178.5	78.5	2.3
7	20830038	9561	3.3	3.8	162.1	78.5	2.1
8	32583827	14956	4.7	4.0	245.2	78.5	3.1

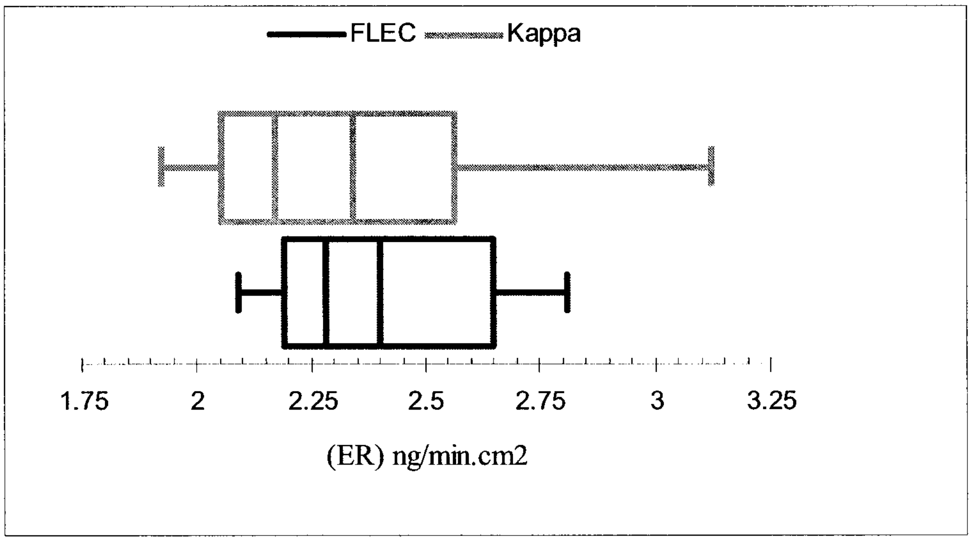


Figure 5.2: Box-and-Whisker plot for ER results obtained using FLEC/REM-X and Kappa/REM-X sampling (min., 25th percentile, median, mean, 75th percentile, max.).

From the results obtained, using two-decimal places, average REM-X emission factors of 2.40 ng/min.cm^2 (SD of 0.28 ng/min.cm^2; CV of 12%) and 2.35 ng/min.cm^2 (SD of 0.45 ng/min.cm^2; CV of 20%) were obtained for the FLEC and the Kappa respectively. Based on Figure 5.2, assuming the normality of data sets, and using a two sample t-test with unequal variances---details on normality testing and t-testing are presented later--, the difference in the mean REM-X ER values, as sampled by the FLEC and the Kappa, is not significant (p=0.82; n=8; df=12; two tail sample; alpha @ 0.05).

The higher CV in the Kappa sampling could be attributed to its exposure to the real indoor air conditions. Sampling air to the Kappa was supplied by the indoor air itself, as opposed to the FLEC, where clean ultra-zero air was used for its sampling air. Kappa tests were all performed under actual indoor air humidity levels. FLEC tests, with the exception of three last samples (sample 6, 7 and 8; Table 5.1) were conducted using humidity controlled dry air. In the three last FLEC samples, with sampling air being humidified using a Nafion transfer line, average REM-Xs emission rate of toluene were at least 15% higher than the average concentration of toluene found during dry air sampling, a mean of 464 ng/min versus a mean 401 ng/min, respectively. This is in agreement with the findings of other researchers on the influence of indoor conditions on emissions from interior finishes and furnishings. An increase in VOC emissions from building materials has been associated with an increase in indoor air humidity level.[13, 14] Table 5.5 presents three supplementary samples, not tabulated above, with data illustrating the comparative performance of the REM-X with the FLEC under a different sampling cell flow rate condition.

Table 5.5: FLEC REM-X sampling at a higher cell flow rate.

Test	#	FLEC09	FLEC10	FLEC11
Cell Flow rate	cc/min	152	147	150
Sample Flow rate	cc/min	51	50	50
Sample Time	hr	3h00	3h00	3h00
Sample Time	min	180	180	180
Sample Vol	cc	9171	8991	9072
Room Temp	C	23	23	23
Sample RH	%	<5	<5	<5
GCFID Response	peak area	47296833	43514000	59317175
Net toluene	ng per tube	21709	19973	27227
Cell Concentration	ng/cc	2	2	3
ACH	1/min	4	4	4
Emission Rate	ng/min	359	327	449
Loading	cm2	176.6	176.6	176.6
Emission Factor	ng/min.cm2	2.0	1.8	2.5

As it can be seen from Table 5.5, that increasing FLEC's cell flow rate from the 61 cc/min used in the pervious set of samples (average of Table 5.1) to 149 cc/min (average of Table 5.5), has slightly reduced the average estimated emission rate of the REM-X by 5%. The average emission rate from Table 5.5 is 378 ng/min versus the average emission rate from Table 5.3 of 401 ng/min. This slight decrease raises a question on the influence of ventilation parameters: flow rate, air change rate, and surface air velocity, on diffusive-based emissions from planar surfaces.

On the one hand, a higher flow rate should reduce the concentration generated by a constant emitting surface due to the theoretical fact that concentration equals emission rate divided by flow rate. This fact is clearly illustrated in Tables 5.3 and 5.5 under the heading "cell concentration". On average, increasing FLEC's cell flow rate from 61 cc/min to 149 cc/min resulted in a reduction of concentration from 6.6 ng/cc to 2.5 ng/cc. This is in agreement with the theory of concentration, dilution and ventilation.[15]

On the other hand, an increase in air flow rate is accompanied by an increase in the air exchange rate and an increase in surface air velocity over a sampling surface. This increase in surface air velocity may contribute to a potential attenuation of the emission rate by the REM. The concept of the REM, as outlined previously, is a permeation concept. It combines both the solubility and the diffusion processes through a membrane.

Each gas, including toluene, has its own permeation coefficient through a membrane. This permeation coefficient is dependent on the steady-state conditions of transfer through a unit surface area of unit thickness at unit pressure difference.[16] A permeation process involves three stages: a dissolving stage into the membrane, a diffusing stage through the membrane, and a desorbing stage out from the membrane. These three stages are dependent, in whole or in part with different degrees of influence, on the three driving forces of pressure gradient, temperature gradient and concentration gradient.

Permeation in the REM is, more or less, a passive permeation as opposed to the active permeation that characterizes the commercially available permeation tubes. By heating a permeation tube to its recommended temperature (mostly above 50°C), the heat generates a required pressure difference that overshadows the pressure generated by the air velocity on the surface of the membrane of the tube. This allows a constant permeation rate regardless of changes in air velocities, as long as the supply flow rate is kept constant.

However, in the case of the REM, and in the absence of heat, a change in air velocity due to an increase in air change rate triggers a change in pressure hence a change in emission rate. There are limited empirical research available at the present that fully describes the influence of air velocity on diffusive-based, dry, low-emitting, interior finishes.[17,18,19,20]

Indirect results from such reviews suggest that air velocity could influence VOC emission rates from some dry building materials, depending on the VOC. According to a research conducted at the same laboratory were sampling was performed, the influence of surface air velocity on surface emission rates had two distinguishing stages.[21] In the short term, an increase in surface air velocity on a dry planar material increases emission rate. In the long term the effect starts to diminish and tends to reduce emission rate over time. This phenomenon could have played some role in the lower emission rates observed by the FLEC/REM-X during the above supplementary tests.

As it pertains to the Kappa, the sampling rate and cell flow rate are the same. Both flows are driven by the same source, a micro pump. The rate is calibrated by a fixed needle adapter attached to the micro-pump. No external source for zero-air or different supply and sampling flow rates are required.

Based on the above tests, the Kappa has shown, so far, that sampling a planar emitting source is possible by using a simple inverted cup sampler. This "inverted cup", similar to the FLEC, is especially profiled to control surface air velocities. However, unlike an "inverted cup", the Kappa is a dynamic emission cell. And unlike the FLEC, the Kappa provides it own supply air. It uses its own sampling air as the supply air through an O-ring filtering felt made from activated carbon. This O-ring, once placed on top of an emitting surface, establishes and predefines the surface area and hence the loading factor. In the aforementioned tests, the loading of the Kappa was determined based on the area of the circular O-ring carbon felts (∅ 10 cm). Each Kappa test has used a clean activated carbon O-ring felt. These felts were individually prepared, cut and re-generated by placing them inside an oven for 48hrs at 200°C.

The thickness of the activated carbon felt, the O-ring ACF used by the Kappa, was 1mm thick. Placing several such felts on top of each other generates a relatively thick and a flexible layer of a filtering medium that would follow the surface contour of the emitting material. The latter provides a cushioning effect that allows sampling from uneven and fleecy surfaces to be conducted without concern for potential peripheral leaks due to uneven surfaces of finishes and furnishings. Most interior finishes and furnishings have surfaces that are uneven and hardly smooth, except for select materials such as glass and some PVC flooring materials.

The Kappa was designed with these considerations in mind. Due to the nature of interior finishes and furnishings and their settings, designing an in-situ material emission sampler without a peripheral leak is almost impossible unless a test-sample of the interior material is removed and sent for in-lab emission sampling. Peripheral leak is a common problem in the FLEC, observed in this study and also reported by other researches.[22,23] In fact, the use of a modified sealing system such as lead-based inserts or the use of clamps were recommended for the FLEC during in-lab emission studies, let alone in the field. During this study, clamps were used to guarantee a sealed system for the FLEC/REM assembly.

In the next section, the second set of tests along with their experimental setup will be described. These tests are conducted to compare the Kappa with both the FLEC and the ASTM-based chamber during sampling emissions from one of the most fleecy and abundant interior finish ever used indoors, the carpet. It should be emphasized that neither the ASTM-based chamber nor the FLEC are able to sample carpets in-situ. Both the ASTM-based and the FLEC are thus treated in the upcoming series of tests as laboratory-based emission chambers.

Only the Kappa, due to its design and configuration, will be utilized as an in-situ carpet emission sampler. The reader should bear in mind that sampling VOC emissions from a carpet requires different samples of the same type and age of the carpet in question. For comparative purposes, once a carpet spot is sampled, it can not be sampled again since emissions could be changed and altered by the preceding sampling campaign.

Although all carpet samples used in the upcoming set of tests are from a single type, kind, age and batch of a carpet, one can not resample the same carpet sample. This presents a challenge in comparing the three different samplers during the upcoming set of tests. In the previous set of tests, all the REMs used so far had a constant emission profile. Each REM, relatively speaking, could be alternated and sampled at different times and for different durations without influencing the emission profile of their surfaces. This made comparing the three different samplers a relatively easy task. In the upcoming section, the methodology of sampling several samples of the same carpet using three different material emission samplers will be presented and their results discussed. The aim of the following set of tests is two fold: 1) to compare the Kappa with both the ASTM-based chamber and the FLEC in terms of its ability to capture the same emitting VOCs relative to both the ASTM-based chamber and the FLEC; 2) to compare the Kappa with both the ASTM-based chamber and the FLEC in terms of its ability to sample emission rates of the VOCs captured relative to both the ASTM-based chamber and the FLEC.

5.5 Carpet Sampling with three Different Emission Samplers

The objective of this section is to compare the Kappa with both the FLEC and the ASTM-based emission chamber using an actual interior finish. In the previous set of tests different REMs were used to compare emission sampling between the FLEC and the ASTM-based chamber. Results of those tests have concurred with findings by other researchers who have reported similarities and differences between the FLEC and ASTM-like laboratory emission chambers.[24,25,26]

In this section, a comparison is made between the ASTM based chamber, the FLEC and the Kappa, as a step in the preliminary validation of the latter, the Kappa. The terms “sampling device”, “sampling method”, “device”, "chamber" or “sampler” will be used interchangeably as reference to the FLEC the Kappa and the 50-L ASTM-based chamber, henceforth refereed to as ASTM.

Results of the upcoming set of tests will shed light on the effectiveness of the newly developed Kappa and its applicability as an in-situ emission sampler for VOCs from interior finishes and furnishings.

The experience gained from using the ASTM and the FLEC during the three REMs sampling, supports the contention that the FLEC is indeed a much simpler emission sampler than its ASTM counterpart. However, the limitations observed from using the FLEC for in-situ emission sampling became obvious when the FLEC was compared to the Kappa during the REM-X sampling campaign. This has highlighted the potential benefits of using a more practical field emission sampling method that would be able to identify sources of indoor VOC emissions, in-situ.

Results of this chapter present the overall degree by which the Kappa-- which was designed and developed to deliver the main objective of this research-- could be compared with both the FLEC and the ASTM in sampling and quantifying VOC emissions by an interior finish. Carpet was selected as the interior finish of interest due to: a) it is an abundant material that is largely used indoors, and b) it is a difficult material to sample emissions from, especially in-situ.

5.5.1 Experimental Setup, Sampling and Analysis

The following set of tests presents the first deployment of the Kappa to sample VOC emissions from an interior finish. Results of the tests are qualitatively compared with both the FLEC and the ASTM. Data generated in this section will be imported into the following section for quantitative analysis based on area specific emission rates (SER) from the carpets tested. The analytical method employed in this chapter will not target the identification or the names of any VOC emitted. A VOC is identified by its retention time (RT) as per its respective sample chromatogram. In addition, only the most abundant VOCs are considered in comparing carpet sampling results by the three different samplers.

The sampling loop system used during the three REMs (REM-L, REM-M, and REM-S) sampling campaign, chapter four, was modified to accommodate active sampling using standard charcoal tubes. In this set of tests, chemical desorption (CD) charcoal tubes were selected for sampling rather than the thermal desorption (TD) tubes used during the previous REM-X tests.

Based on experience gained during the REM-X sampling campaign, the process of preparing and cleaning each TD tube was deemed very time consuming. Certification of each tube, running a baseline chromatogram for each before sampling, was a lengthy process. The thermal desorption system that is used at the laboratory was not equipped with an automated thermal desorber. Each sample tube had to be placed inside the thermal desorption system one at a time. Due to this fact, and some other considerations such as costs of liquid Nitrogen, favored the use of standard CD charcoal tubes over the TD Carbosieve/Tenax tubes.

The setup used during this sampling campaign was the same setup used during the three REMs sampling campaign described in the previous chapter. Two venting valves were, however, added to the setup. These valves, one for each the ASTM and the FLEC, were added to control the flow of and to release the backpressure observed during sampling. The added vents valves helped to control and maintain the desired positive pressure needed for FLEC and ASTM sampling. Emission sampling of the carpet samples by the ASTM and the FLEC was performed on positive pressure driven flow into the charcoal tubes rather than on negative pressure pump driven flow. Only during Kappa sampling, Kappa's micro-pump (RENA Air 200) was used to draw air into the charcoal tube.

Inlet flows to the chamber/cell of each sampler and to each sampling tube was measured using a primary standard bubble meter. Air flow to the ASTM and the FLEC was from a single source of ultra high purity (UHP) nitrogen cylinder. The flow to the system was set at 480 cc/min and branched downstream into two separate and independent flows with one serving the FLEC and an other serving the ASTM. The average flow rate to the FLEC was 219 cc/min and the average flow rate to the ASTM was 223 cc/min. The balance of the flow (38 cc/min; 8% of the original 480 cc/min) was attributed to leakage in the system. Fluctuation in both the FLEC and the ASTM inlet flow rates were estimated at ±12%.

Fifteen (n=15) carpet samples were obtained from a large roll of a single carpet batch. This carpet roll was scheduled to be installed on a newly renovated office floor at the Computing Department of McGill University. Each carpet sample was used as the emitting source for each test. Although testing of the Kappa should have involved placing the Kappa directly on top of the newly installed carpet in the computing department, the fresh glue used beneath the installed carpet would have complicated the nature of this comparative study. Thus, for Kappa sampling, fresh carpet samples that were not yet glued, from the same carpet batch used for the FLEC and the ASTM, were placed on a table counter-top at the lab.

Placing the Kappa and the carpet sample in a laboratory environment generated a worst-case scenario of indoor air chemistry. In other words, if the O-ring felt of the Kappa was able to filter the numerous VOCs present in the air of a chemical laboratory and provide a clean sample air to Kappa's inner chamber, then the utility of the Kappa in delivering a purified air from within a partially contaminated indoor air can be established. Thus, Kappa sampling was performed using indoor laboratory air as the source of sampling air while both the FLEC and the ASTM used an UHP nitrogen, instead.

From the above carpet batch, 15 carpet samples were cut and prepared (30.5 cm by 30.5 cm). All carpet samples were placed together inside a sealed plastic bag and allowed to equilibrate with their own emissions for a week. Before each sampling set (five sampling set all together), three individual carpet samples were removed from the bag and prepared for their respective FLEC, ASTM and Kappa sampling. Each FLEC carpet sample was cut in circular shape to match the inner size of the carpet cell adapter manufactured by the FLEC (diameter 15 cm; sample area 177 cm^2). As previously mentioned, sampling VOC emissions in-situ from a fleecy material such as a carpet can not be conducted by the FLEC. Placing the FLEC on top of a carpet sample does not establish the seal necessary for a dynamic emission sampling. It is only through cutting a piece from the carpet and placing it inside a FLEC-based cell adapter that carpet sampling by the FLEC can be conducted. The latter renders the FLEC as a mere laboratory emission sampler rather than a field emission sampler.

Each carpet sample for the ASTM was kept as is (30.5 cm by 30.5 cm; sample area 930 cm^2). The main size of Kappa carpet samples were the same as the ones for the ASTM (30.5 cm by 30.5 cm. However, as per Kappa's mode of operation, the size of Kappa's O-ring AC felt would determine the sampling area. In this

Kappa sampling campaign, O-ring AC felts were prepared and pre-cut in circular shapes with a diameter of 8.5 cm, hence the Kappa carpet sampling area was 57cm^2.

Table 5.6 outlines the number of sampling performed. The net emitting surface area of each carpet sample was thus 930 cm^2, 177 cm^2, and 57 cm^2 for the ASTM, the FLEC and the Kappa respectively.

Table 5.6: ASTM/FLEC/Kappa carpet sampling campaign.

Carpet Sample	ASTM	FLEC	Kappa	Baseline (1/sample)	Sampling Blanks	Lab Blanks	Spiked Samples	Total
(n)	5	5	5	15	8	4	3	45

Room temperature during the FLEC and the ASTM tests ranged from 23°C to 26°C (CV 5%). Room relative humidity during the FLEC and the ASTM tests ranged from 35% to 37% (CV 3%). Relative humidity inside the FLEC and the ASTM was 70% (± 18%). This level of humidity was achieved using a humidification bubbler (Restek cat. #24282). The level of the humidity was controlled by combining the dry UHP nitrogen with a 100% humidified nitrogen.

Sampling flow rates (average flow to the sampling tubes) from the FLEC and the ASTM were 64 cc/min (SD 4 cc/min; CV 7%; n=5) and 64 cc/min (SD 8 cc/min; CV 12%; n=5), respectively. The balance of the inlet flow rates into the FLEC and the ASTM were vented through the two venting valves. The two venting valves, mentioned above, controlled the sampling flow into each charcoal tube through controlling the flow of the vents. The Kappa, on the other hand, was pre-configured to sample at a preset capillary needle-controlled micro-pump driven flow. Average sampling flow rate by the Kappa was 144 cc/min (SD 11 cc/min; CV 8%; n=4). During the Kappa sampling, one sample test was rejected, see below. FLEC, ASTM and Kappa sampling flow rates (sampling rate into sampling tube) were measured at least three times, at the beginning, at mid point and at the end, of each sampling run.

Tables 5.7, 5.8, and 5.9 present the parameters of the carpet sampling campaign for the three samplers respectively. A* mark on a cell indicates that the corresponding value was calibrated at the outset of the experiment (the start of sampling campaign) and was continuously monitored using a surrogate parameter. For example, the inlet flow rates to both the FLEC and the ASTM were calibrated and measured at the outset of the experiment. Both flow rates were monitored daily using a mark on the floating ball scale. Minor adjustments to each flow were performed using a micro-needle value. However, no attempt was made to re-measure (by a bubble flow meter) the main supply flow, since such an attempt would have disturbed the balance of the entire flow to the system.

Nevertheless, sampling flow rates in the FLEC and the ASTM were periodically measured, at least three times during each carpet test. Since the sampling flow in both the FLEC and the ASTM was supplied by the main supply flow, any variation in the former would trigger a variation in the latter. The highest variation observed in a sampling flow in both the FLEC and the ASTM had a CV value of 12% (Table 5.8). This value was thus used as an estimate of the CV value for the supply flow. As for the Kappa sampling parameters, the flow rates were based on the micro-sampling pump. All samples had consistent flow rates except for Carpet sample # 2 (Carpet S2). The sampling rate had dropped almost 60% from its original rate (144 cc/min to 60 cc/min).

After investigating the reason for this significant drop, it was found that the end tip of the tubing material connecting the sampling pump to the tip of the sampling tube may have slightly slipped away from the tip of the sampling tube. The connecting end of the tube was changed with a softer Teflon tube as a preventative measure. Carpet sample # 2 was eliminated form the comparison, regardless. Table 5.9 presents the Kappa sampling campaign with Carpet S2 removed from the set.

Table 5.7: FLEC Carpet Samples (* estimated).

FLEC-Carpet	unit	Carpet S1	Carpet S2	Carpet S3	Carpet S4	Carpet S5	Mean	SD	CV %
Sample Time	min	1403	1402	1398	1489	1487	1436	48	3
Sample Flow	cc/min	57	64	62	69	65	64	4	7
start	cc/min	58	65	62	69	65	64	4	7
end	cc/min	57	64	62	69	65	63	4	7
min.	cc/min	57	64	61	68	65	63	4	7
max.	cc/min	58	65	63	69	66	64	4	7
SD	cc/min	<1	<1	<1	<1	<1	-	-	-
CV	%	<1	<1	<1	<1	<1	-	-	-
Sample Vol.	cc	80532	90008	86536	102443	97250	91354	8658	9
Cell Flow*	cc/min	219	219	219	219	219	-	-	12*
Cell Vol.	cc	35	35	35	35	35	-	-	-
Carpet Area	cm^2	177	177	177	177	177	-	-	-
ACM*	(min.^-1)	6	6	6	6	6	-	-	12*
ACH*	(hr^-1)	375	375	375	375	375	-	-	12*

As mentioned above, sampling was performed using CD charcoal tubes (SKC coconut charcoal, Cat. #226-01 or Supelco equivalent – ORBO 32 small, Cat.

#20267-U). After sample collection, each tube was desorbed with carbon disulfide and analyzed by the Varian GC-FID system. Samples were collected over a twenty-four hour period. A baseline sample is completed before each carpet sample, at similar flow settings and conditions used during carpet sampling.

Table 5.8: ASTM Carpet Samples (* estimated).

ASTM-Carpet	unit	Carpet S1	Carpet S2	Carpet S3	Carpet S4	Carpet S5	Mean	SD	CV %
Sample Time	min	1402	1400	1493	1322	1490	1421	72	5
Sample Flow	cc/min	59	58	76	61	66	64	8	12
start	cc/min	59	58	77	61	65	64	8	12
end	cc/min	58	58	75	61	66	63	7	12
min.	cc/min	58	57	75	61	65	63	7	12
max.	cc/min	60	58	78	62	66	65	8	12
SD	cc/min	1	<1	1	<1	<1	-	-	-
CV	%	2	<1	1	<1	<1	-	-	-
Sample Vol.	cc	82297	80780	113916	80906	97684	91117	14593	16
Cell Flow*	cc/min	223	223	223	223	223	-	-	12*
Cell Vol.	cc	53000	53000	53000	53000	53000	-	-	-
Carpet Area	cm^2	930	930	930	930	930	-	-	-
ACM*	(min.^-1)	0.004	0.004	0.004	0.004	0.004	-	-	12*
ACH*	(hr^-1)	0.252	0.252	0.252	0.252	0.252	-	-	12*

Table 5.9: Kappa Carpet Samples (with test S2 removed).

Kappa-Carpet	units	Carpet S1	Carpet S3	Carpet S4	Carpet S5	Mean	SD	CV %
Sample Time	min	1326	1447	1516	1438	1432	79	5
Sample Flow	cc/min	158	137	148	133	144	11	8
start	cc/min	161	142	145	126	143	14	10
end	cc/min	155	134	151	138	145	10	7
min.	cc/min	155	133	144	125	140	13	9
max.	cc/min	161	142	152	139	148	10	7
SD	cc/min	3	4	3	6	-	-	-
CV	%	2	3	2	5	-	-	-
Sample Vol.	cc	209243	198384	223610	191815	205763	13900	7
Cell Flow	cc/min	158	137	148	133	144	11	8
Cell Vol.	cc	13	13	13	13	-	-	-
Carpet Area	cm^2	57	57	57	57	-	-	-
ACM	(min.^-1)	12	11	11	10	11	1	8
ACH	(hr^-1)	728	633	681	616	664	51	8

A 24 hour flush run was completed for the FLEC and the ASTM, between each sample. The general sampling order for the FLEC and the ASTM was: 1) Flush run; 2) Baseline sample run without carpet; and 3) Carpet sample run.

For the Kappa sampling campaign, the order was: 1) Baseline sample run without a carpet; and 2) Carpet sample run. During Kappa baseline sampling runs, clean glass plates were used instead of carpet samples for quality control. No flush runs were performed during Kappa sampling campaign since results of baseline tests were used to monitor cross contamination from previous sample runs.

Sampling blanks and lab blanks were incorporated periodically for quality control. Certified pre-spiked SKC charcoal tubes (SKC AnaChek Prespiked on 50/100 mg Anasorb Coconut-shell Charcoal Model No: 227-101A; toluene at 0.5 PEL) were administered for response and quality control.

The concentrations of toluene in the pre spiked sampling tubes were relatively high when compared to the collected VOCs from the carpet samples. These pre-spiked tubes were prepared for industrial sampling campaigns, rather than low emission carpet sampling campaign. A 0.5 of the PEL of toluene is 25 ppm in volume. This translates into a concentration of almost 96 mg/m^3. That is at least 100 times higher than the average indoor Total VOC concentrations, let alone toluene concentration generated by emissions form a single sample of a carpet. Thus, although the per-spiked, ready-made and certified charcoal tube samples were excellent and practical, their application to indoor "non-industrial" environment sampling is not appropriate.

All samples collected including baseline samples, carpet samples, sample blanks and lab blanks, were solvent desorbed using 0.5 ml of carbon disulfide (CS_2). An aliquot of each sample solution was transferred to a second micro volume insert vial (0.5ml). Micro vial inserts had to be used since desorptions of samples collected were performed using 0.5 ml CS_2 as opposed to the standard 2 ml CS_2 recommended by NIOSH sampling and analysis protocol.[27] This modification is implemented to reduce the dilution effect inherent in chemical desorption and to boost the analytical detection limit.

The use of micro-volume vial inserts (Figure 5.3) allowed the desorbed solution from each sample to fill the sampling vial and reach the required level/height so that the tip of the injection needle (Autosampler Varian 8100) could be immersed in a sufficient depth of solution. A 5ul-sample solution from each sample vial was drawn out for injection in to a gas chromatograph.

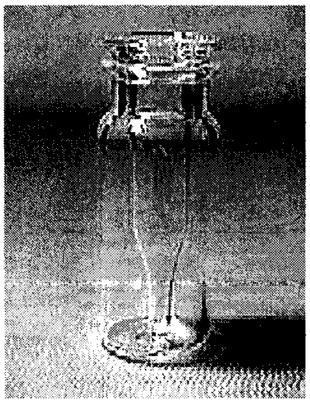


Figure 5.3: A 0.5 ml micro vial insert used for sample concentration (Picture curtsey of www.TechLab.de).

Samples were analyzed using a gas chromatography-flame ionization detector (GC-FID) system (Varian 3400) equipped with a 30m fused silica capillary column (VOCOL Capillary Column, Cat. #2-5320). A temperature program ramp of 5°C/min. increasing from 40°C to 200°C (injector temperature 200°C, detector temperature 250°C) was used, resulting in a total analysis run time of 36 minutes. Blank vials were periodically included in sample analysis to detect column background peaks between sample runs for possible cross contamination. Several vials with pure carbon disulfide were also included in each analysis set for quality control.

5.5.2 Chromatographic Fingerprints

The average sample volumes during FLEC and ASTM sampling were calculated at 0.09 m^3 (SD 0.01 m^3; CV 9%; n=5) and 0.09 m^3 (SD 0.01 m^3; CV 16%; n=5), respectively. The average sampling volume during Kappa sampling was calculated at 0.21 m^3 (SD 0.01 m^3; CV 7%; n=4). The doubling of sampling rate and hence sample volume in the Kappa versus both the FLEC and the ASTM was due to a few precautionary assumptions based on lessons learned from the REM tests.

These assumptions were: 1) a higher sampling rate would assure a continuous momentum of flow through the O-ring felt of the Kappa; 2) a larger sampling volume would partially compensate for the smaller surface area of the carpet sample in the Kappa; and 3) a higher flow rate may be needed as a preventive measure against loss of sensitivity due to the reliance of the Kappa on the indoor air for its inlet flow as opposed to the UHP N_2 used in both the FLEC and the ASTM.

After sample analysis, it was found that none of these assumptions were indeed correct. In fact, it would have been much easier to use the same flow rate in the Kappa as in the FLEC and the ASTM. Regardless of the inconveniences caused by the different sampling flow rates, responses factors of each test were normalized and were corrected for, nevertheless.

FID responses and hence concentrations of all samples collected were normalized on respective sampling volume. Throughout the sampling campaign, samples were analyzed less than two weeks after sampling during which time they were stored at -20°C.

The overall "fingerprints" of peaks resulting from the analysis of carpet samples from each sampler were more or less similar, but some were partially shifted left or right compared to each other, if analyzed on different days. To correct these shifted results, retention times (RT) were adjusted based on the retention time of their respective benzene peak contained in CS_2 and used as an internal standard for retention time correction. Thus, all retention times of the shifted results, if any, were adjusted by an amount based on benzene retention times. Accordingly, the five carpet samples from each the ASTM, the FLEC and the four carpet samples from the Kappa were matched according to the adjusted retention times.

The result of this matching process created adjusted carpet "fingerprints / chromatographs" unique to each sampler used. Qualitatively speaking, these RT adjusted and normalized chromatograms could be used to compare the similarities and the differences between the three samplers. The differing factors in the three sampling methods such as flow rates, exposed sampling area, sink effects, chamber size, and sampling volume should not pose a major influence on the overall chromatographic pattern of VOC emissions by each carpet sample.

Although all carpet samples were from a single carpet batch, large variations in emissions from different spots within a material sample are common in building materials due to the manufacturing processes.[28] These differing factors would greatly influence the net mass collected in each sampling tube, hence the estimated concentration. Estimated concentrations would consequently affect the calculation of emission rate (ER) results. These sampling variations should somehow be accounted for especially when the objective is to establish a realistic comparative analysis between different emission chambers. However accounting for some of the variations including the variations in the primary emissions from same-type-same-batch carpet samples is likely impractical, if not impossible.

The chromatographic pattern that is generated by each sampler was used as a metering method for material emission profiling. The focus of the following discussion is on the shape/pattern/picture of each chromatogram, the retention time of each peak, representing a specific VOC, and on the most shared and abundant peaks. The size of each peak as represented by its FID response area and the relative magnitude of each peak to other peaks within a single sample was taken into consideration during mapping and analysis of peaks within each set of samples.

FID responses of baseline samples (empty chamber/cell) were subtracted from the corresponding carpet samples. Chromatographic results of each sampler were sorted to filter the data to the most prevalent peaks. Results of each sampler were then compiled and mapped according to the retention time of each matching peak. Figure 5.4 presents the chromatograms (finger prints) of the five carpet samples performed by the FLEC. Figure 5.5 presents the chromatograms of the five carpet samples performed by the ASTM. Figure 5.6 presents the chromatograms of the four carpet samples performed by the Kappa. All associated Tables (Table 5.10, Table 5.11, Table 5.12) are placed below each corresponding Figure.

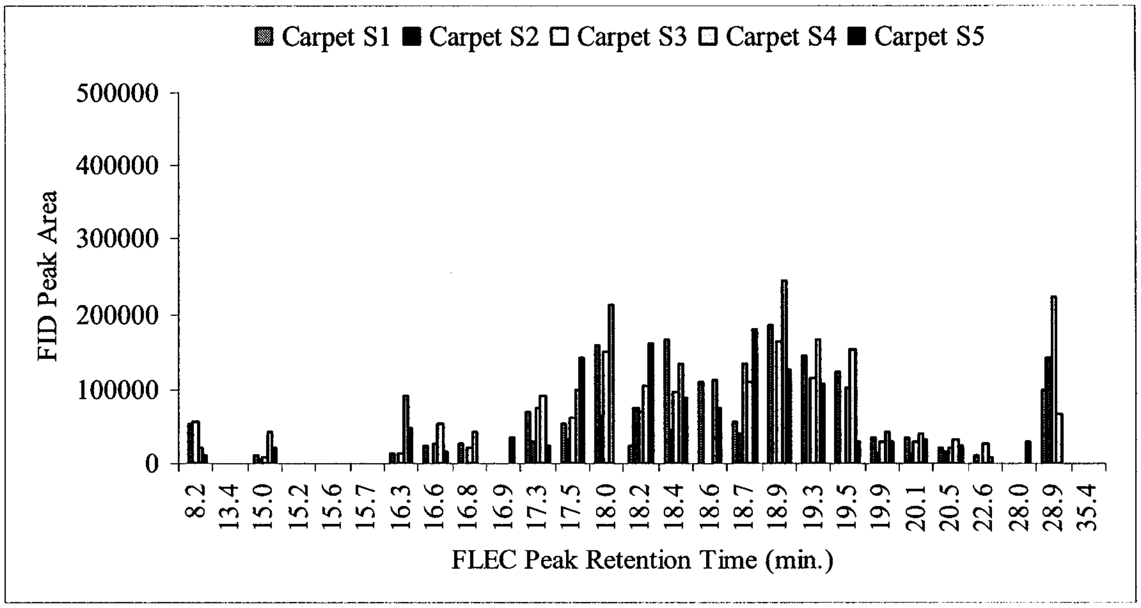


Figure 5.4: Matched peak chromatograms of the five carpet samples conducted by the FLEC sampler.

Table 5.10: FLEC most abundant peaks in terms of FID peak area.

RT	**Carpet S1**	**Carpet S2**	**Carpet S3**	**Carpet S4**	**Carpet S5**	**Average**	**SD**	**CV**
min.	*FID Area*	*Fid Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*%*
8.2		54628	57029	21883	11270	36203	23093	64
13.4								
15.0	11401	6260	6832	42466	21757	17743	15153	85
15.2								
15.6								
15.7								
16.3	14717		14158	91470	48524	42217	36557	87
16.6	24829		25550	54548	15530	30114	16916	56
16.8	27822		20232	42544		30199	11344	38
16.9					35295	35295		
17.3	68863	28344	74081	91870	24510	57534	29681	52
17.5	53606	31205	62634	99745	142472	77932	43733	56
18.0	157261	63959	151624	211728		146143	61126	42
18.2	24250	74182	70295	103523	161110	86672	50363	58
18.4	166333	45287	96105	134657	89246	106326	46167	43
18.6	110313			112187	74891	99130	21013	21
18.7	57545	39118	135448	109676	178901	104138	57007	55
18.9	186644		164921	245083	127340	180997	49249	27
19.3	145904		114476	167759	108230	134092	27849	21
19.5	124217		102421	152419	30250	102327	52229	51
19.9	35858	12900	28255	43437	29641	30018	11297	38
20.1	35442	14363	28694	41547	31529	30315	10137	33
20.5	20325	17338	21406	31636	23755	22892	5405	24
22.6	11001		28016	7699		15572	10903	70
28.0					28439	28439		
28.9	100091	143220	223153	67272		133434	67415	51
35.4								

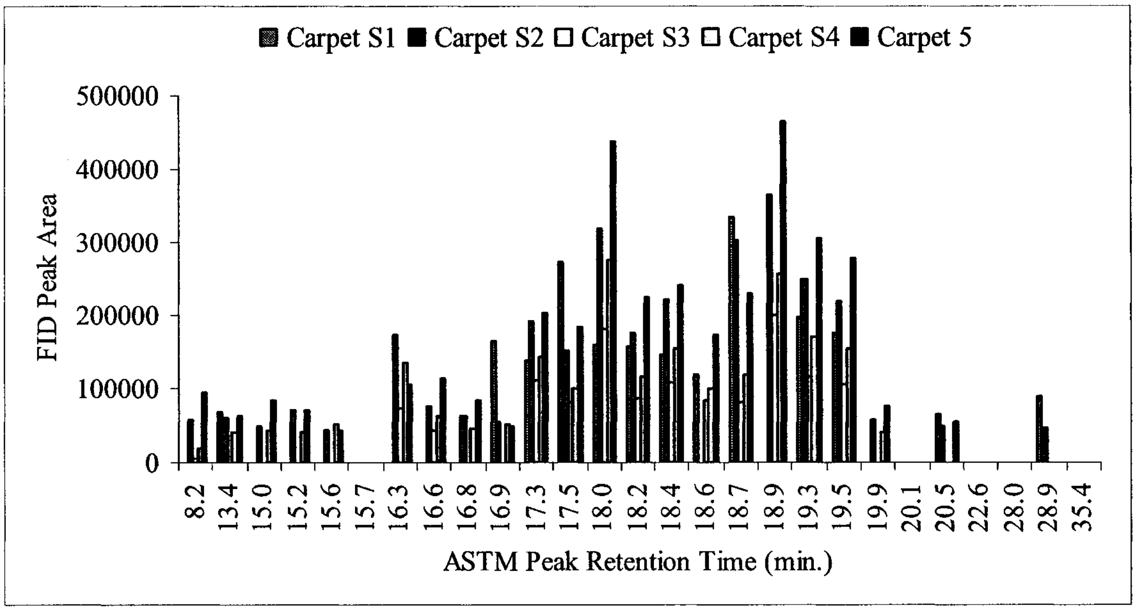


Figure 5.5: Matched peak chromatograms of the five carpet samples conducted by the ASTM sampler.

Table 5.11: ASTM most abundant peaks in terms of FID peak area.

RT	**Carpet S1**	**Carpet S2**	**Carpet S3**	**Carpet S4**	**Carpet S5**	**Average**	**SD**	**CV**
min.	*FID Area*	*Fid Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*%*
8.2		57681	6528	18365	93652	44057	39639	90
13.4	68861	58232		40964	61818	57469	11856	21
15.0		48213		43013	84525	58584	22616	39
15.2		69703		41156	70143	60334	16610	28
15.6		44483		50681	42094	45753	4432	10
15.7								
16.3		173295	74199	135133	106219	122212	42180	35
16.6		74709	43802	62557	112902	73493	29187	40
16.8		61493		45608	84370	63824	19486	31
16.9	165493	54439		50501	47411	79461	57427	72
17.3	138691	191249	110426	142197	201510	156815	38332	24
17.5	273477	151501	81671	100026	183884	158112	76214	48
18.0	160170	319055	182288	275380	437296	274838	111873	41
18.2	155620	175050	87225	117472	224558	151985	52908	35
18.4	145122	221666	106827	154840	240483	173788	55689	32
18.6	119625		82638	100362	171765	118597	38529	32
18.7	335035	301561	80837	120220	228804	213291	110748	52
18.9		363928	200752	257461	464168	321577	116670	36
19.3	198549	248943	116597	170166	305597	207970	72589	35
19.5	175966	218535	104911	153991	277933	186267	65594	35
19.9		57062		40732	74903	57566	17091	30
20.1								
20.5	65670	47616			53215	55500	9241	17
22.6								
28.0								
28.9	90188	46737				68462	30724	45
35.4								

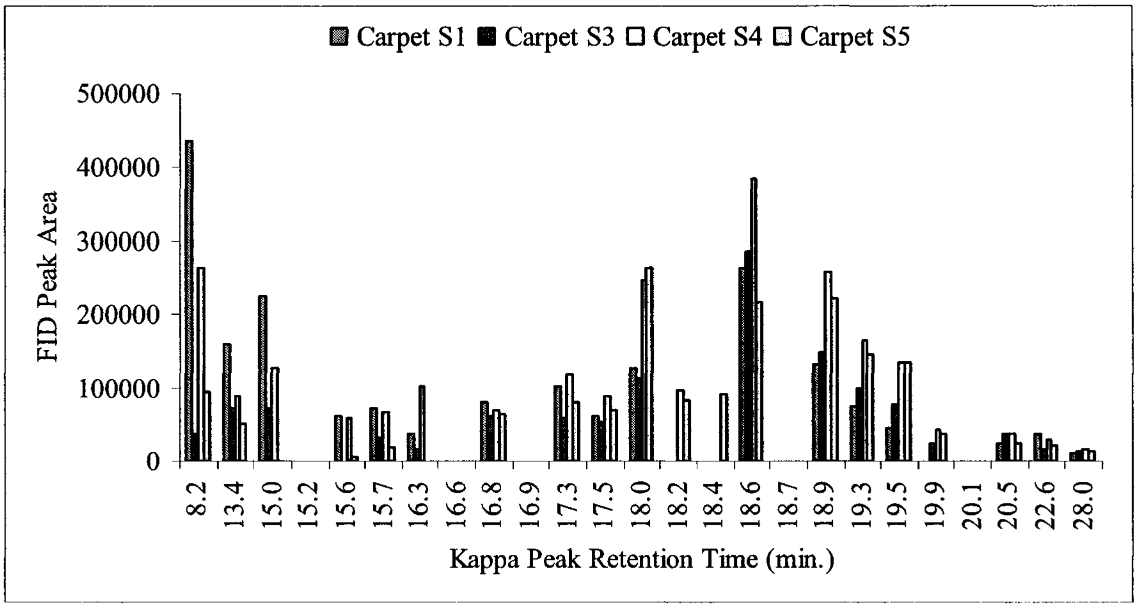


Figure 5.6: Matched peak chromatograms of the four carpet samples conducted by the Kappa Sampler.

Table 5.12: Kappa most abundant peaks in terms of FID peak area.

RT	**Carpet S1**	**Carpet S3**	**Carpet S4**	**Carpet S5**	**Average**	**SD**	**CV**
min.	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*FID Area*	*%*
8.2	434823	39291	264771	95467	208588	178696	86
13.4	159896	72999	90585	52105	93896	46727	50
15.0	225852	72394	128982		142409	77605	54
15.2							
15.6	63405		59452	4717	42525	32802	77
15.7	73501	33631	66592	19105	48207	26059	54
16.3	38462	16352	103605		52806	45361	86
16.6							
16.8	82515	62263	70362	65498	70160	8884	13
16.9							
17.3	103085	60928	119740	81284	91259	25629	28
17.5	61771	53708	89392	70208	68770	15310	22
18.0	128387	115332	247152	264478	188837	77845	41
18.2			98036	84660	91348	9458	10
18.4				93154	93154		
18.6	264299	285786	382461	217463	287502	69436	24
18.7							
18.9	132934	149861	258527	223704	191257	59703	31
19.3	76081	99296	165476	146612	121866	41311	34
19.5	46363	79372	135576	134683	98999	43844	44
19.9		25450	42407	36956	34938	8657	25
20.1							
20.5	24440	37648	36777	23687	30638	7606	25
22.6	39389	17353	30735	20864	27085	9969	37
28.0	9583	12879	17113	12516	13023	3101	24
28.9		44616	52341	56073	51010	5843	11
35.4	18332	16049	26983	20001	20341	4715	23

The following formulas were used to calculate the concentrations and to estimate the emission rates of the samples collected.

Concentration = (FID response x Calibration Factor) / Sampling Volume [eq.1]
Emission Rate = (Concentration x ACH x Chamber Volume) / Surface Area [eq.2]

The calibration factor is established from a 9-point toluene calibration curve outlined in Figure 5.7. Table 5.13 presents the chamber/cell sampling parameters including the cell/chamber volume (V), surface area (SA), sampling volume (SV) and air change rate (ACH) with corresponding CVs, if applicable, per sampler. Tables 5.14, 5.15, and 5.16 present the estimated emission rate data per sampler and associated graphs (Figures 5.8, 5.9 and 5.10).

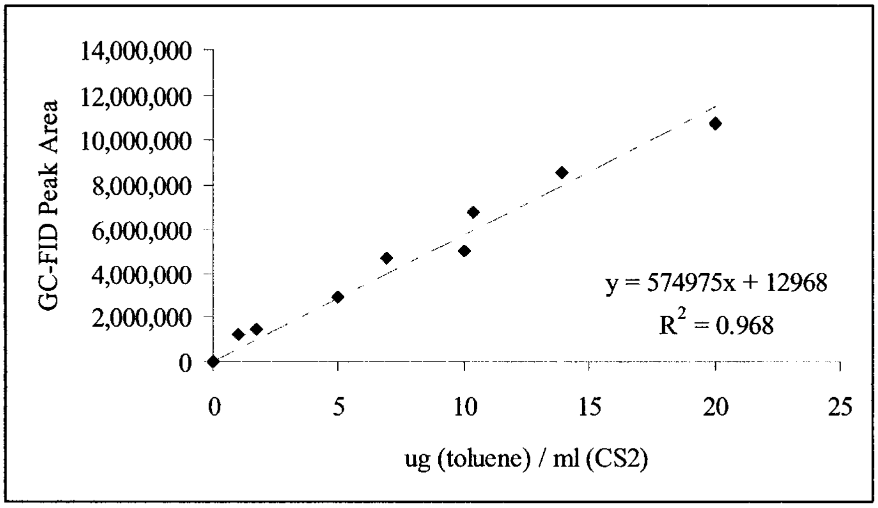


Figure 5.7: GC-FID 9-point calibration curve (5ul injection).

Table 5.13: Chamber / Cell Sampling Parameters.

	ASTM	CV %	**FLEC**	CV %	**Kappa**	CV %
V m3	5.3E-02	na	3.5E-05	na	1.3E-05	na
SA m2	0.093	na	0.0177	na	0.0057	na
SV m3	0.09	16	0.09	9	0.21	7
ACH	0.252	12	375	12	664	8

Table 5.14: FLEC Carpet Emission Rates

RT	Carpet S1	Carpet S2	Carpet S3	Carpet S4	Carpet S5	Average	SD	CV
min.	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*%*
8.2		0.39	0.43	0.14	0.07	0.26	0.18	69
13.4								
15.0	0.09	0.04	0.05	0.27	0.14	0.12	0.09	76
15.2								
15.6								
15.7								
16.3	0.12		0.11	0.58	0.32	0.28	0.22	79
16.6	0.20		0.19	0.34	0.10	0.21	0.10	48
16.8	0.22		0.15	0.27		0.21	0.06	28
16.9					0.23	0.23		
17.3	0.55	0.20	0.55	0.58	0.16	0.41	0.21	51
17.5	0.43	0.22	0.47	0.63	0.95	0.54	0.27	50
18.0	1.26	0.46	1.13	1.33		1.05	0.40	38
18.2	0.19	0.53	0.52	0.65	1.07	0.59	0.32	53
18.4	1.33	0.32	0.72	0.85	0.59	0.76	0.37	49
18.6	0.88			0.71	0.50	0.70	0.19	28
18.7	0.46	0.28	1.01	0.69	1.19	0.73	0.38	52
18.9	1.50		1.23	1.54	0.85	1.28	0.32	25
19.3	1.17		0.85	1.06	0.72	0.95	0.20	21
19.5	1.00		0.76	0.96	0.20	0.73	0.37	50
19.9	0.29	0.09	0.21	0.27	0.20	0.21	0.08	37
20.1	0.28	0.10	0.21	0.26	0.21	0.21	0.07	33
20.5	0.16	0.12	0.16	0.20	0.16	0.16	0.03	17
22.6	0.09		0.21	0.05		0.12	0.08	73
28.0					0.19	0.19		
28.9	0.80	1.03	1.66	0.42		0.98	0.52	53
35.4								

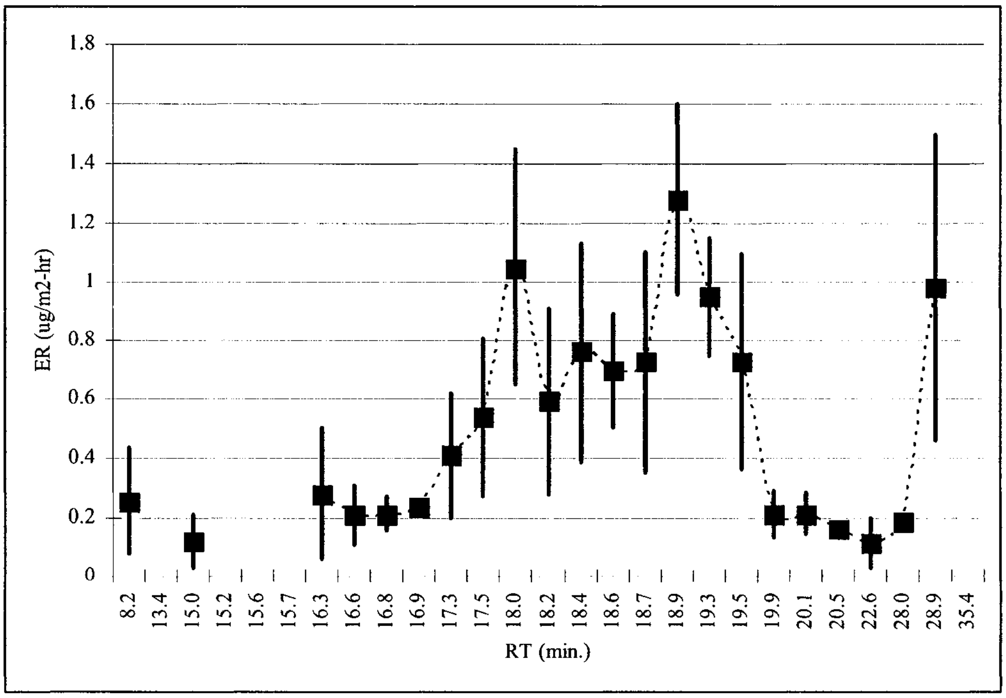


Figure 5.8: FLEC carpet ER values with associated CVs. Dashed lines are for mapping purpose only.

Table 5.15: ASTM Carpet Emission Rates

RT	Carpet S1	Carpet S2	Carpet S3	Carpet S4	Carpet S5	Average	SD	CV
min.	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*%*
8.2		0.09	0.01	0.03	0.12	0.06	0.05	86
13.4	0.10	0.09		0.06	0.08	0.08	0.02	21
15.0		0.07		0.07	0.11	0.08	0.02	27
15.2		0.11		0.06	0.09	0.09	0.02	26
15.6		0.07		0.08	0.05	0.07	0.01	18
15.7								
16.3		0.27	0.08	0.21	0.14	0.17	0.08	47
16.6		0.12	0.05	0.10	0.14	0.10	0.04	40
16.8		0.10		0.07	0.11	0.09	0.02	21
16.9	0.25	0.08		0.08	0.06	0.12	0.09	75
17.3	0.21	0.30	0.12	0.22	0.26	0.22	0.07	30
17.5	0.42	0.23	0.09	0.15	0.24	0.23	0.12	54
18.0	0.24	0.49	0.20	0.43	0.56	0.38	0.16	41
18.2	0.24	0.27	0.10	0.18	0.29	0.21	0.08	36
18.4	0.22	0.34	0.12	0.24	0.31	0.25	0.09	36
18.6	0.18		0.09	0.16	0.22	0.16	0.05	34
18.7	0.51	0.47	0.09	0.19	0.29	0.31	0.18	58
18.9		0.56	0.22	0.40	0.59	0.44	0.17	39
19.3	0.30	0.39	0.13	0.26	0.39	0.29	0.11	37
19.5	0.27	0.34	0.12	0.24	0.36	0.26	0.10	36
19.9		0.09		0.06	0.10	0.08	0.02	21
20.1								
20.5	0.10	0.07			0.07	0.08	0.02	21
22.6								
28.0								
28.9	0.14	0.07				0.10	0.05	44
35.4								

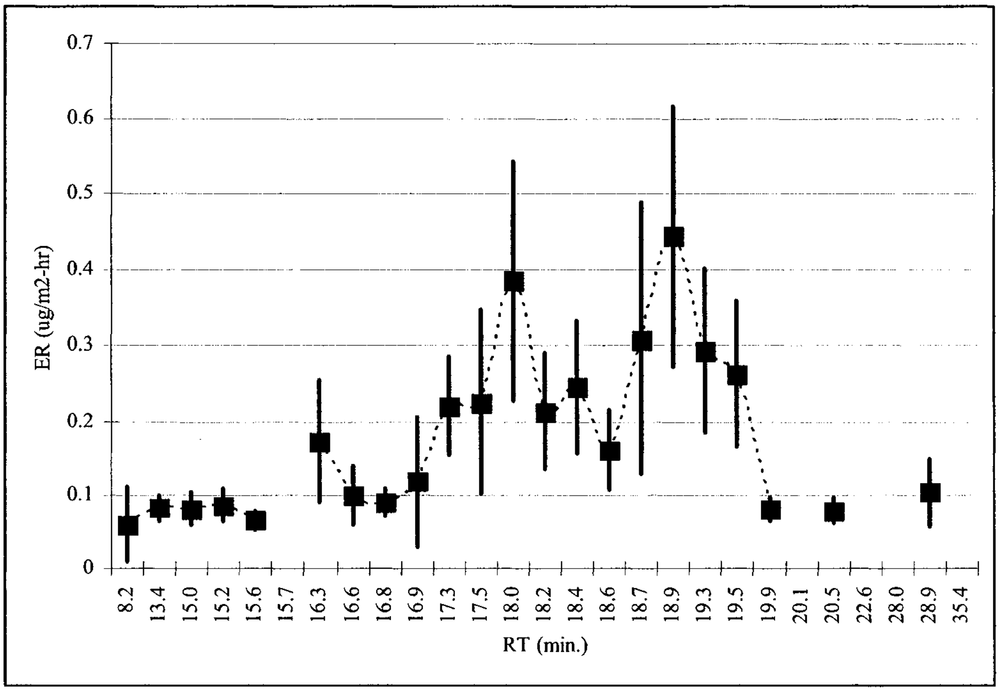


Figure 5.9: ASTM carpet ER values with associated CVs. Dashed lines are for mapping purpose only.

Table 5.16: Kappa Carpet Emission Rates

RT	Carpet S1	Carpet S3	Carpet S4	Carpet S5	Average	SD	CV
min.	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*ug/m2-hr*	*%*
8.2	3.00	0.25	1.60	0.61	1.36	1.23	90
13.4	1.10	0.46	0.55	0.33	0.61	0.34	56
15.0	1.56	0.46	0.78		0.93	0.57	61
15.2							
15.6	0.44		0.36	0.03	0.28	0.22	78
15.7	0.51	0.21	0.40	0.12	0.31	0.18	56
16.3	0.27	0.10	0.63		0.33	0.27	81
16.6							
16.8	0.57	0.39	0.42	0.42	0.45	0.08	18
16.9							
17.3	0.71	0.39	0.72	0.52	0.58	0.16	28
17.5	0.43	0.34	0.54	0.45	0.44	0.08	19
18.0	0.89	0.73	1.49	1.68	1.20	0.46	39
18.2			0.59	0.54	0.57	0.04	7
18.4				0.59	0.59		
18.6	1.82	1.81	2.31	1.38	1.83	0.38	21
18.7							
18.9	0.92	0.95	1.56	1.42	1.21	0.33	27
19.3	0.53	0.63	1.00	0.93	0.77	0.23	30
19.5	0.32	0.50	0.82	0.86	0.62	0.26	41
19.9		0.16	0.26	0.24	0.22	0.05	23
20.1							
20.5	0.17	0.24	0.22	0.15	0.19	0.04	21
22.6	0.27	0.11	0.19	0.13	0.18	0.07	41
28.0	0.07	0.08	0.10	0.08	0.08	0.02	19
28.9		0.28	0.32	0.36	0.32	0.04	12
35.4	0.13	0.10	0.16	0.13	0.13	0.03	19

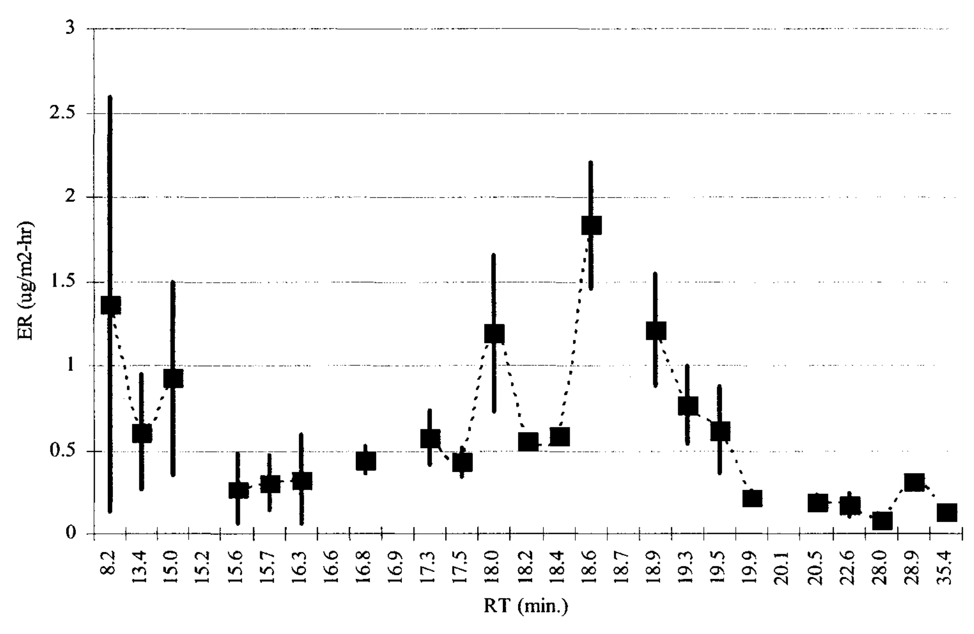


Figure 5.10: Kappa carpet ER values with associated CVs. Dashed lines are for mapping purpose only.

The detection limit used for the calculation of concentrations sampled was 0.1ug/m^3. The IDL (Instrument Detection Limit) was used, rather than the MDL or the QDL (Method Detection Limit; Quantitation Detection Limit) since the objective of this sampling campaign was to establish a baseline for relative comparative analysis of the three samplers rather than assessing the absolute emission rate of the test material. This IDL was established based on a mean FID response (peak area) of 10,000 for the three samplers. For the system used, any response (peak area) below the 2000 range was considered to be response noise. An average response-to-noise ratio of five was considered an appropriate IDL for the purpose of this semi-quantitative/comparative sampling campaign.

Having aggregated the resulting peaks, nine VOCs (defined by their retention times) were selected to establish the basis for comparing the three samplers. The selection of these VOCs was based on mapping the pattern of the chromatograms generated. An example of such mapping can be observed by the dashed lines overlaid over the mean ER values presented in Figures 5.8 through 5.10, above. Two identifiable and common sets of patterns appear in all the three aforementioned Figures. The first is a pattern generated by connecting the five consecutive RTs of 17.3, 17.5, 18.0, 18.2, and 18.4. The second is a pattern generated by connecting the four consecutive RTs of 18.9, 19.3, 19.5, and 19.9.

The mapping of these nine shared and uniquely identified VOCs and their respective ER values is presented by a radar map in Figure 5.11.

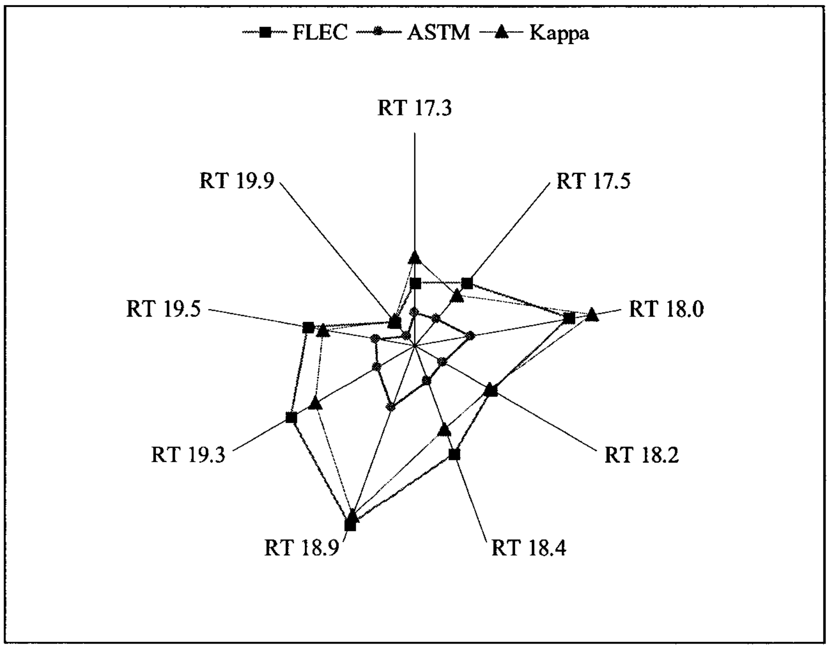


Figure 5.11: Mapping of the 9-VOCs and their ER values as captured by the three different samplers.

The radar map above indicates that these 9-VOCs have had a common source, irrespective of their absolute values. One could conclude that the three samplers did indeed match in their ability to capture at least 9-VOCs from a common emitting source and the source of these 9-VOCs was indeed the carpet samples. There are other notably detected VOCs that were captured by at least two of the three samplers; however mapping or finding a trend for those other captured VOCs is not as straightforward as the trend observed by the aforementioned 9-VOC. A closer look at some of the other captured VOCs has revealed few interesting observations. Figure 5.12 illustrates the mean response of the three samplers to all the VOCs captured.

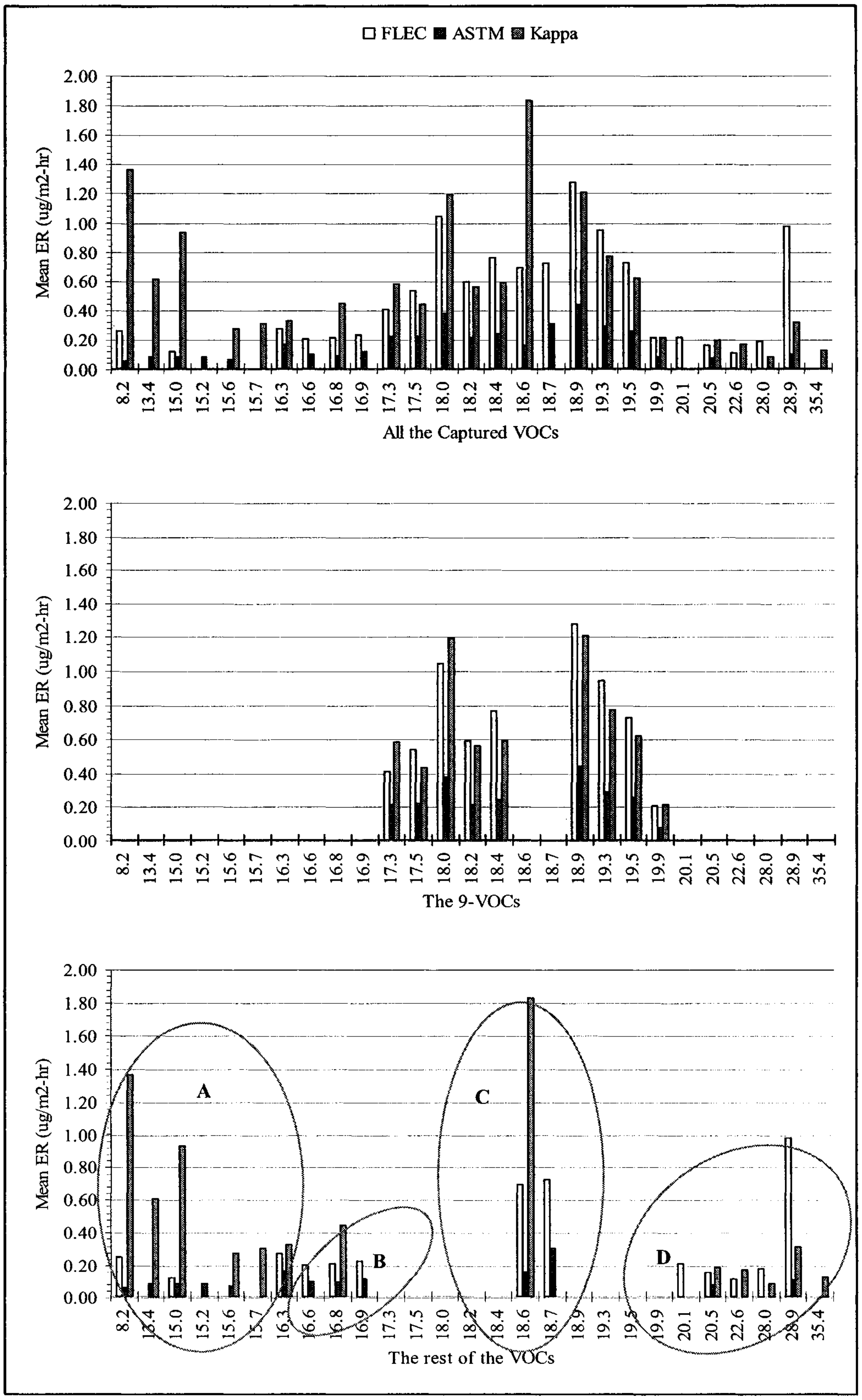


Figure 5.12: Top- all the VOCs captured by the three samplers; Middle- the "9-VOCs"; Bottom: the "rest of" the VOCs.

From the Figure above, one can determine the total number of VOCs that are captured by all the samplers, at least two of the sampler and only one sampler. Out of the total 27 VOCs detected, 16 VOCs were captured by all the three samplers (59%). From the remaining 11 VOCs, 7 VOCs were captured by only two samplers (26%). 2 VOCs were captured by both the ASTM and the FLEC; 2 by both the ASTM and the Kappa, and 3 by both the FLEC and the Kappa. Only 4 VOCs (15%) were captured individually either by the FLEC (2 VOCs) or by the Kappa (2 VOCs). No VOC was captured only by the ASTM. Interestingly, each of the samplers, the FLEC, the ASTM and the Kappa, captured 22 out of the 27 VOCs. In other words, if comparing the three samplers was based on the number of VOCs they captured, they all scored equally.

5.5.3 Qualitative Analysis

As per the VOC that each sampler is more likely to capture, this was based on the retention time (RT) of each VOC. RT is a good indication of the volatility, the boiling point, the vapor pressure and the molecular size of a VOC. Generally, the lower the retention time the more volatile the VOC, the lower the boiling point, the higher the vapor pressure and the smaller the molecular weight.

The retention time axis (the x-axis of Figure 5.12) was divided into four bins (A, B, C, and D): a relatively volatile VOC bin (RT 8.2 to RT 16.3); a moderately volatile VOC bin (RT 16.6 to RT 16.9); a slightly volatile VOC bin (RT 17.3 to RT 19.9); and, a less volatile VOC bin (RT 20.1 to RT 35.4).

The VOCs present in these four bins are considered for qualitative evaluation while the 9-VOCs presented in the middle part of Figure 5.12 are considered for quantitative evaluation, presented later, since not all of the "bin-categories" VOCs were captured by all the three samplers. The 9-VOCs, on the other hand, have all been captured by the three samplers. In this study, a VOC is considered to be of interest if it was captured and matched by the three samplers in at least three of the five repeated sampler per sampler. A detailed qualitative analysis for those "four-bin" VOCs is presented next, while the quantitative comparative analysis for those matched 9-VOCs is presented later.

5.5.3.1 The Sink and its Effect

Examining the VOCs captured in each of the four bins (A, B, C, and D in Figure 5.12), it becomes apparent that the ASTM sampler was better in capturing the more volatile VOCs than the less volatile VOCs. This supports the assumption that many of the lesser volatile VOCs, because they are larger in molecular size, tend to adsorb on the interior surfaces of a chamber/cell. The more volatile the organic compound is (low boiling point or high vapour pressure), the weaker its sink strength or adsorption capacity becomes. The availability of a sink surface is more abundant in the ASTM than in either the FLEC or the Kappa. The chamber/cell volume surface areas for the ASTM, the FLEC and the Kappa are 8793 cm2, 227 cm2, and 117 cm2, respectively. The ASTM had 39 times more surface area available for VOCs to adsorb on to than does the FLEC, and 75 times more than does the Kappa.

The sink effect lessens the concentration of each sample and accordingly the calculation of emission rates. Studies have indicated that the higher the boiling-point of a VOC the higher its sink or adsorption potential.[29] This does not exclude, however, the notion that the low boiling point VOCs do also adsorb on chamber surfaces. In fact lower boiling point VOCs have adsorption capacities and do contribute to the sink effect, but at a lesser magnitude.[30] Sink effect is lower for the smaller molecule VOCs and higher for larger molecules.[31] This could explain the reason why almost all the emission rates were lower in the ASTM than in either the FLEC or the Kappa. A similar trend is exhibited for the FLEC and the Kappa, but to a much lesser degree.

The volume of an emission chamber does indeed influence the calculated emission rate of a material, even if the calculations were normalized on loading factors. A loading factor is the surface area of an emitting material divided by the volume of the chamber in which the material is placed. It has the unit of m^2/m^3. In a multi-chamber study that was performed using different sizes of chambers, including a 50 liter chamber, a 3-liter chamber and a 35cc FLEC, a similar sink effect was observed.[32] The chambers were used to sample VOC emissions from a carpet. One of the results of the study indicated that the area specific emission rate of 2-ethylhexanol (MW 130, a relatively larger VOC compared with toluene MW 92) was the highest in the FLEC (a small chamber) and the lowest in the 50 liter chamber. Other researches have also reported that the area specific emission rates, for relatively larger compounds such as di-2-ethylhexyl phthalate (DEHP), emitted from PVC flooring, are inversely proportional to the loading factor of the emission chambers used to sample these flooring materials.[33] In the latter study, two chambers were used, a 50L ASTM-like and the 35cc FLEC.

While the ASTM chamber is less likely to adsorb the more volatile VOCs on its inner surfaces, results of this sampling campaign (according to Figure 5.12) also suggest that both the FLEC and the Kappa are less likely to adsorb the less volatile VOCs on its inner surfaces; a mutual inclusive argument of the sink-effect. This is clearly noticeable in the bin D category of Figure 5.12. The capturing ability of both the FLEC and the Kappa, the two smaller chambers with the least inner surface areas, are far more superior to the ASTM in sampling, capturing and hence reporting the less volatile VOCs. This is a direct testimony to the presence of a large sink effect in the ASTM and its deterring effect on the less volatile VOCs.

5.5.3.2 The FLEC and its Cavity

The FLEC, did not match the ASTM or the Kappa in its capacity to capture the higher volatile VOCs (Figure 5.12, bin A). There are limited studies that attributed some of the variations observed in VOC emission sampling to the profile of the FLEC and its inner cavity. Several studies have demonstrated that the air flow at the surface of an emitting material under the mouthpiece of the FLEC may not be homogeneous. [34,35]

There are specific spots, at the centre and on two opposite locations at the peripheral rim of the mouthpiece of the FLEC, that sampling air, in terms of flow rate or velocity, is almost nil. This causes VOC emissions on affected spots/areas of the sampling material to be reduced. To illustrate this slowing down phenomenon of surface emission, Figure 5.13 below illustrates an approximate schematic diagram of the inverted FLEC showing its bottom cavity or mouthpiece. The arrows on the Figure indicate the two locations of the sampling air where it enters into FLEC cavity. The dashed line represents the slit that is integrated into the design of the FLEC. This slit was provided to channel the inlet air to the edges of the test material first and then move inward to the center of the material.

However, based on results obtained from a recent CFD (Computational Fluid Dynamic) study[36] as well as the earlier flow field study mentioned above,[37] air velocity profile in the cavity of the FLEC, at the surface of the test material varied according to the location of the two air inlets with respect to the test material. Schematically, the sampling mouthpiece of the FLEC can be divided into sectors of varying flow fields. These flow fields are approximately illustrated by the five shaded areas shown in the Figure 5.13; the darker the shade, the lower the air velocity. Accordingly, sampling air barely reaches the center and the two opposite ends of the test material.

The FLEC has in fact failed to capture ~50% of the more volatile VOCs that were captured by either the ASTM or the Kappa. The term "capture" in the context of this study refers to capturing VOCs at levels above the detection limit. The flow field effect may have contributed to the results obtained during this sampling campaign.

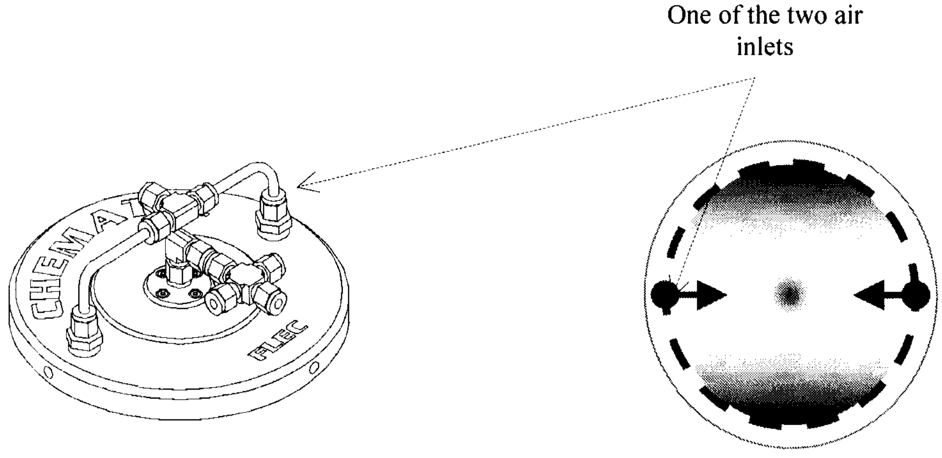


Figure 5.13: The FLEC (left) and a schematic of an inverted FLEC showing its sampling mouthpiece (right) with different flow field intensities; the darker the zone the less the air flow.
(After: Uhde et al. 1998 & Murakami et al. 2002)

5.5.3.3 The Kappa and its Cavity

All VOCs captured by the Kappa were equally distributed over the entire range of the retention times presented above. Qualitatively, there was no preference as such by the Kappa towards capturing certain categories of VOCs as observed in both the ASTM and the FLEC. This could be due to either the novel air flow delivery system developed for Kappa, the smaller cell volume of the kappa, the higher sampling flow rate used during Kappa sampling or all of the above. The latter reason is analyzed later. As per the former reason, there is indeed a major difference between the Kappa and either the FLEC or the ASTM in terms of the inlet air delivery and the sampling flow fields. As per the smaller cell volume of the Kappa compared to the other two samplers, a comparative analysis that includes cell volumes was performed and results discussed in the upcoming section.

In the Kappa, the sample air flows directly into a cavity without any diversions or splits. Kappa's inlet air, which is also the entire sampling air (split-less sampling), skims over the test material at a steady rate and at a constant velocity. Figure 5.14 is a schematic of the inverted Kappa. The square piece with its circular hole represents the activated carbon felt, the "corner stone" of the Kappa.

To sample emissions from a building material, the square felt is placed first on top of the test material and then the Kappa on top of the felt. The term O-ring, which was used during Kappa's description above, makes reference to the hole at the center of the square ACF piece. The size of the ACF piece is 20 cm by 20 cm, and the size of the centre hole (O-ring opening) could vary from 5cm ∅ to 10cm ∅ depending on the sampling material.

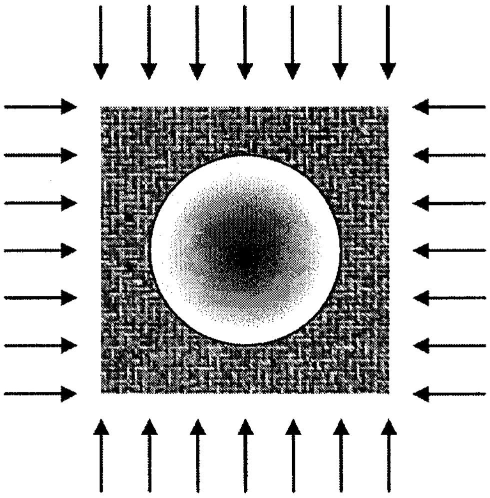


Figure 5.14: A schematic of Kappa's inverted mouthpiece showing the activated carbon felt O-ring and the flow field zones (shaded gray) at the centre.

The arrows around the square piece (the ACF) represent the air flow as it enters into the Kappa's mouthpiece. This inlet air, which is supplied by indoor air where sampling is taking place, is pulled into the Kappa by the action of a sampling pump at a pre-defined rate. The sampling pump is attached to the sampling tube. The sampling tube is a standard charcoal tube, the inlet end of which is placed perpendicular to the center of the central O-ring and positioned slightly above the surface of the test material. As indoor air enters the Kappa from all the directions around the ACF, it passes through the activated carbon filter before it reaches the test material.

The amount of active sites that are present at the path of the inlet air while it traverses from the outer edge of the ACF (the square shape felt) to the inner edge (the circumference of the inner circular O-ring) is equivalent to thousands of square meters of free adsorbing sites. In a typical ACF, the surface area is approximately 1000 m^2 per gram felt. These sites are the filtering mediums for the VOCs present in indoor air and also those emitting from the test material that is directly in contact (beneath) the ACF. Once the purified indoor air passes the ACF, it enters into the sampling cell, where the sampling site is and where surface VOC emissions from the test material are taking place.

The novel air supply technique used by the Kappa has several advantages and also comes with some disadvantages. The main advantage is the ability to sample in-situ, using the same indoor air where sampling and emission are taking place without the need for complex air supply and humidification systems. The potential drawback of the ACF O-ring system is that it may be possible for the very volatile indoor VOCs to breakthrough the ACF and mix with emissions from the test material. This is partly observed in the "Bin A" category, Figure 5.12 above, of VOCs captured by the Kappa. The amount of these VOCs is relatively higher than those captured by either the ASTM or the FLEC. These highly volatile VOCs along with other many organic acids present indoors are not filtered by the Kappa's ACF O-ring. These highly reactive chemicals are mixed up with the primary emission process of the testing material promoting the so called "secondary emissions" and many reactive by products.

The influence of such highly volatile and reactive chemicals to emissions from interior finishes and furnishings will be reviewed in some detail below. The fact that the presence of reactive indoor air chemicals does alter the emission profile of interior finishes supports the argument that VOCs from interior sources should be sampled in-situ. Through mapping and fingerprinting techniques one can distinguish between the primary and the secondary emissions, provided that a whole indoor air sample is performed along side the Kappa and its material emission sampling campaign. The latter is a standard practice in IAQ investigations, regardless.

5.5.3.4 Indoor Air Chemistry

The ASTM and the FLEC have both effectively captured all the three VOCs in the Bin B category. The Kappa, on the other hand, has only captured a single VOC, RT 16.8, in the Bin-B category. Interferences such as indoor humidity, indoor daylight, indoor pH level and indoor oxidizing processes may have played a role.

It has been reported that the chemical composition of indoor air and the environmental factors present in indoor microenvironments interact and take part in modifying the composition of emitted VOCs from interior surfaces. [38] Chemical reactivity of indoor air pollutants and the reaction by-products of material emissions in indoor environments is a new field in IAQ research that is known as "indoor air chemistry".[39] This field is beyond the scope of this investigation. It should be mentioned however that the influence of indoor air chemistry would likely play a more significant role during Kappa sampling than during FLEC or ASTM sampling.

The Kappa is an in-situ material emission sampler. It receives its sampling air from the indoor microenvironment where other VOCs are present and interact with the indoor air and the indoor microenvironment. The ASTM and the FLEC, on the other hand, receive their sampling air from a zero-air or an UHP nitrogen cylinder. In this investigation an UHP cylinder was used during the ASTM and the FLEC sampling campaign while the indoor air of a university laboratory was used during the Kappa sampling.

Emission sampling during the ASTM and the FLEC were performed in their respective dark cells. During the Kappa sampling, the carpet was exposed to indoor day light since the cell material of the Kappa is made from a clear and a translucent Plexiglass. The influence of indoor air chemistry during an in-situ sampling campaign would be more significant than its influence during a closed cell environmental chamber sampling. This in-situ sampling could have influenced the capturing ability, the sensitivity and the specificity of the Kappa to certain VOCs. The influence of indoor air chemistry on the variations observed between the Kappa and the FLEC/ASTM could be investigated further by placing the Kappa inside a sealed chamber supplied with own UHP nitrogen during emission sampling. The latter, however, was not the objective of this research.

The differences observed in the ER results of VOC RT 16.8 and VOC RT 16.9, Figure 5.12, between the Kappa and the other two samplers, could suggest that an indoor air chemistry determinant may have had an influence on the selectivity of the there samplers to these two very adjacent VOCs, in terms of their chromatographic RT responses. Comparing the emission rate values of the two VOCs in each of the FLEC and the Kappa, since both samplers are relatively similar in size, it becomes intriguing to notice that the Kappa has almost captured twice the amount of the RT 16.8 VOC as the FLEC, while the Kappa did not capture any amount of the RT 16.9 VOC. The FLEC, on the other hand, has captured half the amount of the RT 16.8 VOC compared to the Kappa, and almost a similar amount of the RT 16.9 VOC as RT 16.8 VOC.

The relative ratio of the amount of these two adjacent VOCs captured by both the FLEC and the ASTM are also strikingly similar. This observation promotes two suggestions: a) these two VOCs are too close to be resolved and they are probably the same substance whose retention time was affected by the presence of other eluants-- not unusual in GC analysis; b) that the Kappa could have been influenced by some concealed indoor air chemistry factor(s) that may have caused these two very adjacent VOCs, if compared to the other captured VOCs, to possibly collate together during the Kappa-carpet sampling.

These suggestions are only hypotheses and further experiments are required to confirm each. It suffices to mention, however, that the influence of indoor air chemistry on VOC emissions by interior finishes and furnishings has been reported in many scientific reviews and is certainly a determining factor in changing the emission profile of interior finishes and furnishings.

The later was indeed the *raison d'être* of this research study. After all, the objective of sampling emissions from interior finishes and furnishings, aside from the academic interest, is to acquire knowledge on the type and magnitude of VOCs that are being emitted from an interior finish or furnishing, on-site. Ultimately this should include their contribution to the indoor pollution concentration and to the dose inhaled by the indoor occupants in real settings.

The aforementioned phenomenon of indoor air chemistry could also be noticed in the next category; bin C (RT 18.6 and RT 18.7). Due to the scale and the magnitude of both VOCs present in bin C, the effect of indoor air chemistry, if it is the case, in the Kappa is much more pronounced than in the former bin-B category. Similar to the previous two VOCs (RT 16.8 and RT 16.9), the two VOCs in bin C are also chromatographically close, (RT 18.6 min. and RT 18.7 min, much too close to be resolved).

Similar to the aforementioned example in bin B, the amount of RT 18.6 VOC in the Kappa is almost twice that of the amount in the FLEC, while none of RT 18.7 VOC is captured by the Kappa. The ratio of these two adjacent VOCs is also noticeably similar in both the FLEC and the ASTM as the case was in bin B. Once again, this fact may suggest that the Kappa has been influenced by an indoor air chemistry factor that have caused these two relatively adjacent VOCs to either collate together or react and mask the effect of each other.

5.5.3.5 Inlet Flow, Sampling Flow and Ventilation

Before examining the influence of sampling airflow rate and inlet airflow rate, these two terms need to be defined. Sampling airflow rate is the rate of airflow generated by the sampling pump into the sampling tube. Inlet airflow rate is the rate of airflow supplied into the sampling chamber (the ASTM) or the sampling cell (the FLEC and the Kappa). Sampling airflow rate was approximately 50% higher during Kappa sampling compared with sampling airflow rate during the FLEC or the ASTM. The inlet airflow rate to the Kappa, on the other hand, was approximately 50% lower than the inlet airflow rate to either the FLEC or the ASTM.

If the sampling airflow rate in the Kappa was set to be equal to the sampling airflow rate in either the FLEC or the ASTM, this would have caused the inlet airflow rate into the Kappa to be almost three times lower than of either the FLEC or the ASTM. Similarly, if the inlet airflow rate to the Kappa was set to be the same as that of the FLEC or the ASTM, this would have caused the sampling airflow rate in the Kappa to be almost three times higher than that of the FLEC or the ASTM. This situation related to the design and operation of the three samplers was the reason for choosing a mid range airflow rate for the Kappa. It should be noted that the sampling airflow rate of the Kappa, unlike that of the FLEC or the ASTM, is the momentum that generates the inlet airflow to its sampling cell and hence controls the inlet airflow rate into the Kappa. Based on the actual airflow rates used during this sampling campaign, the area specific ventilation in the Kappa, the FLEC, and the ASTM were 2.47, 1.19 and 0.23 (cc air /cm^2-min) respectively.

$$\textit{Area Specific Ventilation} = (\textit{Chamber Volume} / \textit{Surface Area}) * \textit{ACH} \qquad [eq.3]$$

$$\textit{ACH} = \textit{Chamber flow rate} / \textit{Chamber Volume} \qquad [eq.3.1]$$

Considering the large differences in the area specific ventilation between the FLEC or the Kappa with that of the ASTM and the relatively comparable area specific ventilation in both the FLEC and the Kappa, any difference in the capturing ability of the Kappa as compared to that of the FLEC or the ASTM, based on the type of VOCs emitted (bin A, bin B, bin C, or bin D; Figure 5.12) may not be largely attributed to the differences in the sampling or the inlet airflow rates. This is due to the fact that the capturing ability of the Kappa did not lean towards one of the samplers, the FLEC or the ASTM, per se. The Kappa scored better than the FLEC against the ASTM in the more-volatile VOC category, while the Kappa scored slightly better than the ASTM against the FLEC in the less-volatile VOC category.

The area specific ventilation (ASV) in the FLEC, the ASTM and the Kappa were not the same. The area specific ventilation were however relatively comparable in both the FLEC and the Kappa. Unlike the ASTM, the Kappa could be set to have almost the same area specific ventilation as in the FLEC by adjusting the sampling airflow rate of the Kappa to that of the inlet airflow rate to the FLEC by using an airflow rate adjustment ratio. This ratio is dependent on the surface area of the testing material. However, this dependency is only applicable to the Kappa, since the surface area of any testing material placed under the FLEC has been preset by the design of the FLEC at $177 cm^2$.

Considering the chamber/cell volumes of the FLEC, the ASTM and the Kappa, Figure 5.15 presents airflow rate ratio equations for the three samplers. Due to the scale and chamber/cell volumes of the three samplers, some of these equations could be used to match the area specific ventilation of both the Kappa and the FLEC but not the ASTM. Figure 5.15 has two Kappa equations that are based on the two sample surface areas used during Kappa sampling campaigns, the REM-X @ 10cm diameter sample size as presented previously, and the carpet samples @ 8.5 cm diameter sample size.

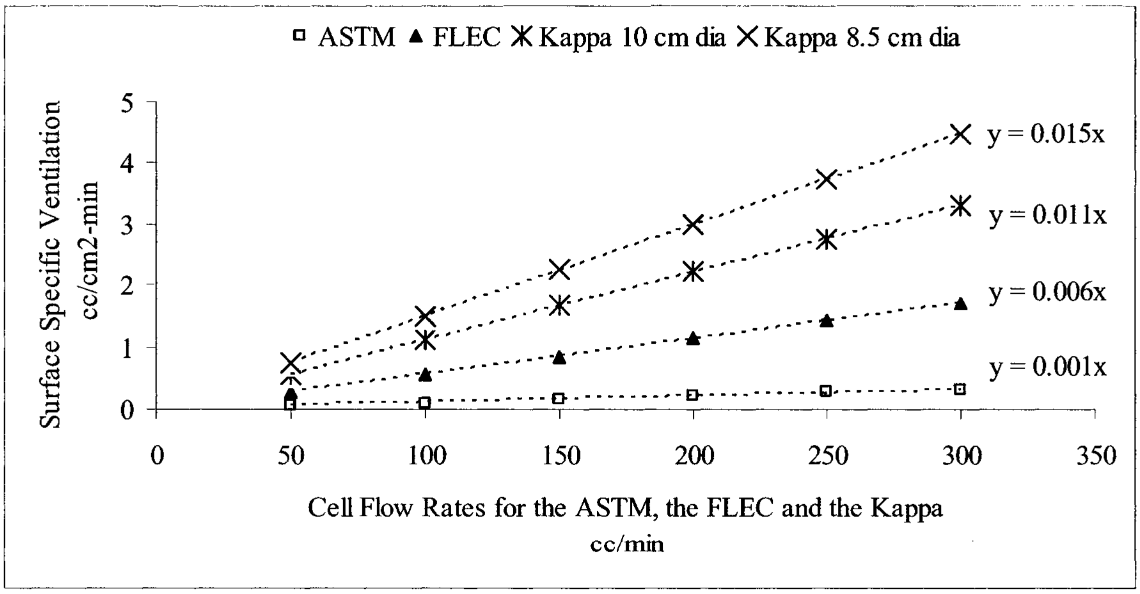


Figure 5.15: Relationship between the inlet flow rates with the surface specific ventilation based on equation 3; see text above.

Derived form Figure 5.15 above, the flow rate Q (cc/min), in equation 4 below, is applicable for a Kappa test surface area of 56.7 cm^2 (Kappa test sample ∅ 8.5 cm; used during the carpet sampling campaign). The flow rate Q (cc/min), in equation 5 below, is applicable for a Kappa test surface area of 78.5 cm^2 (Kappa test sample ∅ 10 cm; used during the REM-X sampling campaign).

$$Q\,Kappa_{\,sampling\ air\ flow} = 0.4\ Q\,FLEC_{\,inlet\ airflow} \qquad [eq.4]$$

$$Q\,Kappa_{\,sampling\ airflow} = 0.5\ Q\,FLEC_{\,inlet\ airflow} \qquad [eq.5]$$

During the FLEC/Kappa carpet sampling campaign, the carpet area used by the Kappa was 56.7 cm^2, and the average inlet airflow rate, the rate of which is the same as the sampling airflow rate in the Kappa, was 144cc/min.

Based on the equation: $y = 0.015\ x$ (Figure 5.15), Kappa's area specific ventilation (ASV) during this sampling campaign was 2.7 cc/cm^2-min. Meanwhile, the FLEC sampling area was 177 cm^2, and its mean inlet airflow rate was 219 cc/min. Based on equation: $y = 0.006\ x$ (Figure 5.15) FLEC's area specific ventilation (ASV) was 1.3 cc/cm^2-min. In the Kappa, carpet VOC emissions were sampled using almost twice ASV (2.7cc/cm^2-min versus 1.3 cc/cm^2-min) than in FLEC. The larger ASV during Kappa sampling may have influenced the emission profile of the more volatile VOCs emitted by the carpet.

Recalling from the FLEC/Kappa REM-X sampling campaign, presented in the preceding section, the REM-X area exposed to the Kappa was 78.5 cm^2. During the REM-X sampling campaign, two different airflow rate ratios (Kappa : FLEC) were used. In one set of samples an airflow rate ratio close to 1.0 was used, while in another set of samples an airflow rate ratio of 0.3 was used. The theoretical Kappa to FLEC ratio during the REM-X sampling campaign and according to equation 5 is 0.5, since Kappa's surface area was based on a 10 cm diameter. Even with such a wide range ratio and different ASVs, differences in toluene emission rates sampled by both the FLEC and the Kappa were less than 5%. It should be noted that toluene belongs, more or less, to the bin A retention time category, Figure 5.12.

Along with the differences in airflow rates, sampling area, and area specific ventilation, there are other factors that could have played other deterministic roles in the differences observed between the Kappa, the FLEC and the ASTM such as sink effects and indoor air chemistry.

As it pertains to the volatile VOCs (the bin A category), the Kappa matched that of the ASTM. As it pertains to the less volatile VOCs (the bin D category), the Kappa matched that of the FLEC. For those VOCs that are in-between the two volatility spectrums, they were divided into three categories: 1) the bin B category; 2) the bin C category; and 3) the 9-VOCs category. Both the ASTM and the FLEC matched each other in both the bin B and the bin C categories, while the Kappa only matched 2 out of the 5 VOCs in bin B and C categories. As for the 9-VOC category, all the three samplers matched each other in all the 9-VOCs (Figure 5.12; middle graph).

In the next section a quantitative analysis of these 9-VOCs will be performed to further evaluate the in-situ sampling performance of the novel Kappa against the two in-lab emission samplers, the ASTM and the FLEC.

5.5.4 Quantitative Analysis: The 9-VOCs

To compare between different emission-samplers, two important measurements are needed: a qualitative metric, and a quantitative metric. The former, as presented above, is developed through matching the pattern of chromatograms generated by each sampler. The latter however, is a more challenging endeavor. VOC emissions from building materials are time-dependent; they change with time and follow a first or second order decay model. The rate constants of such models can be estimated by conducting several continuous and consecutive short term samples, using the same material with the same sampler, to generate a concentration-time profile. From the rate of the slope of the profile generated, one would estimate the rate constants. This dynamic modeling and curve-fitting approach was set aside in favor of an empirical area specific emission rate (SER) approach. The latter is the standard approach usually adopted by those performing material emission testing.

5.5.4.1 Area Specific Emission Rate

For all the tests performed in this study, the concentration of each emitted VOC (ug/m^3) are converted to an areas specific emission rate (ug/m2-hr @ 24 hour sampling) by multiplying the calculated concentration by an area specific ventilation factor. The latter is the ratio of the chamber/cell volume to the volumetric inlet airflow rate normalized on the surface area of the test material. In the literature, there are different notations used that make reference to the area specific ventilation factor. All the notations lead to the same result. In the preceding section one notation was already used (see equation 3 and 3.1 above). The following is yet another notation that is commonly used:

$$\mathit{Area\ Specific\ Ventilation} = \mathit{ACH} \,/\, \mathit{Loading\ Factor} \qquad [eq.6]$$

$$\mathit{Loading\ Factor} = \mathit{Surface\ Area} \,/\, \mathit{Chamber\ Volume} \qquad [eq.6.1]$$

Regardless of the notations used, determination of emission rate values entails the assumption of a steady-state condition in each chamber/cell. No test was conducted in this sampling campaign to confirm this assumption. However, based on earlier tests performed during the REM sampling campaign, chapter 4, the assumption of a steady state condition seemed not far from the actual case. This is especially true when emission sampling is being conducted using a dry material such as a carpet. Selecting the method of area specific ventilation to estimate the area specific emission rate under the steady-state assumption in this sampling campaign was dictated by practical concerns.

One such concern was on the long sampling duration-- several weeks per sample per sampler --that would have been required to establish a set of representative decay model constants. The other concern was on the latent errors that would have been introduced when using a less-than-ideal mathematical model to fit the data generated. Ideally, a second-order decay model should be used to fit concentration-time data when the material under investigation is a dry low-emitting material with an emission that is controlled by diffusive transport, e.g., a carpet.[40] The second-order decay model includes the contribution of sink effect and VOC adsorption to the walls of the sampling chambers/cell. However, applying a second-order decay model entails extended tests with very longer durations (several months to a year).

The main objective of this sampling campaign, as mentioned before, was to compare the sampling performance of a novel in-situ sampler with the FLEC and the ASTM under comparable conditions, rather than to assess the emission rate or profile of a material. In a research study that was conducted by the European Collaborative Action on Indoor Air Quality, comparing the performance of different emission chambers/cells, the notion of having identically biased results were preferred to unbiased results but affected by unknown errors that are generated by the application of the less-than-ideal decay models.[41]

Another challenge in conducting comparative material-emission sampling studies is on finding an exact replica of the testing material for pair-wise comparison. Unlike sampling emissions from a constant emitting source such as a REM, emissions from building materials are not constant, their rates change per each sample performed. The issue of repeatability and reproducibility and the relevancy of their definitions in material emission sampling have been discussed earlier.

Keeping in mind the aforementioned concerns and the magnitude of the variations observed within the five carpet samples and in-between the three samplers, and having reviewed some of the statistical treatments suggested by other researchers who have conducted similar comparative and chemometric studies the concept of relative ratio, relative to the emission rate, has been suggested as the most appropriate method to be used for comparing the performance of emission chambers against each other, in a pair wise manner.[42]

In this study, a pair-wise comparative analysis of selected VOC and their emission rates as measured by two respective samplers will be conduced. The VOCs selected for this quantitative analysis are those most abundant and shared VOCs captured by the three samplers, the 9-VOCs as shown previously in Figure 5.12. Figure 5.16 and Table 5.17 present the mean ER values of the 9-VOCs as captured by each sampler with associated data.

Along with a pair-wise VOC ER ratio analysis, the applicability of other statistical tools to compare the VOC ER data between the three samplers will also be investigated. In the parametric domain, both the ANOVA (Analysis of Variance) for single factor and the student t-test for two independent variables are reasonable approaches that can be used to treat the data and compare between the three samplers.

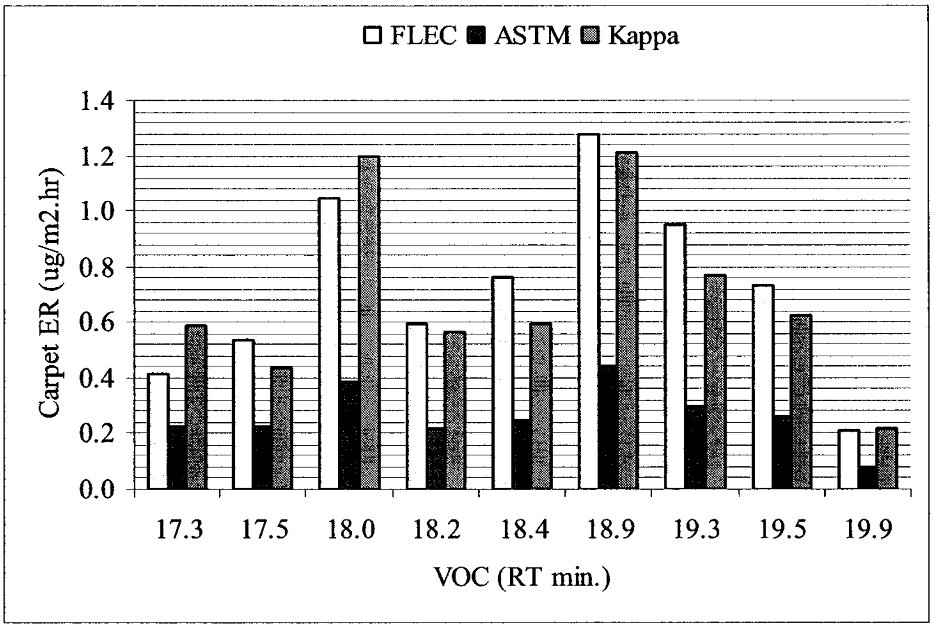


Figure 5.16: Mean VOC ER carpet values of the most commonly shared VOCs by the three samplers, the 9-VOCs.

Table 5.17: Mean VOC ER carpet values of the 9-VOCs selected.

		FLEC			**ASTM**			**Kappa**		
VOC		*# Samples*	*Mean ER*	*CV*	*# Samples*	*Mean ER*	*CV*	*# Samples*	*Mean ER*	*CV*
#	*RT min.*	*n*	*ug/m2-hr*	*%*	*n*	*ug/m2-hr*	*%*	*n*	*ug/m2-hr*	*%*
1	17.3	5	0.4	51	5	0.2	30	4	0.6	28
2	17.5	5	0.5	50	5	0.2	54	4	0.4	19
3	18.0	4	1.0	38	5	0.4	41	4	1.2	39
4	18.2	5	0.6	53	5	0.2	36	2	0.6	7
5	18.4	5	0.8	49	5	0.2	36	1	0.6	-
6	18.9	4	1.3	25	4	0.4	39	4	1.2	27
7	19.3	4	0.9	21	5	0.3	37	4	0.8	30
8	19.5	4	0.7	50	5	0.3	36	4	0.6	41
9	19.9	5	0.2	37	3	0.1	21	3	0.2	23

The limited number of samples collected and the relatively large variations observed in the ER values (46% to 76% based on the square root of the sum of the squares of the coefficients of variation per VOC) by the three samplers could limit the applicability of the ANOVA and t-test. Regardless of the limitations in sample size, normality tests and homogeneity tests are conducted since even parametric tests and ratio tests (ratio of means) ought to satisfy these two fundamental statistical assumptions, normality and homogeneity.

5.5.4.2 Normality of Data Sets

Every statistic, parametric or nonparametric, has assumptions which must be met prior to its application to a data set. Parametric statistics have an assumption that each sample point from the data is from a population that "follows" a normal distribution. Here the term "follows" should be underlined since hardly any experimental data follow a distribution that is normal. This deviation from normality is indeed normal, especially in the field of occupational health, environmental sciences, air and emission sampling. Most empirical distributions in the field of emission sampling are closer to being log-normally distribution than to being normally distributed. With this fact in mind, and based on the comparative nature of this sampling campaign, deviating from the log-normal to the normal counterpart would not pose a major bias in the over all analysis.

However, if the objective of this sampling campaign was to report the exact emission rate values of each carpet sample individually, then a deviation from the log-normal to the normal could result in biased estimates.

Before attempting to use, test or perform any parametric test or sub-test, the normality of the distribution of each emission rate data set will be confirmed. Each data set (by data set it is meant the ER results of the five-- or four in the case of the Kappa --repeated samples for a single VOC) was submitted to one or more of the available statistics that tests for normality.

There are a handful of tests that could be used for normality testing. The Shapiro-Wilk test, the Kolmogorov-Smirnov test, the Lilliefors test, the Anderson-Darling test, and the Jarque-Bera test are some of the most common tests used.[43] The power of all these normality tests are weak if the number of data points is less than ten. In this sampling campaign, the number of carpet emission rate data points collected per VOC in the 9-VOC category is between 11 and 14.

The Shapiro-Wilk test (S-W) test, as developed by Shapiro and Wilk during 1965, is one of the most powerful overall tests for normality. It is the ratio of two estimates of variance and it is roughly a measure of the straightness of the Q-Q plot (quintile – quintile). The closer the W is to 1, the more normal the sample population is.

Kolmogorov-Smirnov (K-S) test is historically the most commonly applied test. The test is based on the maximum difference between the observed distribution and expected cumulative-normal distribution; the smaller the maximum difference the more likely that the distribution is normal. The K-S test for normality is valid only when the mean and standard deviation of the distribution are known a-priori and not estimated from the data. This test has been shown to be less powerful than the other normality tests and it is considered to be a poor test if a data set has less than 30 samples.

An improved version of the K-S test is known as the Lilliefors test after its developer H.W. Lilliefors in 1967. In this test both the mean and the standard deviation are computed from the actual data, a post-priori process. The test involves a complex conditional hypothesis examining the likelihood of obtaining a normality statistic of a magnitude that is contingent upon the mean and standard deviation computed from the observed data. The Lilliefors probabilities are used to determine whether the K-S difference statistic is significant or not.

The Anderson-Darling (A-D) test is a popular normality test that is based on empirical distribution function statistics. The Anderson-Darling test tests the goodness-of-fit of the data to a specific distribution. It is also a modification of the K-S test and gives more weight to the tails of the distribution than does the K-S test. As the K-S test is distribution free in the sense that the critical values do not depend on the specific distribution being tested, the A-D test makes use of the specific distribution in calculating critical values. This has the advantage of allowing a more sensitive test.

Another normality test is the Jarque-Bera (J-B) test, proposed by Jarque and Bera (1980). This test can only be generalized for distributions where the third and fourth moment exist, an assumption which often does not hold. In statistics, the mean of a distribution is the first moment, the variance is the second moment, the skewness is the third moment, and the kurtosis is the fourth moment.[44] Since the Jarque-Bera test is based on the classical measures of skewness and kurtosis, and as these measures are based on moments of the data, this test has a zero breakdown value; a single outlier can make the test reject normality, even though the data set could well be normally distributed.[45]

From these set of tests the four tests, Shapiro-Wilk, Lilliefors, Anderson-Darling and Jarque-Bera tests are applied to the carpet VOC ER data set. Table 5.18 presents the results of the normality tests for each set of ER data per VOC for the three samplers combined. As per the results of each data set (per VOC), at the level of significance alpha 5%, $\alpha = 0.05$, the decision was not to reject the null hypothesis that each data set follows a normal distribution. All the 9-VOCs, with only one partial exception of VOC RT 19.5, have suggested that the non-normality in each data set is not significant.

5.5.4.3 Homogeneity of Variances

The equality of variances in each data set collected in this sampling campaign across the three samplers is called homogeneity of variances or homoscedasticity. Testing the equality of the means by a t-test or an ANOVA, not only requires that the data follow a normal distribution but also assume that the data set per VOC has the same variance, even if the final result of either the t-test or the ANOVA test rejects the null hypothesis of equality of the means of ER data between any one of two samplers (2-sample t-test) or the three samplers combined (ANOVA).

If both the normality and the condition of homogeneity of variance are not met, the results of the statistical test may not be valid. Both the 2-sample t-test and the ANOVA test can lead to meaningless results if the equality of variances condition is not met. Unlike the 2-sample t-test, the ANOVA although not very sensitive to the normality assumption, it is only moderately insensitive to minor violations of the homogeneous variance assumption, provided the sample sizes are equal across the samplers and are not too small. Unfortunately, from the top 9-VOCs selected, two VOCs (RT 18.2 and RT 18.4) could pose a problem with the ANOVA since the sample sizes for these two VOCs are indeed small; see the circle on Table 5.17, above.

Table 5.18: Tests of Normality per VOC ER data, the three samplers combined. (S-W: Shapiro-Wilk; Lilliefors, A-D: Anderson-Darling; J-B: Jarque-Bera)

	VOC #	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
	RT (min.)	***17.3***	***17.5***	***18.0***	***18.2***	***18.4***	***18.9***	***19.3***	***19.5***	***19.9***
	SER per VOC per Sample per Sampler (µg/m2-hr)									
FLEC	Carpet S1	0.55	0.43	1.26	0.19	1.33	1.50	1.17	1.00	0.29
	Carpet S2	0.20	0.22	0.46	0.53	0.32				0.09
	Carpet S3	0.55	0.47	1.13	0.52	0.72	1.23	0.85	0.76	0.21
	Carpet S4	0.58	0.63	1.33	0.65	0.85	1.54	1.06	0.96	0.27
	Carpet S5	0.16	0.95		1.07	0.59	0.85	0.72	0.20	0.20
ASTM	Carpet S1	0.21	0.42	0.24	0.24	0.22		0.30	0.27	
	Carpet S2	0.30	0.23	0.49	0.27	0.34	0.56	0.39	0.34	0.09
	Carpet S3	0.12	0.09	0.20	0.10	0.12	0.22	0.13	0.12	
	Carpet S4	0.22	0.15	0.43	0.18	0.24	0.40	0.26	0.24	0.06
	Carpet S5	0.26	0.24	0.56	0.29	0.31	0.59	0.39	0.36	0.10
Kappa	Carpet S1	0.71	0.43	0.89			0.92	0.53	0.32	
	Carpet S3	0.39	0.34	0.73			0.95	0.63	0.50	0.16
	Carpet S4	0.72	0.54	1.49	0.59		1.56	1.00	0.82	0.26
	Carpet S5	0.52	0.45	1.68	0.54	0.59	1.42	0.93	0.86	0.24
Number of samples		14	14	13	12	11	12	13	13	11
S-W	P value	0.126	0.256	0.352	0.150	0.117	0.317	0.605	0.077	0.227
	Alpha	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Lilliefors	P value	0.269	0.404	0.341	0.205	0.112	0.529	0.531	0.048	0.218
	Alpha	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
A-D	P Value	0.121	0.303	0.371	0.163	0.142	0.417	0.611	0.061	0.264
	Alpha	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
J-B	P value	0.483	0.100	0.559	0.223	0.113	0.605	0.596	0.418	0.511
	Alpha	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05

A circle on a data point signifies a significant result.
A hexagon on a data point is an outlier (referenced later).

Several tests are available to test the homogeneity of variances. One common test is the Bartlett's test, which tests if "k" samples (the three samplers) have equal variances. The Bartlett test is designed to test for equality of variances across groups against the alternative that variances are unequal for at least two groups. It compares the geometric mean of the group variances to the arithmetic mean. The

Bartlett's test is a Chi-square statistic with (k-1) degrees of freedom-- where k is the number of samplers (three samplers in this case) --in the independent variable. Although the number of carpet samples per sampler per VOC did not need to be equal (dependent variables), as in the case of this sampling campaign, the Bartlett test requires at least 5 samples (per VOC per sampler).

The number of carpet samples (per VOC per sampler in this study) is very close to the minimum limit of the Bartlett test. However, this test was used as a first initial test, followed by other supporting tests, on the homogeneity of the variances of the VOC ER data obtained. It should be mentioned that the Bartlett test statistic is very sensitive to deviations from normality. Thus, one should take into consideration that a low P value resulting from a Bartlett test (a theoretical confirming of unequal variances) may have been generated due to small deviation from normality rather than to actual unequal variances in the data set.

Another, though more common, test of homogeneity of variances is the Levene test. This test is insensitive to sample size or normality. Usually the Levene test is based on deviations from the group mean. There are other versions of Levene test based on deviations from the group median, deviations from the group median that is adjusted for degrees of freedom, and the 5% trimmed group mean. In this study the deviations from the group median was used.

All the VOC ER data were redefined by subtracting the median of each sampler and conducting a one-way ANOVA on the redefined data. As mentioned earlier, the Levene test is more robust in the face of non-normality than other more traditional tests such as the aforementioned Bartlett's test.

Table 5.19 presents the 9 data sets of the 9-VOCs along with the results of these two tests. In both the Levene test and Bartlett test, failing to reject the null hypothesis at the level of significance alpha 5%, $\alpha = 0.05$, suggests that variances are equal.

From the results obtained, and at the level of significance α (alpha) = 0.05, one could suggest not to reject the null hypothesis of equality of the variances since the inequality of variances is not significant for almost all the sample sets, except for three VOCs (RT 18.2, 18.4 and 19.3) that have exhibited a partial (one test out of two) significance in their lack of homogeneity of variances. However, the relative proximity of the p-values to the alpha level is an indication that the data set are in the boarder of homoscedasticity and heteroscedasticity.

Table 5.19: Tests of homogeneity of variances per VOC ER data set for the three samplers combined
RT is the retention time in minutes.

	VOC 1 (RT 17.3)			VOC 2 (RT 17.5)			VOC 3 (RT 18.0)		
	FLEC	ASTM	Kappa	FLEC	ASTM	Kappa	FLEC	ASTM	Kappa
Carpet Sample 1	0.55	0.21	0.71	0.43	0.42	0.43	1.26	0.24	0.89
Carpet Sample 2	0.20	0.30		0.22	0.23		0.46	0.49	
Carpet Sample 3	0.55	0.12	0.39	0.47	0.09	0.34	1.13	0.20	0.73
Carpet Sample 4	0.58	0.22	0.72	0.63	0.15	0.54	1.33	0.43	1.49
Carpet Sample 5	0.16	0.26	0.52	0.95	0.24	0.45		0.56	1.68
Bartlett's test:	p-value = 0.136 > alpha 0.05			p-value = 0.108 > alpha 0.05			p-value = 0.180 > alpha 0.05		
Levene's test (median):	p-value = 0.391 > alpha 0.05			p-value = 0.305 > alpha 0.05			p-value = 0.174 > alpha 0.05		

	VOC 4 (RT 18.2)			VOC 5 (RT 18.4)			VOC 6 (RT 18.9)		
	FLEC	ASTM	Kappa	FLEC	ASTM	Kappa*	FLEC	ASTM	Kappa
Carpet Sample 1	0.19	0.24		1.33	0.22		1.50		0.92
Carpet Sample 2	0.53	0.27		0.32	0.34			0.56	
Carpet Sample 3	0.52	0.10		0.72	0.12		1.23	0.22	0.95
Carpet Sample 4	0.65	0.18	0.59	0.85	0.24		1.54	0.40	1.56
Carpet Sample 5	1.07	0.29	0.54	0.59	0.31	0.59	0.85	0.59	1.42
Bartlett's test:	p-value = 0.029 < alpha 0.05			p-value = 0.016 < alpha 0.05			p-value = 0.559 > alpha 0.05		
Levene's test (median):	p-value = 0.301 > alpha 0.05			p-value = 0.132 > alpha 0.05			p-value = 0.280 > alpha 0.05		

	VOC 7 (RT 19.3)			VOC 8 (RT 19.5)			VOC 9 (RT 19.9)		
	FLEC	ASTM	Kappa	FLEC	ASTM	Kappa	FLEC	ASTM	Kappa
Carpet Sample 1	1.17	0.30	0.53	1.00	0.27	0.32	0.29		
Carpet Sample 2		0.39			0.34		0.09	0.09	
Carpet Sample 3	0.85	0.13	0.63	0.76	0.12	0.50	0.21		0.16
Carpet Sample 4	1.06	0.26	1.00	0.96	0.24	0.82	0.27	0.06	0.26
Carpet Sample 5	0.72	0.39	0.93	0.20	0.36	0.86	0.20	0.10	0.24
Bartlett's test:	p-value = 0.404 > alpha 0.05			p-value = 0.092 > alpha 0.05			p-value = 0.194 > alpha 0.05		
Levene's test (median):	p-value = 0.047 < alpha 0.05			p-value = 0.254 > alpha 0.05			p-value = 0.362 > alpha 0.05		

A circle on a data point signifies a significant result.
** indicates that data from the specified column was not included in the calculation, an alternative two sample comparison of variances was used instead.*

5.5.4.4 Descriptive Statistics

Having obtained a reasonable satisfactory result on both the normality test and the equivalency of variances test, a descriptive parametric statistics for each data set (ER values per VOC by the three samplers) was conducted. The results obtained are collated and plotted as box plots and presented in Figure 5.17. The scale of the y-axis (emission rate values) was kept the same for all the data sets to facilitate the visual comparison between the sets.

The data, as presented in Figure 5.17, are divided into nine sets. Each data set is composed of the ER values of one of the nine VOCs selected for this quantitative analysis. The mean, median, minimum, maximum and the 95% confidence interval of the ER values of each of the nine VOCs captured by one of the three samplers are presented with own box plot. Together, each VOC has three box plots, one per sampler. The three ER box plots of each VOC were placed inside a rectangle (dashed line). The number of the carpet samples per sampler is indicated in each respective rectangle. All together there are 113 data points (ER data) that make up the 9 data sets, one per VOC. Each data set is made up of a maximum of 14 to a minimum of 11 data points. A data set consists of 3 sub-sets, one per sampler. On average, there were 4 data points per sub-set.

5.5.4.5 Outliers

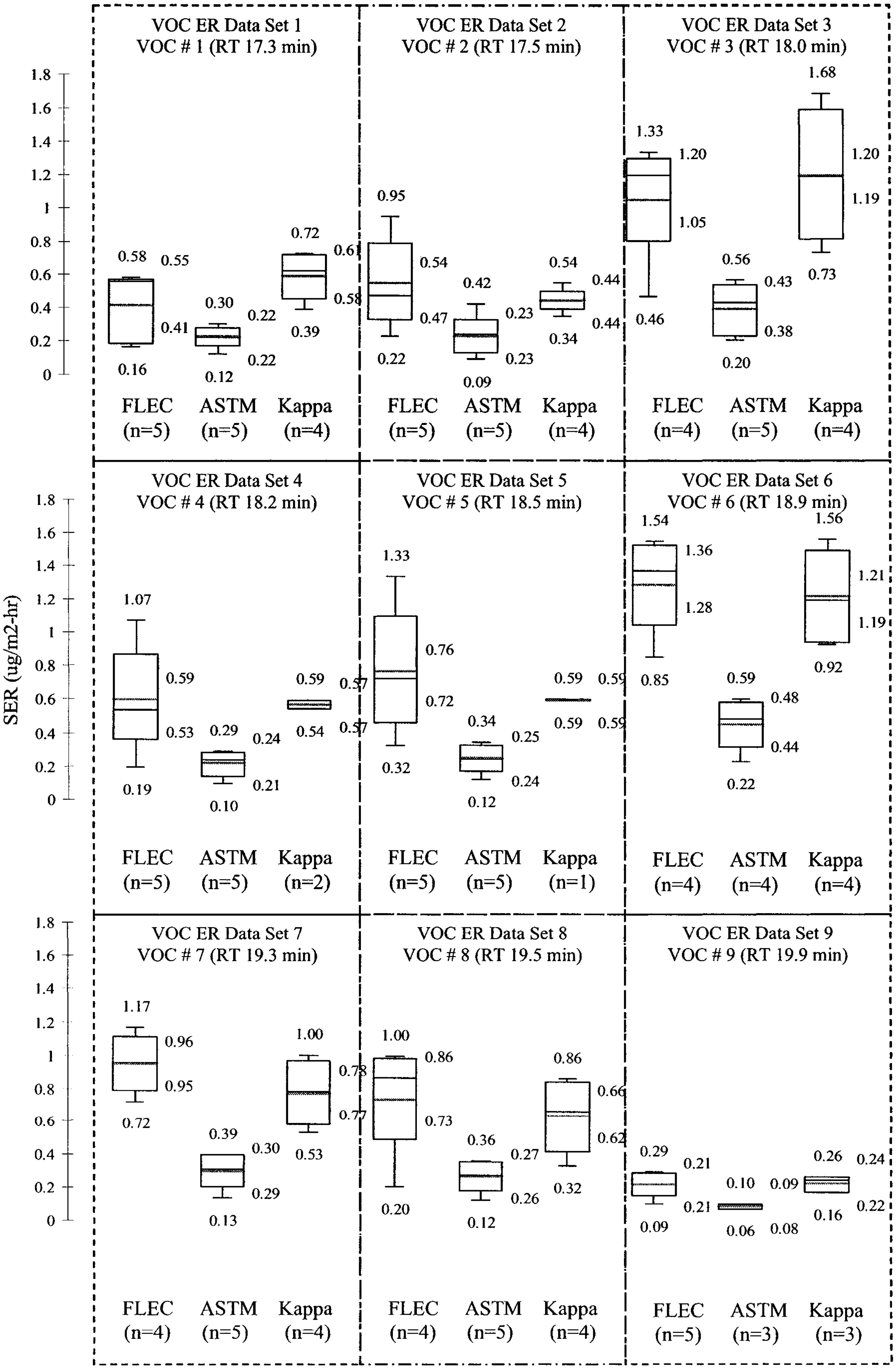
Figure 5.18 presents data of the three sub-sets (each rectangle of Figure 5.17) into a single mean of the means box plot per VOC per the there samplers combined, for the FLEC and the ASTM, for the ASTM and the Kappa and for the FLEC and the Kappa, respectively. A data point with a circle indicates an outlier. These outliers were also highlighted with a hexagon in Table 5.18 above. Almost all the outliers are associated with the FLEC sampler with the exception of one, which is from the Kappa. The latter is indeed a single data point in its category; hence the term "outlier" may not be a valid term to use for this particular data point.

An outlier in a set of data is "an observation that appears to be inconsistent with the remainder of that set of data".[46] The five ER outliers observed are considered anomalous values in the data. Such outliers will have an influence over the fitted slope and the intercept for any statistical data treatment hence rendering a poor fit to the bulk of the data points.

There are many causes that could have lead to the presence of these outliers. They may have been due to retention time matching and mapping errors, sampling errors, analysis errors, cross contamination errors, and other errors inherent in most empirical research and sampling campaigns.

Regardless of the aforementioned errors, which are probable, but unlikely since several quality control with check and balance procedures were used during this sampling and analytical campaign, one major source for the outliers could be due to the non-homogeneity of the sampling material.

Figure 5.17: The 9-VOC data sets per VOC per the three samplers.



VOC emission rates from different carpet samples are not the same even though the carpet samples are from the same carpet batch. Significant differences ($P<0.01$) of 50% to 250%, depending on the VOC emitted, were reported from sampling emissions at different spots of a single carpet in a laboratory controlled environment.[47] This leads to the theoretically correct but empirically untrue assumption that the data collected may have not come from the same population, although it actually did come from the same carpet.

Outliers may also be present due to the fact that emission rate values belong to a non-normal population. This is a valid assumption in most air quality and environmental data sets. In addition, since most of the outliers are from the FLEC sampler, the aforementioned variability in the flow field of the FLEC could yet be one more reason to consider.

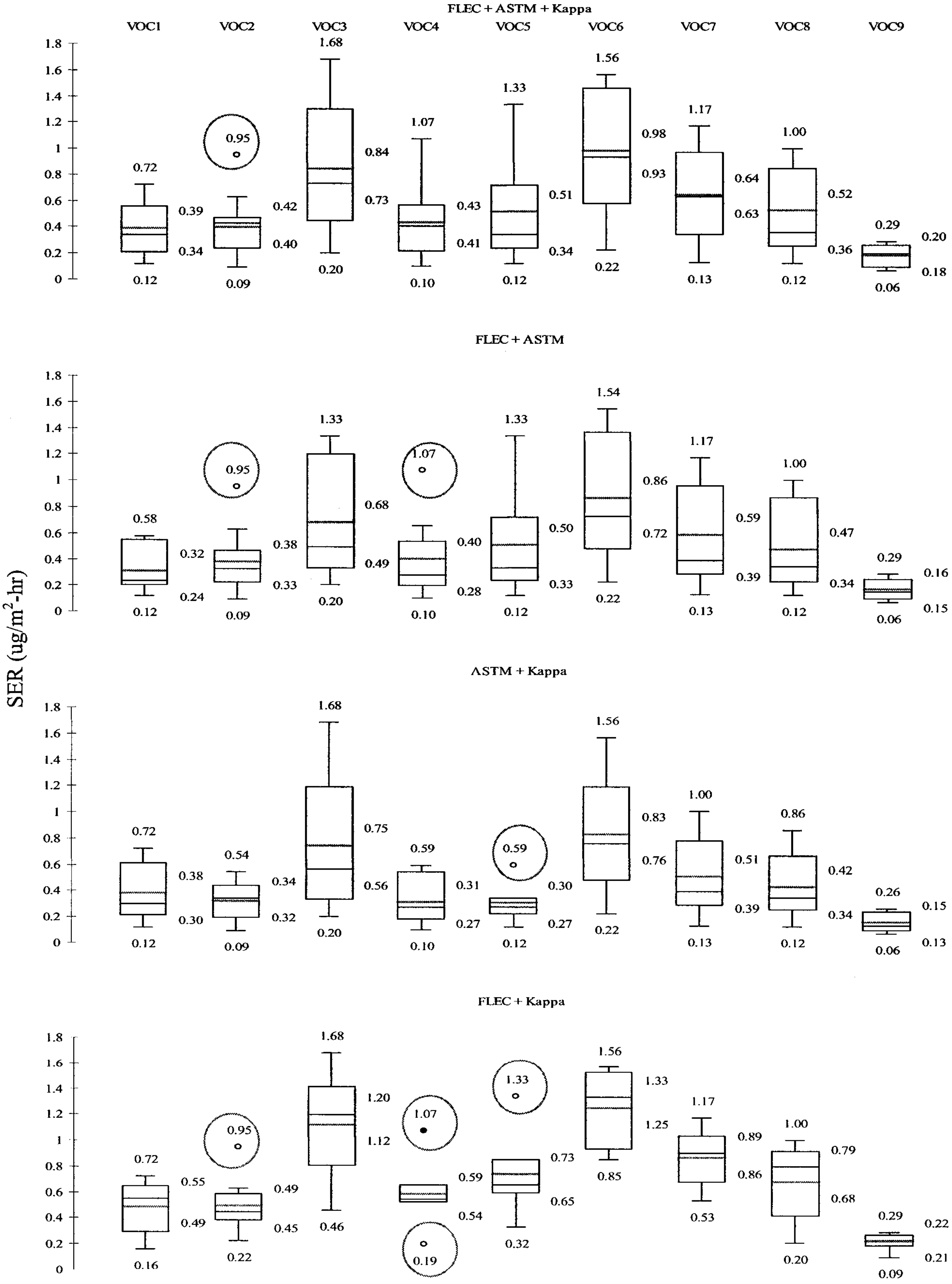
Outliers clearly appeared when the data of the three samplers were disaggregated into two-sampler category. Depending on the number of data points, outliers do get diluted when sample data are aggregated into a larger category. Outliers tend to increase the estimate of residual variance, thus lowering the chance of rejecting the null hypothesis of equal variances. In this sampling campaign, the objective was to verify that the three samplers or any two of them including the Kappa capture VOC emissions from a planar interior finish in a comparable way. Removing or even treating the outliers may bias the outcome of this investigation since failing to reject the null hypothesis is the pursuit of this comparative analysis.

5.5.4.6 Two Sample t-Tests

The two sample t-test is a statistical approach that tests the degree of equality of two means. Each mean is the average of the VOC ER values per VOC per sampler. Only two samplers at a time are compared. Hence three t-tests (FLEC/ASTM; ASTM/Kappa and FLEC/Kappa) need to be conducted per VOC data set. There are fundamental assumptions that need to be validated before attempting a two-sample t-test.

First and foremost, the data should be continuous, not discrete. This is indeed the case in the VOC ER carpet data obtained. Second, each data set should follow the normal probability distribution. This assumption has been tested and most of the results do satisfy the normality assumption with some outliers. Thirdly, data sets should be independent. There should be no systematic relationship, association or co-variation between ER results of one sampler to the other. Each carpet sample was sampled independently from the other samples and samplers. Fourthly, each VOC ER result should be a random sample from its own respective population. This random sample criterion was satisfied since carpet samples were randomly selected from a large piece of a carpet and assigned to each sampler on the day of sampling using a simple random-pick method.

Figure 5.18: The 9-VOC data sets per the three and two-of-the-three samplers.



Finally, the variances of the two populations should be tested for homogeneity (equal variances) or heterogeneity (unequal variances) so that the appropriate t-test is carried out.

The homogeneity tests that were conducted so far were based on the collated data by the three samplers. In the 2-sample t-test, data by the two respective samplers need to be tested separately for equality of variances. Table 5.20 presents the results of three tests that were conducted to test for the variance equivalency of the ER data sets per VOC per two samplers respectively. The three tests used to compare the variances in each data set were the Fisher F test, and both the aforementioned Bartlett test and the Levene test. The former is based on conducting a two-sample ANOVA of the difference of each ER value with its median to get an F value for the redefined difference values. Each test has it own advantage and shortcoming based on the sample size as well as on the sensitivity of each test to the normality of the data. If one of the tests failed (p-value < alpha of 0.05) then the data was considered heterogeneous with unequal variances, regardless.

Having segregated the equal variances data sets from the unequal variances data sets, two different t-tests were performed to each data set. One t-test assumes that the variances of emission rate results of the two samplers are equal. This is the homogenous variance t-test, sometimes called homoscedastic t-test.

Table 5.20: Tests for rejecting or not rejecting the null hypothesis (Ho) of equality of the variances is two samples comparison of variances; two samplers at a time.

	Two Samplers	Fisher's F test	Bartlett's test	Levene's test	Ho
VOC 1	FLEC/ASTM	0.046	0.046	0.264	Reject
	ASTM/Kappa	0.110	0.123	0.042	Not to reject
	FLEC/Kappa	0.716	0.677	0.852	Not to reject
VOC 2	FLEC/ASTM	0.156	0.156	0.301	Not to reject
	ASTM/Kappa	0.538	0.504	0.598	Not to reject
	FLEC/Kappa	0.080	0.073	0.236	Not to reject
VOC 3	FLEC/ASTM	0.102	0.114	0.418	Not to reject
	ASTM/Kappa	0.064	0.072	0.004	Reject
	FLEC/Kappa	0.821	0.821	0.447	Not to reject
VOC 4	FLEC/ASTM	0.019	0.020	0.212	Reject
	ASTM/Kappa	0.690	0.496	0.479	Not to reject
	FLEC/Kappa	0.178	0.126	0.363	Not to reject
VOC 5	FLEC/ASTM	0.016	0.016	0.132	Reject
	ASTM/Kappa	0.036	0.030	0.182	Reject
	FLEC/Kappa	0.008	0.009	0.234	Reject
VOC 6	FLEC/ASTM	0.335	0.334	0.338	Not to reject
	ASTM/Kappa	0.318	0.317	0.035	Reject
	FLEC/Kappa	0.970	0.970	0.709	Not to reject
VOC 7	FLEC/ASTM	0.256	0.278	0.101	Not to reject
	ASTM/Kappa	0.176	0.193	0.021	Reject
	FLEC/Kappa	0.835	0.834	0.507	Not to reject
VOC 8	FLEC/ASTM	0.025	0.030	0.193	Reject
	ASTM/Kappa	0.086	0.097	0.020	Reject
	FLEC/Kappa	0.576	0.574	0.820	Not to reject
VOC 9	FLEC/ASTM	0.096	0.078	0.187	Not to reject
	ASTM/Kappa	0.213	0.214	0.426	Not to reject
	FLEC/Kappa	0.629	0.537	0.516	Not to reject

This test was conducted to determine whether the ER results from two respective samplers (FLEC/ASTM, ASTM/Kappa, FLEC/Kappa) were likely to have come from a carpet sample with equal VOC ER means, hence an indication of the comparability of each sampler with the other in their emission rate sampling. This entails that the null hypothesis of the 2-sample t-test not to be rejected.

Another t-test assumes that the variances of both sets of emission rate results of any two samplers are not equal. This is the heterogeneous variance t-test or the heteroscedastic t-test. In this test the analysis is performed using a 2-sample t-test but with an adjusted degrees of freedom. The test is used to determine whether the ER results from any two respective samplers are likely to have come from the same carpet with equal VOC ER means, even though their respective variances are different. Generally speaking, this t-test is preferred over the homoscedastic t-test since it accommodates the characteristics of carpet emission process which makes each VOC ER result relatively distinct. From the comparison of variances results as outlined in Table 5.20, 10 out the 27 data sets were considered candidates for the heteroscedastic t-test and the remaining 17 as candidates for the homoscedastic t-test. However, for the purpose of comparative assessment, both the t-tests were conducted to the entire 27 data sets and the results presented in Table 5.21.

If however the VOC ER variances were heterogeneous and they could not be corrected for by either transformation or outlier manipulation, which neither were performed in this study, then a nonparametric option of the t-test is used instead. The latter is the Mann-Whitney test, the nonparametric equivalence of the parametric 2-sample t-test, as explained later.

Results of the parametric t-tests were filtered using the three steps outlined below:

1. Highlighting the appropriate t-test results based on the equality and the inequality of variances by making reference to Table 5.20. The circles placed on Table 5.21 highlight the significant results that suggest the rejection of the null hypothesis of equality of the means between two respective samplers. Any two samplers with a circle is an indication that the samplers did not match each other, quantitatively, in their respective VOC ER sampling. One VOC ER result was also included, which was at the border line of the significance level of 0.05. In the latter case the circle was dashed and included in Table 5.21.

2. Removing data sets with an outlier by making reference to Figure 5.18 or Table 5.18.

3. Excluding the two VOCs (VOC 4 and VOC 5) that were captured by the Kappa. These two VOCs were captured in only 2 and 1 of Kappa's repeated 4 carpet samples, respectively. These VOCs were included at the outset because both the FLEC and the ASTM have captured them in all of the 5 repeated carpet samples, respectively. Kappa's ER values of these two VOCs were only temporarily included as dummies in the analysis to maintain the design matrix of this comparative analysis.

The hexagon marks on Table 5.21 highlight the excluded data sets that include the outliers and the aforementioned two VOCs, regardless of the significance of the t-test results obtained.

From the above selection and filtering criteria, six of the nine VOCs captured by both the FLEC and the Kappa were quantitatively matched. In other words, the differences between the means of the VOC ER values of these six VOCs were not significant, hence suggesting that both the FLEC and the Kappa are quantitatively similar in their dynamic emissions sampling from a surface such as the carpet.

Quantitatively, neither the FLEC nor the Kappa matched the ER values of the ASTM in any one of the 9-VOCs captured and shared by the three samplers. The differences in the results were significant at an alpha value of 0.05. The results of the differences between the VOC ER means of the FLEC and the VOC ER mean of the ASTM, and also between the VOC ER mean of the ASTM and the VOC ER mean of the Kappa, indicate that both the FLEC's and the Kappa's means were significantly higher than those captured by the ASTM.

Table 5.21: Two sample t-tests for VOC ER results for FLEC/ASTM, ASTM/Kappa and FLEC/Kappa, respectively (alpha, α @ 0.05).

		t-tests; independent samples					
		equal variances			not equal variances (Satterthwaite's method)		
		left-tailed test	two-tailed test	right-tailed test	left-tailed test	two-tailed test	right-tailed test
		P-value	P-value	P-value	P-value	P-value	P-value
VOC 1	FLEC/ASTM	-	-	0.04	-	-	0.06
	ASTM/Kappa	0.001	-	-	0.01	-	
	FLEC/Kappa	0.11	0.21	-	0.10	0.20	-
VOC 2	FLEC/ASTM	-	-	0.02	-	-	0.03
	ASTM/Kappa	0.01	-	-	0.01	-	-
	FLEC/Kappa	-	0.50	0.25	-	0.46	0.23
VOC 3	FLEC/ASTM	-	-	0.01	-	-	0.02
	ASTM/Kappa	0.004	-	-	0.02	-	-
	FLEC/Kappa	0.32	0.91	-	0.32	0.85	
VOC 4	FLEC/ASTM	-	-	0.02	-	-	0.03
	ASTM/Kappa	0.001	-	-	0.001	-	-
	FLEC/Kappa	-	0.91	0.45	-	0.85	0.42
VOC 5	FLEC/ASTM	-	-	0.01	-	-	0.02
	ASTM/Kappa	0.002	-	-	0.0004	-	-
	FLEC/Kappa	-	0.57	0.28	-	0.36	0.18
VOC 6	FLEC/ASTM	-	-	0.002	-	-	0.004
	ASTM/Kappa	0.003	-	-	0.01	-	-
	FLEC/Kappa	-	0.78	0.39	-	0.78	0.39
VOC 7	FLEC/ASTM	-	-	0.0002	-	-	0.002
	ASTM/Kappa	0.002	-	-	0.01	-	-
	FLEC/Kappa	-	0.29	0.14	-	0.29	0.14
VOC 8	FLEC/ASTM	-		0.01		-	0.04
	ASTM/Kappa	0.01	-	-	0.03	-	-
	FLEC/Kappa	-	0.65	0.33	-	0.66	0.33
VOC 9	FLEC/ASTM	-	-	0.02	-	-	0.01
	ASTM/Kappa	0.01	-	-	0.02	-	-
	FLEC/Kappa	0.46	0.92	-	0.46	0.91	-

Although the three samplers did qualitatively and collectively match in 16 out of the total 27 different VOCs emitted and captured by the three samplers, only 9 out of the 16, as explained above, were considered appropriate for a quantitative analysis. The selection criteria of the 9-VOCs was based on the number of times a VOC was captured during the repeated five carpet samples per sampler, the within-sampler coefficient of variation per VOC per sampler, and the number of samplers capturing the same VOC. From this nine most abundant, matched and shared VOC list, the area specific emission rates of six VOCs (VOC 1, 3, 6, 7, 8 and, 9) were matched by both the Kappa and the FLEC with alpha > 0.21, 0.91, 0.78, 0.29, 0.56, and 0.92, respectively (refer to the rectangles on Table 5.21).

5.5.4.7 Analysis of Variance (ANOVA)

ANOVA for single factor performs a simple analysis of variance on each VOC ER value for any two or the three samplers together. The t-tests performed above were in fact a "2-sampler" test ANOVA.

Repeatedly performing statistical tests on the same data set increases the chance of committing a Type-I error, since probability values are additive, performing three separate t-tests (as conducted above), the overall P with an alpha value of 0.05 would be 0.15 (3 x 0.05 = 0.15). However, the additive model influence on repeating several t-tests (FLEC/ASTM, ASTM/Kappa and, FLEC/Kappa) on the ER data collected during this investigation may not present a major deviation from the actual observation. In other words, as the ASTM sampler did match neither the FLEC nor the Kappa in any of the 9-VOCs ER results, pulling and comparing the three samplers together would most probably indicate that they do not match, as a group, regardless.

As opposed to the t-tests, an ANOVA provides a test of the null hypothesis that each carpet VOC emission rate result is in fact from the same/similar carpet regardless of the sampler used. This would be an indication of the degree of comparability between the three samplers combined. The null hypothesis is thus tested against an alternative hypothesis which states that the VOC ER values seem to be so different that they may not have come from the same carpet per se. In the later case, this would indicate that the three samplers are not comparable since their VOC ER sampling results may well have provided the VOC ER values most probably from two or more different populations of carpets. If there were only two samplers to compare, the student t-test, as reviewed above, was equally sufficient. However, with more than two samplers to compare (FLEC, ASTM and the Kappa) there is no convenient generalization of the t-test and hence the single factor ANOVA is a recommended practice, apart from the 2-sample t-test results.

Homogeneity of VOC ER variances are also a fundamental assumption in the ANOVA. The results of the aforementioned three samplers' homogeneity tests (see Table 5.19) including the modified Levene equal variance test were considered before conducting an ANOVA test. The modified Levene test is one of the appropriate tests since it is considered insensitive to sample size or normality. As already mentioned, the modified Levene test redefines the variates of all the data sets by subtracting the median of each subgroup and performing a one-way ANOVA on the redefined variates. Failing to reject the null hypothesis concludes that variances are equal. If however the VOC ER variances were heterogeneous and they could not be corrected for by either transformation or outlier manipulation, which neither were performed in this study, then a nonparametric option of the ANOVA can be used instead. The latter is the Kruskal-Wallis test, the nonparametric equivalence of the parametric ANOVA, explained later.

From the above brief introductory note to the AVOVA, the question is whether ANOVA would be an appropriate statistical tool that could be used to compare the VOC ER values of the three samplers (combined) for this sampling campaign? ANOVA is an extremely useful statistical tool for designed experiments with random sampling. Sampling VOC emission rates from interior finishes and furnishings may well satisfy, if appropriately designed, the randomness criterion. However, along with the randomness criterion, there are other factors that do limit the application of the ANOVA in material emission sampling in general and in this carpet sampling campaign, in particular.

Spatial variability of VOC emissions from an interior material such as a carpet is, no doubt, a confounding factor that confounds the results between a carpet sample versus another carpet sample, even if the samples are from the same type and batch of a carpet. In this study, 9-VOC emission rates by 14 same-type-same-batch carpet samples were sampled and reported. This means that the VOC ER data came from 14 different "spots" from one carpet block. As mentioned earlier and according to numerous investigations by several other researchers, VOC emission rates of a single type carpet vary by as much as 50% to 250% depending on the VOC, the more volatile (lower boiling point) the higher the variation. [48]

ANOVA is more sensitive to spatial variability, smaller but consistent difference in emissions between samples, than to a larger but highly variable difference. The reason is that ANOVA compares between sample variability (the variability of VOC ER results from the five carpet samples using a single sampler) to within sample variability (the variability of the VOC ER results from three carpet samples using three different samplers).

In the absence of a difference in temporal variability, an assumption that does not hold in dynamic emission sampling, within-sample variability becomes a combination of spatial and analytic variability, whereas between-sample variability is more associated with the spatial variability and less with the analytical variability. Since spatial variability in carpet emissions is invariably large relative to the combination of temporal and analytic variability, the ANOVA will mostly conclude that the ratio of "between-sample" variability to "within-sample" variability is significantly larger than zero. Of course, the assumption of ANOVA is that under the null hypothesis-- no differences between the emissions captured by the three samplers --all samples are drawn from the same population distribution (carpet samples) with the same ER mean results. Although this assumption is justifiable, provided it is under random sampling, it is harder to justify when it comes to VOC emissions from carpet samples in which initial emission rate conditions, spatially and temporally, is different to start with.

One good application of ANOVA in a carpet sampling campaign is in testing whether or not the amount of spatial variability of each VOC ER is statistically significant. In such a case a simple restriction of the analysis could be done to a set of controlled and repeated carpet samples that are obtained from a carpet batch/role which is freshly produced from the manufacturer, isolated, prepared, conditioned and tested by three or more identical and controlled environmental chambers. This however was not the objective of this study or of this carpet sampling campaign. In this comparative analysis, ANOVA is unlikely the appropriate tool to be used as a metric to compare the differences and the similarities between the three emission samplers.

However, as a general screening tool, and considering the inherent multi-fold emission rate variation in carpet emissions from a single sampler, let alone a group of samplers, ANOVA tests were conducted and results compared against an alpha of 0.05 and an adjusted Bonferroni-alpha of 0.017 significance. The latter is based on a per-sampler-alpha of 0.05 divided by 3, the number of comparisons between the three means. The intention of presenting both the unadjusted alpha and the adjusted alpha was simply to shed light on the data sets from two different perspectives and presenting the possible interpretations of the results obtained. Regardless of the appropriateness of applying the Bonferroni adjustment to this comparative analysis, since it increases the probability of committing a type II, beta (β), error, presenting both the unadjusted and the adjusted level of significance would enable the reader to reach a reasonable conclusion without being influenced by a specific statistical adjustment.[49] Results of the ANOVA are presented in Table 5.22.

Table 5.22: ANOVA of the 9-VOCs performed on the emission rates obtained by the three samplers, the FLEC, the ASTM and the Kappa.

			Fail to reject Ho*	
VOC #	RT (min.)	P-value	< 0.050	<0.017
1	*17.3*	0.017	N	Y
2	*17.5*	0.057	Y	Y
3	*18.0*	0.012	N	N
4	*18.2*	0.049	N	Y
5	*18.4*	0.031	N	Y
6	*18.9*	0.004	N	N
7	*19.3*	0.001	N	N
8	*19.5*	0.045	N	Y
9	*19.9*	0.037	N	Y

**Failing to reject the null hypothesis of the equality of the means between the FLEC, the ASTM and the Kappa hints to a quantitative match between the three samplers, collectively.*

5.5.4.8 Non Parametric Test: Three Samplers

One question that is often asked during ANOVA is whether the nonparametric ANOVA corrects the limitations of its parametric counterpart? The only difference between the nonparametric and the parametric ANOVA is that the nonparametric ANOVA, Kruskal-Wallis (K-W), does not assume a specific distributional form for the data obtained, ER results, whereas the parametric

ANOVA assumes normality of the data sets. However, in the K-W test it is assumed that the shape of the distribution is equal for all the groups hence the homogeneity of variances assumption remains relatively necessary. Both parametric and non-parametric ANOVA models assume independence of the measurements and both are severely compromised by spatial variability.

Table 2.23 presents the results of the K-W test conducted on the VOC ER data obtained by the three samplers combined.

Table 2.23: Quantitative comparison between the three samplers with the p-values associated with the Kruskal-Wallis test.

VOC #	RT (min.)	P-value
1	*17.3*	0.07
2	*17.5*	0.04
3	*18.0*	0.03
4	*18.2*	0.06
5	*18.4*	0.03
6	*18.9*	0.02
7	*19.3*	0.01
8	*19.5*	0.12
9	*19.9*	0.08

H0: The distribution of scores is equal across the three samplers if P >0.05.
H1: The distribution of scores is NOT equal across the three samplers if P <0.05.

5.5.4.9 Non Parametric Test: Two Samplers

The Mann-Whitney (M-W) test is a nonparametric equivalent to the two sample t-test comparing two unpaired groups. The key outcome of the M-W test is a P value that attempts to answer the question of whether the carpet ER values of each VOC captured by a pair of samplers have the same median. It also sheds light on whether the chance of random sampling would result in medians as far apart as observed in the ER values obtained during this sampling campaign.

If the P value is small, the idea that the difference is a coincidence can be rejected favoring the idea that the two samplers do indeed sample differently with different VOC ER medians. If the P value is large, the ER data suggest no reason to conclude that the overall medians of the ER values between the two samplers differ. However, the latter does not suggest that the VOC ER medians are the same. It only offers no compelling evidence that they are indeed different.

It should be noted that due to the small sample size per sampler in this sampling campaign, the Mann-Whitney test has limited power. Hence, the applicability of a non-parametric test is limited in this comparative analysis. Regardless of the sample size, Table 5.24 presents the results of the M-W test on the 9-VOC ER data sets.

If the P value is greater than the level of significance of alpha at 0.05, the decision would be not to reject the null hypothesis that the samples are not different. In other words, the difference between the two respective samplers is not significant. However, if the P value is less than the level of significance of alpha at 0.05 the decision would be to reject the null hypothesis that the samples are not different. In other words, the difference between the two respective samplers is significant.

Table 5.24: Mann-Whitney Test on the ER values of the 9-VOCs captured by two samplers respectively

Mann-Whitney test		two-tailed test	
		P-value	
VOC 1	FLEC/ASTM	0.35	←
	ASTM/Kappa	0.01	
	FLEC/Kappa	0.33	←
VOC 2	FLEC/ASTM	0.05	
	ASTM/Kappa	0.03	
	FLEC/Kappa	0.46	←
VOC 3	FLEC/ASTM	0.05	
	ASTM/Kappa	0.01	
	FLEC/Kappa	0.56	←
VOC 4	FLEC/ASTM	0.05	
	ASTM/Kappa	0.05	
	FLEC/Kappa	0.70	←
VOC 5	FLEC/ASTM	0.02	
	ASTM/Kappa	0.05	
	FLEC/Kappa	0.44	←
VOC 6	FLEC/ASTM	0.02	
	ASTM/Kappa	0.02	
	FLEC/Kappa	1.00	←
VOC 7	FLEC/ASTM	0.01	
	ASTM/Kappa	0.01	
	FLEC/Kappa	0.25	←
VOC 8	FLEC/ASTM	0.14	
	ASTM/Kappa	0.05	
	FLEC/Kappa	0.56	←
VOC 9	FLEC/ASTM	0.05	
	ASTM/Kappa	0.05	
	FLEC/Kappa	0.88	←

(Arrows indicate no significant difference between the two respective samplers).

5.5.4.10 Pairs of Two Samplers: SER Ratios

Having conducted a handful of relatively-appropriate statistical tests on the VOC ER data sets, it became apparent that among the three samplers, the ASTM leaned towards underestimating VOC emission rates when compared with either the FLEC or the Kappa. It also became apparent that both the FLEC and the Kappa are comparable samplers. The similarities in both the Kappa and the FLEC in their ER values were prominent especially when both samplers exhibited similar trends against the ASTM. Based on Figure 5.16 and Table 5.17 which presented the mean ER values of the 9-VOCs as captured by each sampler, Table 5.25 presents the pair-wise VOC ER ratios of the three samplers.

Table 5.25: Area Specific Emission Rate Ratios per pair of samplers

VOC #	*RT min.*	ASTM / FLEC	ASTM / Kappa	FLEC / Kappa
1	17.3	0.5	0.4	0.7
2	17.5	0.4	0.5	1.2
3	18.0	0.4	0.3	0.9
4	18.2	0.4	0.4	1.1
5	18.4	0.3	0.4	1.3
6	18.9	0.3	0.4	1.1
7	19.3	0.3	0.4	1.2
8	19.5	0.4	0.4	1.2
9	19.9	0.4	0.4	1.0
Mean SER Ratios		*0.4*	*0.4*	*1.1*
SD SER Ratios		*0.1*	*0.1*	*0.2*
CV SER Ratios		*18%*	*14%*	*18%*

The FLEC and the Kappa have matched very closely in their quantitative capturing of the shared and the most abundant VOCs emitted by the carpet samples. The ASTM sampler has matched both the FLEC and the Kappa with a mean underestimation factor of 0.4 (CV <20%) for each VOC among the 9-VOCs. The latter is a measure of precision of this sampling camping. This underestimation in emission sampling is not surprising, since the ASTM chamber, as explained above, has a much larger sink effect due to it larger interior surface area.

5.6 Concluding Remarks

Qualitatively, VOCs captured by the Kappa have matched those captured by the FLEC and the ASTM. Quantitatively, VOC emission rates obtained by the Kappa and the FLEC were matching for the most abundant VOCs captured. Both the Kappa and the FLEC have comparable volumes and hence similar free surfaces for sink effects. The ASTM sampler underestimated surface emissions rates by almost 60% compared with both the Kappa and the FLEC. The latter would likely be due to the larger volume of the ASTM and the larger surfaces available for sink effects to take place. Emission rates reported by the Kappa and the FLEC are matched and are compared with the ASTM by a similar ratio. The similarities in the differences between the Kappa:ASTM and the FLEC:ASTM emission rate results favor the null hypothesis of no differences between the Kappa and the FLEC.

One question, however, remains to be answered. Why did the ASTM match the FLEC during toluene emission sampling using the three REMs (REM-S, REM-M, and REM-L; chapter four) but failed to match the FLEC during sampling of VOCs emitted by the carpet samples? Factors that could have played a role in this discrepancy include the molecular size, vapor pressure, polarity and boiling point of the VOC, toluene, emitted by the REMs if compared with the 9-VOCs emitted by the carpet samples. Toluene is a "bin A" VOC-category. Not a single VOC that belonged to "bin A" category has passed the screening criteria placed to justify quantitative analysis. The within-samplers variation of each VOC that belonged to bin-A category and that was emitted by the carpet samples was grater than 50%.

It should also be noted that toluene emission rate by the REMs was much higher than all the VOC emissions from the carpet samples combined. The rate of emission by the REMs, if compared with the most abundant VOC emitted by the carpet samples, is almost 3000 times higher. Even with the re-designed REM-X, toluene emission was approximately 600 times higher than the emission of the most abundant VOC from the carpet samples. The constant emission profile of the REM versus the transient emission profile of the carpet samples may yet be another factor that likely contributed to the differences observed. Further research is needed to develop an ultra low emitting REM using a less volatile VOC and to compare the latter with the three samplers, the Kappa, the FLEC and the ASTM, in parallel. Regardless of the above, it is promising to report that the newly developed Kappa has indeed matched the FLEC in sampling VOC emissions from an interior finish such as a carpet, however unlike the FLEC, the Kappa was able to capture emissions in-situ.

Endnotes

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Chapter Six

Kappa's Sampling Alternatives

The Kappa sampler has so far provided a promising answer to some of challenges of in-situ material emission sampling. The Kappa has demonstrated the application of a simplified and a practical approach to sampling emissions from interior finishes and furnishings, in-situ. In this chapter, the application of two alternative sampling methods, capillary-canister sampling and passive diffusive badge sampling, were investigated. These sampling methods are two potentially alternative methods that could substitute the active charcoal tube sampling method used in the Kappa. This chapter presents a summary of two parallel studies conducted during the course of this research. These were the application of the capillary flow canister and the passive diffusive badge in surface emission sampling. Details of these two studies are presented in appendix B and appendix C, respectively.[1,2]

6.1 Capillary-Canister Sampling

Few initial tests were conducted to evaluate the potential application of capillary flow in evacuated canisters for surface emission sampling. The concept of capillary-canister sampling method was originally developed by Simon et al. as an alternative method for sampling VOC in air.[3] In this investigation, the application of the capillary-canister sampling method to sample VOC emissions from surfaces of interior finishes and furnishings were however unsatisfactory for the intended and the anticipated use. The involved processes in the preparation of each canister for sampling and the uncertainties in the capillary flow sampling rates were two limiting factors that favored the use of the standard active charcoal tube sampling method over the capillary-canister sampling method during the course of this research.

The application of capillary flow canister sampling is yet a now concept and its practicality for surface emission sampling remains to be uncovered. The fundamental theory of capillary flow in a column in a rarefied condition, c.f., pressurized condition, and using the analogy of an orifice to regulate and control the flow into an evacuated canister has not yet been established. More research is needed to support the assumption of steady flow in capillaries in vacuum conditions.

Preliminary results have indicated that sampling flow rate in a capillary-canister system could vary with time at a dimensioning rate. This rate depends on the diameter and the length of the capillary column, the size of the canister, and the level of the vacuum inside the canister.[4] Although, promising results of the capillary-canister sampling method in industrial hygiene sampling has been reported by other researchers[5] the application of the capillary-canister sampling method in surface emission sampling has not yet been fully evaluated.

For the benefit of future researchers, the following is a summary of the lessons learned while attempting the use of the capillary-canister sampling method for potential adaptation, as an alternative sampling method, for the Kappa sampler.

An experimental setup was developed to study the practicality of the capillary-canister sampling method in surface emission sampling using the FLEC. Two capillary-canisters were used, one to supply a zero-air to the FLEC and the other to collect emissions from an emitting surface placed inside the FLEC. Such a sampling train demonstrated the possibility of performing FLEC sampling without any reliance on electrical provisions. The sampling train has continuously sampled emissions for a duration exceeding 10 hours. The duration could have been extended to days depending on the size of the canister and the length/diameter of the capillary.

However, based on the experience gained during the development of the experimental setup and the capillary-canister-FLEC sampling campaign, some lessons were learned.

1. Empirically, there seems to be a difference between the flow in a capillary due to differential pressure that is based on a pressurized canister, and the flow in a capillary due differential pressure that is based on a depressurized canister (evacuated canister). More research is needed in this area.
2. Canister evacuation and cleaning is an involved operation that needs specialized and dedicated tools and expertise.
3. Valves that were tested for pressure leaks do not necessary mean that their use would be valid in a vacuum application.
4. Self-locking quick-connects, a trademark of Swagelok, are not appropriate for evacuated canisters. Not only the self-locking mechanism of a quick-connect system depends on a positive pressure to maintain seal, the mere action of pushing the two parts of a quick connect system generates a leak

enough to raise the pressure in an evacuated canister from 0.05 torr to 1 torr (mm-Hg).

5. Pressure gauges commonly used in laboratories mostly likely do come with a partial vacuum gauge. These however could only indicate the presence of a vacuum and not the level of it. Special vacuum-only gauges are indeed needed to read the level of vacuum inside a canister.
6. The original design of the capillary-canister configuration, as developed by Simon et al., had several connections, each increasing the likelihood of a leak. A new configuration was designed and proposed with only a single connection rendering the capillary-canister assembly less prone to leaks.
7. Sampling flow rate in a capillary-canister system is not constant and tends to exhibit a polynomial S-curve decay. The rate constant of this decay curve could only be determined empirically.

The complex procedure involved for canister preparation and vacuuming, the need for pre and post analysis of canisters for quality control, and the empirical validation needed for each capillary column before use, and other limitations as outlined above, deemed the capillary-canister sampling method impractical, at this stage, as a sampling medium alternative for the Kappa.

In line with the objective of this research, any approach for sampling surface emissions from interior finishes and furnishing should be simple and practical. The capillary-canister sampling method did not pass the requirements of simplicity and practicality, let alone the much involved and the much higher costs of sampling with and the analyses of evacuated canisters. Appendix B provides the details and the results of the capillary-canister-FLEC experiment.

6.2 Passive Badge Sampling

The reason that active tube sampling was used rather than passive badge sampling during the course of this research project, including the Kappa sampling campaigns, was due to the uncertainties reported in uptake rates and the background impurities observed in passive badge sampling. The application of the current and commercially available passive diffusive badges in non-industrial indoor environments, especially in-situ surface emission sampling from interior finishes and furnishing, needs much further investigation.

The diffusive uptake rate in a passive badge is empirically validated using air velocities that are higher than what is normally encountered indoors. According to a study conducted by OSHA, the US Occupational Safety and Health Association, the application of passive badges are appropriate at environments were concentrations and air velocities are relatively high.[6] The following two paragraphs are extracts from the referenced study:

> *The sampling rate and capacity of 3M 3520 OVMs* [a passive sampler] *was determined by taking samples from a dynamically generated test atmosphere of toluene (nominal concentration of 400 ppm or 1507 mg/m^3) for increasing time intervals. The atmosphere was at approximately 75% relative humidity, 29°C and 647 mmHg. The flow of the atmosphere through the exposure chamber provided for face velocities on the diffusive samplers of approximately 0.4 m/s.* [7]
>
> *The sampling rate and capacity of the SKC 575-002 Sampler* [a passive sampler] *were determined by taking samples from a dynamically generated test atmosphere of toluene (nominal concentration of 400 ppm or 1507 mg/m^3) for increasing time intervals. The atmosphere was at approximately 76% relative humidity, 26°C and 650 mmHg. The flow of the atmosphere through the exposure chamber provided for face velocities on the diffusive samplers of approximately 0.4 m/s.* [8]

From the above it is evident that OSHA's uptake rate validation study was performed at a velocity that is at least four times higher than what is usually encountered in a non-industrial indoor setting. An average air velocity in a typical non industrial indoor microenvironment is within the range of 0.05 to 0.1 m/s.[9]

For the kappa, the issue of air velocity at the face of the passive badge was addressed by incorporating a special adapter. The adapter was designed to generate the needed air velocity at the face of the passive badge using an auxiliary micro-fan. The micro-fan adapter, a Kappa accessory, provided the Kappa with the ability to sample surface emissions using a passive diffusive badge such as the 3M 3520 or the SKC 757-002. When operated with its micro-fan adapter accessory, the Kappa maintains the airflow at the surface of an emitting material unperturbed while gradually increasing the air velocity of the sampling air at the face of the passive badge.

However, the impurities observed in several blanks of passive badges, newly purchased for the Kappa passive badge adapter, shifted the objective of the sampling campaign to screening the sources of the observed impurities. For example, some of the impurities observed in the SKC badges were found to be from a component of the SKC badge itself, its O-ring. With the observed impurities the use of the passive badge, as received commercially, was deemed inappropriate for incorporation into the Kappa sampler.

Appendix C presents the findings of an experiment conducted to study the potential adaptability of passive badges in Kappa sampling. Based on the results obtained a decision was made to exclude passive badge sampling during the course of this research. Nevertheless, the possibility of using a quality passive badge that is without impurities and incorporating it into the aforementioned adapter for the Kappa sampler needs to be further investigated.

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Chapter Seven

Conclusions

Concentrations of most volatile organic chemicals (VOCs) are found to be several times higher indoor than outdoor.[1,2,3,4] Results of several field investigations suggest that interior finishes and furnishings are key contributors to indoor air pollution.[5] Many VOCs have been traced to be present in indoor non-industrial microenvironment.[67] Interior finishes and furnishings emit many VOCs. The reactive by products of these indoor VOCs are considered the culprit of indoor air quality complaints.[8] The impact of indoor air quality on the health and productivity of building occupants is not yet clear. Very little is known about the determinants and the contributing factors that lead to Sick Building Syndrome. Developing risk assessment for indoor air entails hazard identification, exposure assessment, dose-response assessment, and risk characterization. The outcome of this research has contributed to the first of the above four, hazard identification. It developed and tested a novel in-situ surface emission sampler to identify source of indoor VOC emissions. The latter is associated with indoor air quality complaints in non industrial microenvironments.

The contribution of interior finishes and furnishings to chronic exposure of building occupants to volatile organic chemicals and the limitation of current sampling methods to identify sources of indoor air pollution in-situ are major challenges facing indoor air quality researches and practitioners. This research focused on providing an answer to how to sample VOC emissions from fleecy surfaces of interior finishes and furnishings, in-situ. Different case studies that aimed to identify sources of indoor VOCs were reviewed from scientific literatures. Different air sampling methods that were used and adapted for sampling sources of indoor VOCs were evaluated and the applicability of current industrial hygiene sampling approaches and related analytical methods to non-industrial indoor air quality and sources emission sampling were examined.

Most sampling approaches and related methods exhibited limited ability to sample VOC emissions from surfaces of interior finishes and furnishings, in-situ. VOC emissions from fleecy diffusive surfaces of interior finishes and furnishings were in particular the most challenging of all. For example, due to the sink effect in fleecy surfaces that are found indoors, emissions are aggregates of other emissions from other sources. Emissions of VOCs from interior finishes and furnishings are unique to each building, each site and each spot. To tag a VOC to its original source requires a creative new measurement approach that is beyond what is currently available and borrowed from the field of industrial hygiene sampling.[9] Currently, and in the domain of indoor air pollution and VOC emission sampling, there is neither a standardized measurement method nor a consensus on what and where to measure.

The current practice in VOC emission sampling from interior finishes and furnishings is mostly conducted using laboratory based environmental chambers.

These environmental chambers, sometimes referred to as emission chambers, come in different sizes, from large room size chambers to small hand-held cells. VOC emissions obtained using these chambers are limited to the condition of the chamber used. Environmental chambers are used to perform baseline comparison between an empty chamber and a chamber housing an emitting material under controlled and exact conditions.

A real indoor microenvironment is not a controlled environment. There are number of factors such as ventilation rate, humidity, temperature, use and occupancy that influence emissions from surfaces of interior finishes and furnishings. There are also a number of other interior finishes and furnishings present indoors that do alter the emission profile of many indoor surfaces. These factors interact with one another. A primary emission from one interior finish may well become a secondary emission from another interior finish. Some air pollutants that are present indoors may also mask and even change the VOC emission profile of interior surfaces.

Sampling VOC emissions from interior finishes and furnishing using laboratory controlled environmental chambers would generate data that is appropriate for source characterization. However, the mandate of an IAQ investigator is to identify the source of the indoor VOC that has been found in indoor air sample collected. Finding the source becomes a needle in the haystack exercise. The latter requires cutting pieces of the different suspected interior finishes and furnishings and sending them to a laboratory for emission testing and possible source identification.

Identifying sources of indoor VOCs requires representative sampling. Cutting pieces from interior finishes or furnishings and placing them individually inside an emission chamber with a controlled environmental condition may not qualify as a representative sampling. Identifying indoor sources should be conducted at the site were emissions do occur. Including the actual indoor parameters during surface emission sampling could only be possible if sampling is performed in-situ, where the actual material resides.

The issue of indoor air chemistry and its influence on altering the emission profile of sources is indeed a challenge that needs to be addressed during material emission sampling. To address this challenge, this research studied the application of different sampling methods. Based on the limitations observed and lessons learned, a new sampling approach to the field of material emission sampling was developed. The approach involved developing two complementary tools, a new reference emitting material, the REM, and a new material emission sampler, the Kappa. These two tools were developed to demonstrate an attempt towards a real representative emission sampling from surfaces of interior finishes and furnishings, in-situ, with specific emphasis on fleecy materials such as an indoor carpet.

As per the results obtained so far during the course of this investigation, both the REM and the Kappa have shown promising applications and have provided satisfactory answers to the challenges of this research. The deployment of these two novel tools demonstrated a simplified and a more practical approach to in-situ material emission sampling.

According to established ASTM and ISO protocols, it has been an accepted norm and practice to use a certified reference material for traceability during any environmental sampling and analysis.[10,11] Ironically, in the field of surface emission sampling there was no available reference as such for accurate realization of emission rates and calibration of emission chambers. To this end, a novel reference emitting material (REM) was developed to support and help achieve the objective and mandate of this research. Results of the REM experiments have demonstrated the relevance of the REM as a reference emitting material with a sufficiently predictable and constant emission rate mimicking diffusive emission from surfaces of interior finished and furnishings. The REM could now be used for the calibration and comparison of different environmental chambers, the assessment of different emission sampling methods and the evaluation of different emission samplers on capturing emissions from a known diffusive and planner emitting source.

Before its use, the REM should be placed in the environment where the testing is to be taken place, either inside the chamber or in a room, depending on the objective of the test. Enough time should be allowed for emissions by the REM to equilibrate and reach a steady state. The equilibrium time may take several weeks, depending on the size of the permeating surface and the thickness of the permeating membrane, the larger the surface and the thicker the membrane the longer the time required to reach equilibrium.

For comparison, REM-S in this study has reached its equilibrium within two weeks while REM-XL took ten weeks. Testing for equilibrium could be either performed by an environmental chamber or through a visual inspection on the level of accumulated pressure inside the REM, a rise of the membrane due to pressure buildup. The vapor presence exerted by the evaporation of liquid toluene inside the sealed REM has nothing to do with the build up of pressure inside the REM. The latter is in fact against the theory of vapor pressure and equilibrium. Nor the effect had to do with the elongation or deformation of the membrane used. In the latter case, a needle was used to punch in one of the inflated REMs to observe if the inflated membrane would instantly deflate. It did and hence proved that the inflation was not due to a permanent elongation of the membrane but rather due to some sort of a pressure build up.

After some investigation through literature reviews and communication with polymer experts, the build up of the pressure inside the REM was attributed to a common but little published phenomenon of back diffusion and permeation of the smaller molecules of the surrounding indoor air, such as O_2 into the reservoir of the REM. To confirm this observation, several trial tests were conducted on different sizes of REMs with different types and sorts of membranes. In every test, this interesting though atypical phenomenon has been observed. To further examine this effect, some of the already inflated REMs were placed inside a Freezer (-20C) to observe if the indoor air temperature had any thing to do with this phenomenon. No change was observed, and the REMs remained inflated.

Another lesson learned during the design and the development of the REMs was the potential interaction between the polymer material used to seal the REM, the O-rings, and the permeating toluene. Teflon should be the only O-ring for use in any VOC application, regardless of being in direct contact with the liquid VOC or with its gas phase. The latter was indeed the precursor that hinted to the source of some observed impurities generated during extraction of samples from the passive diffusive badges.

Assisted by the newly developed REM, the new emission sampler, the Kappa, was tested and compared against the FLEC. Results indicate the ability of the Kappa to capture toluene from an emitting source, the REM-XL, in-situ. The Kappa, unlike the FLEC, uses the indoor air as its sampling gas. The FLEC on the other hand relies on zero air cylinders as a source for its sampling gas. Despite this fundamental difference, the Kappa has managed to sample toluene from the REM and eliminate interferences from other indoor sources, thanks to the activated carbon felt O-ring and its integration into the design of the Kappa. The latter proved the ability of the Kappa to sample an indoor source in the midst of other sources, as typical in indoor environments, while maintaining emission specificity of the sampling source.

The Kappa was designed in response to the needs of IAQ practitioners for a more economical, practical and do-it-yourself sampling method that is able to screen, identify and fingerprint sources of VOCs from the midst of the various sources present in indoor microenvironments. The design criteria for the Kappa supported the following prerequisites deemed important for any surface emission sampling:

1. To be able to perform dynamic emission sampling (c.f. static head sampling);
2. To be able to sample emissions from any sort of indoor material fleecy be it or solid;
3. To be able to sample emission from indoor finishes in-situ without removal.
4. To require the least reliance on external provisions such as zero-air for its sampling air.

Results from the comparative analysis performed using the three different material emission samplers, the ASTM, the FLEC and the Kappa, with data from five repeated carpet samples indicates a systemic match of retention times in sample chromatograms. In other words, the three samplers have qualitatively matched each other in their sampling of the most abundant VOCs emitted by the carpet samples. A matching process was used to generate average carpet fingerprints. Carpet fingerprints generated by the Kappa have matched those generated by the ASTM and those generated by the FLEC. Qualitatively, from a list of 27 most abundant VOCs emitted by the carpet samples, a subset of some 50+ VOCs captured, the three samplers matched on 16 out of the 27 VOCs. Quantitatively, the average variations in these VOCs in terms of their estimated emission rates based on normalized peak responses and steady state model, ranged from 7% to 90% depending on specific VOCs. It should be noted that variations up to 400% in carpet emission sampling between different emission sampling methods are not uncommon in VOC emission studies.[12]

Factors that may have influenced the variations in emission rates of some of the VOCs were sink effects, surface area of the emitting material, volume of the samplers, sampling flow rate and chamber flow rate. Even a slight variation on the amount of the extracting solvent used during sample analysis could lead to variations on emission rate calculations.

The degree of match between the chromatograms obtained by the ASTM, the FLREC and the Kappa represents the qualitative ability of the Kappa to match the two laboratory based emission samplers, though sampling in-situ. From the list of the 16 VOCs that were captured by all the three samplers, 9 VOCs were of particular interest. Both the FLEC and the Kappa were almost identical in estimating the emission rates of these 9 VOCs while the ASTM has systematically underestimated their emission rates, if compared with both the FLEC and the Kappa, by 2.5 folds. This was mainly due to the larger volume of the ASTM and hence its sink effect.

The dynamic emission sampling capability of the Kappa has been achieved due to the filtering O-ring felt placed at the perimeter of its rim. This filtering O-ring eliminated the need for external sources of clean sampling air. The same indoor air that surrounds the material is being used as the sampling air, albeit filtered by the O-ring before entering into the sampling cell of the kappa.

Results of the carpet tests also present the practicality of the Kappa compared with the other two samplers and its unique in-situ sampling ability of a fleecy material such as a carpet where no other sampler could perform. As mentioned earlier, the ASTM is only capable to perform material emission sampling in a laboratory settings using pre cut samples. The FLEC, on the other hand, could not be placed directly on top of a fleecy material such as a carpet; hence the use of a carpet adapter cell was required. The latter is an accessory designed for the FLEC and entails cutting pieces of the carpet for emission sampling by the FLEC. In fact during carpet emission sampling, the FLEC should rather be called the LEC (Laboratory Emission Sampler, c.f. Field and Laboratory Emission Sampler). In principal, there are three fundamental differences between the Kappa and the FLEC:

1. The Kappa is designed to accommodate in-situ/field emission sampling even for a fleecy material such as a carpet, while the FLEC is mainly a lab-based emission sampler and it is only partly a field sampler depending on the type of the material being sampled.
2. The Kappa samples uneven and fleecy surfaces, in-situ, while the FLEC could only sample even and smooth surfaces in-situ.
3. The Kappa does not require an external supply of clean sampling air, while the FLEC requires a supply of clean sampling air either through a canister or by using an external air filtration apparatus.

As per the some of discrepancies observed between the ASTM, the FLEC and the Kappa, it should be acknowledged that variations in excess of 400% between different laboratories that participated in a round-robin sampling campaign for VOC emissions from a specific carpet have been reported elsewhere.[13] VOC emission variability from different locations within same material specimen such as an OSB (Oriented Strand Board) has been reported to range from 26% to 53%, and analytical uncertainty, variation based on sampling and analysis, was found to be strongly compound-specific. The latter ranged from 12% to 35%.[14] Intra-sample variability in emission rates from a single patch of a carpet cushion was found to be as large as between cushion samples collected from different mills/manufactures.[15] In between variations in the amount of a specific VOC (butylated hydroxytolune; a heat stabilizer used in the manufacturing process of urethane carpet under-pads) emitted from multiple pieces of the same patch of a carpet cushion were reported to be 300% to 1300%.[16]

In this research, Kappa versus FLEC variations for the nine most abundant VOCs emitted from the carpet samples including all accumulated variations throughout the entire sampling campaign and taking into account the notion of sampling different locations from within a single material were less than 20%. Results obtained from this experiment demonstrated both the qualitative and quantitative ability of the Kappa as a novel in-situ emission sampler for dynamic emission sampling of interior finishes and furnishings.

Results from this investigation suggest that the novel sampler is comparable with other industry accepted laboratory chambers. If the issue of full validity, both internal and external, is to be resolved, then repeated experimental campaigns using the novel sampler in parallel with a standard sampling method able to perform an "in-situ" VOC emission sampling is required. The latter is not possible since there is no such a tool available for in-situ emission sampling. Thus, the limit of this study rests on repeatability of the novel sampler, the variations within repeated samples, and its reliability as indicated by its comparison with the ASTM and the FLEC. The results of the repeated experiments suggest a good qualitative agreement between the Kappa, the FLEC and the ASTM and an excellent quantitative agreement between the Kappa and the FLEC.

This outcome of this study is thus a novel sampler that is able to perform dynamic in-situ emission sampling with comparable results to that of the FLEC. The dynamic emission sampling capability of the Kappa has been achieved without the need for an external supply of clean sampling air. As per the comparative nature of this investigation and in light of the intertwined factors that may have played a role in the observed variations, the overall trend of the results is assuring. Differences in FID peak areas indicate that certain factors may have been responsible for some of the differences, including specimen variability, spatial variability and temporal variability. Results provided matching fingerprints for some of the most abundant VOCs emitted by the carpet samples, with a consistent and conforming trend. The Kappa thus offered a promising tool for IAQ practitioners to sample VOC emissions "in-situ" and identify the interior surfaces that contribute to indoor VOC pollution. To this end, the objective of this research is practically achieved.

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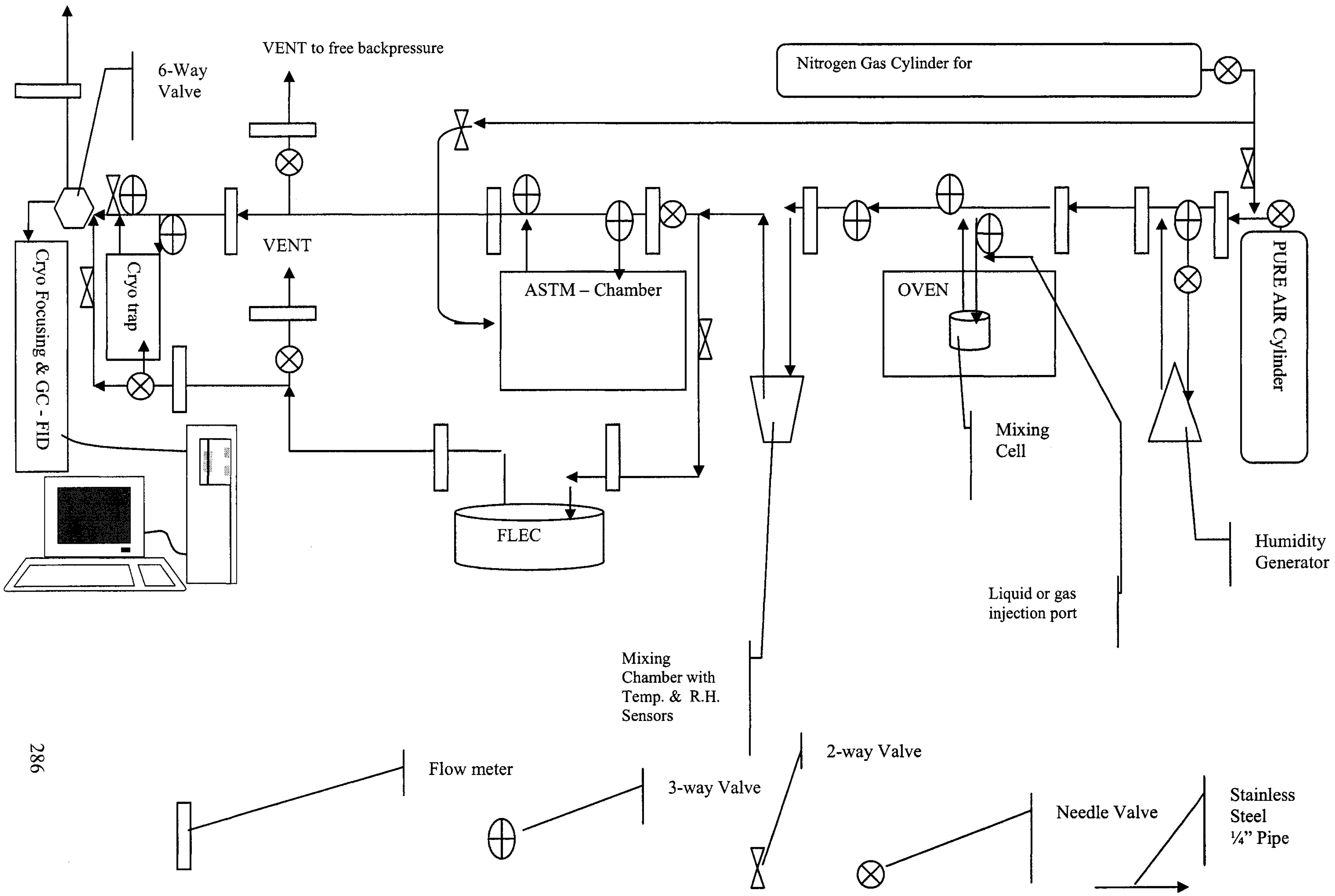
Appendix A

Sampling and Analysis System

GC-FID (104 m Capillary Col. 3um 0.53 mm) with Cryogenic Condenser, Focuser and Separator



Appendix B

Capillary-Canister Sampling

This appendix introduces the experimental setup that was used to test the application of the capillary-canister sampling of surface emissions. The sampling train consisted of two canisters, two capillary sampler flow controllers (CSFC)[1] and the Field and Laboratory Emission Cell (FLEC).

B.1 Background

In response to VOC emissions from interior finishes and furnishings and their impact on the quality of indoor air in non-industrial microenvironments two solutions have been proposed. The first solution is to increase ventilation rate and dilute the concentration of indoor VOCs.[2] This measure however is against current energy conservation practices. The second measure is to control sources that contribute to indoor VOCs.[3] Controlling the source of an indoor VOC requires finding and tagging the source.[4] Finding the source in the midst of interior finishes and furnishings requires an in-situ surface emission sampler.[5] The objective of this investigation was to study the application of a new sampling method to obtain source/surface specific emission data.

B.2 The Sampling Train

The experimental setup used in this investigation consisted of:

1. A small (440cc) pressurized (12 MPa) zero-air canister.
2. A small (1000 cc) evacuated (0.05 torr) stainless steel canister.
3. Two CSFC with an estimated sampling rate of 0.5cc/min.
4. The Field and Laboratory Emission Cell (FLEC).

The FLEC was adapted to receive the ends of two CSFCs. One CSFC was attached to zero-air pressurized canister and the other CFSC was attached to the evacuated canister. Figure B-1 illustrates the sampling train used.

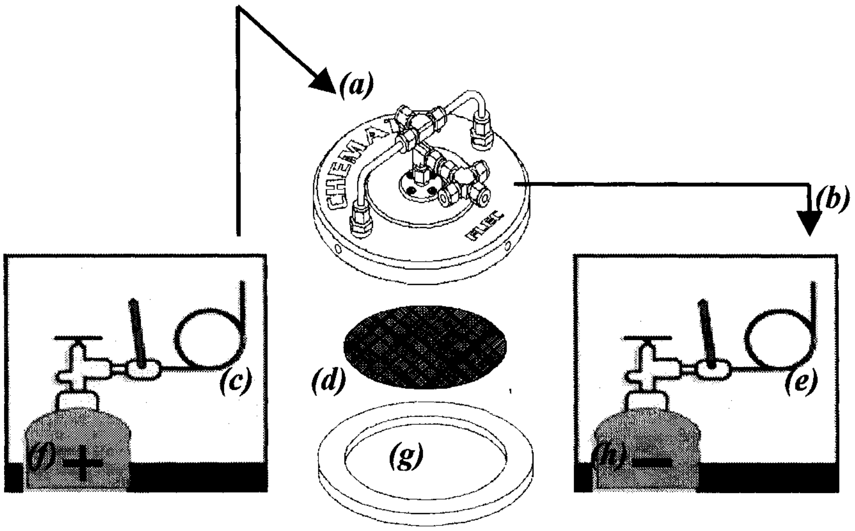


Figure B-1: CSFC-Canister and the FLEC - Sampling Train
(a) inlet flow to the FLEC; (b) sampling flow; (c) CSFC with pressurized flow; (d) painted aluminum plate; (e) CSFC under negative flow; (f) Zero-air pressurized canister; (g) chamber; (h) Evacuated canister.

An aluminum plate, item d, Figure B-1, was first preconditioned by washing it with acetone. The plate was then placed under a laboratory hood for evaporation of the residual solvent. A 10ml low VOC content, white color, 100% acrylic, emulsion, semi-gloss paint was applied in two coats of 5ml each to paint the surface of the plate. Each coat covered the entire surface of the plate. The first coat was allowed to dry for three hours under a laboratory hood. The second coat was allowed to dry for six hour in room conditions (25° C, RH 45%). The plate was then wrapped with aluminum foil and stored for one week. On the day of the sampling, eight other preconditioned unpainted aluminum test-plates were placed inside the test chamber, item g, Figure B-1. The test chamber used is a FLEC accessory (CHEMTEC FL-150).[6] The eight unpainted aluminum plates were used as shims to adjust the depth of the test chamber and to allow the painted plate to be exactly under the mouth of the FLEC. The FLEC was placed on top of the test chamber. The sampling train was tested for leaks. Leaks detected were corrected by using clamps to tighten the FLEC onto the surface of the test chamber.

B.3 The Vacuum Pump

After several attempts to generate and measure an appropriate level of vacuum inside the sampling canister, it became evident that the vacuuming system was not powerful enough to reach the EPA recommended value of 0.05 mm-Hg.[7] It was necessary to measure the vacuum level achieved before the start of the sampling. Initially, the gauge used was an analogue positive pressure gauge with a provisional negative scale indicator. Although the gauge had vacuum scale it was however misleading. Upon closer examination it became evident that the gauge could only indicate that the canister was at a negative pressure without being able to accurately report the level of the vacuum inside the canister. The analogue gauge was replaced with a digital dual sensor vacuum gauge, a thin film Pirani sensor and a piezoresistive sensor (Teledyne Hastings Model 2002)[8]. The piezoresistive sensor is a direct force sensor which gives accurate readings at high pressures from atmosphere down to 1 mm-Hg. The thin film Pirani sensor measures pressures from a 1 mm-Hg down to less than 10^{-4} mm-Hg.

With the help of the new vacuum gauge, it became apparent that the oil-based vacuum pump used in this investigation could not reach the 0.05 mm-Hg level on a reasonable amount of time. It took almost 3 hours to barley reach the required vacuum level. Oil-based pumps are usually used as roughing pumps and are not designed to reach low levels of vacuum. In addition the issue of oil-vapor back draft into the vacuum line and hence into the canister became a concern. A two stage oil mist trapping and VOC filtering system was added and installed into the pumping system as per literature recommendations.[9] Figure B-2 illustrates the vacuum pump used.

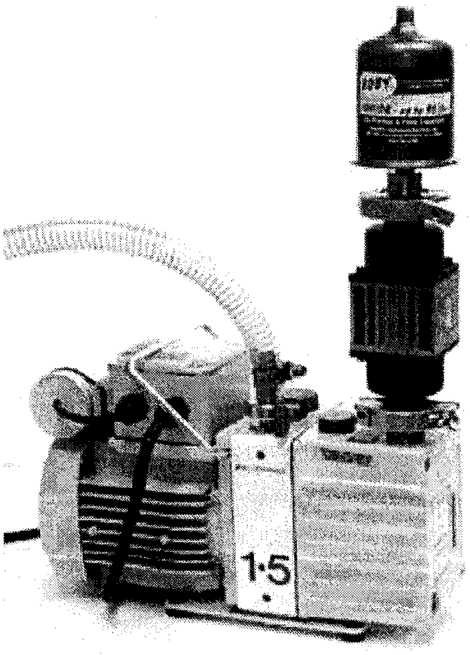


Figure B-2: The vacuum pump with double stage trapping and filtering system.

This however generated further restriction on the pump capacity and severely limited the pump from reaching the desired level of vacuum. A second stage turbo molecular or diffusion pump could have solved this problem. A two stage pumping system is indeed the norm for reaching a low level "clean" vacuum. For the purpose of cleaning canisters, and due to potential contamination of the turbo molecular pump, such a pumping configuration may not appropriate.

After investigating other canister vacuuming systems a new and a relatively recent patented pumping technology, that was introduced by Varian (TriScroll 300 Pump) was acquired and tested. The technology is a multi-stage dry vacuum pumping designed to as an oil-free vacuum system with high speed and low pressure reaching almost 0.03 mm-Hg in less than one hour. It took 20 minutes to reach a desired vacuum level for a 1000 cc canister. Not only the pump was oil-free, no back-draft of mists, but also it was fast and robust. Although the cost of such a pump was $6,000, it needed no additional accessories, filters, traps or auxiliary roughing pumps. The initial vacuum setup was thus modified to include a sensitive vacuum gauge and oil-less vacuum pump. Figure B-3 illustrates the alternative pump used. [10]

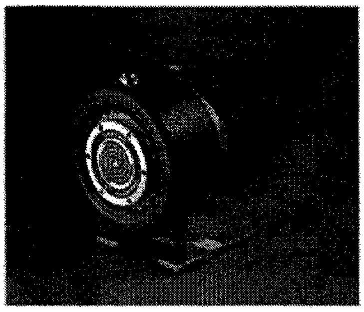


Figure B-3: The oil-less TriScroll 300 vacuum pump by Varian.

B.4 The Canister Valve

Each canister, when purchased, is supplied with own factory installed on/off valve. The valve as originally supplied was for the purpose of sealing a pressurized system. No specification was available for such a valve as supplied under vacuum conditions. Although the original valve supplied with the canister may have kept the level of the vacuum inside the canister, the manufacturer of the valve could not guarantee that the valve would be leak proof under vacuum condition. No data were available to support the applicability of the valve supplied under negative pressure. Although the manufacturer did report a leak testing value of Helium at a rate of 4 x 10–9 std cm3/s (5.3 x 10–9 Torr L/s), the unit Torr is misinterpreted by many as an indication of seal-ability in a vacuum environment.

Figure B-4 illustrates an example of a canister with a metal-seated diaphragm valve. The valve is typically manufactured by Swagelok.[11,12]

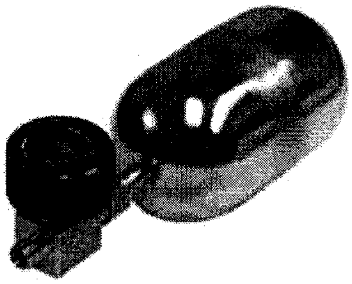


Figure B-4: A canister-valve assembly as supplied by the manufacturer.

In leak testing of valves, a pressure difference between the inlet and the outlet of a closed valve is produced. Subsequently the amount of gas passing through the valve, a measure of leak, is measured. In leak tests, Helium is usually used as the tracer gas. In principle, two methods are used for leak testing, the "vacuum method" and the "overpressure method". According to the specifications of valve that was originally supplied with the canister, the leak test was indeed an overpressure test. An overpressure test is not appropriate for valves that are intended to hold vacuum. Significant efforts and research has been put into designing vacuum sealed valves. Such valves are meticulously made using advanced technologies. The original valve as supplied by the canister manufacturer was replaced with a vacuum-specific valve, Varian Stainless Steel

Block Valve, as illustrated in Figure B-5 (left). The latter valve is especially designed for high level vacuum applications and comes with supporting data and specification on vacuum testing and temperature range.

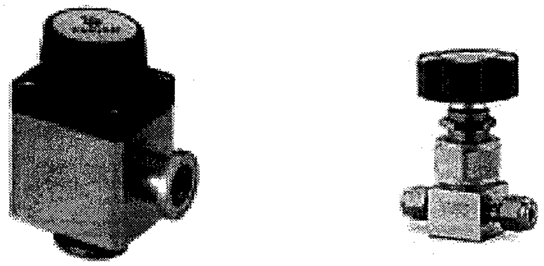


Figure B-5: The Varian vacuum valve[13] (left) replacing the Swagelok pressure valve[14] (right).

B.5 The Quick-Connect Valve

A number of self-locking quick-connect valves, a Swagelok trademark, were originally used in the plumping of the capillary-canister vacuum system. Connecting the two parts of the quick-connect system (see Figure B-6), male with female, entails pushing the two parts against each other for self-lock. During this push-and-lock operation the valve remain open for a minuscule time allowing leaks of vacuum to occur instantaneously. Due to this reason, the quick-connect valves were replaced with aforementioned vacuum valve.

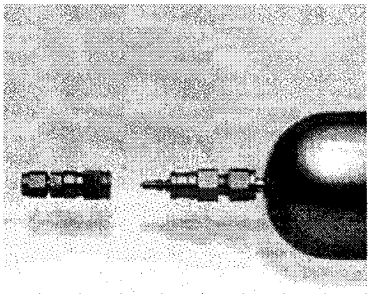


Figure B-6: A Canisters w/ Quick Connect Stem Fittings.
(From: www.restekcorp.com)

B.6 The CSFCs

Inlet flow rate from the pressurized canister through the CSFC to the inlet of the FLEC was set to 0.5 cc/min. Aided by the pressurized canister, this flow rate was controlled by a capillary column. Inlet flow rate was stable as long as the pressure inside the pressurized canister remained above 5.4 MPa (500 psi). Sampling flow rate into the evacuated canister was controlled by a second CSFC and was measured with a digital flow mete. The sampling rate was 0.5cc/min. This sampling rate was also empirically estimated by the length and diameter of the capillary column used, and the initial vacuum and size of the evacuated canister according to an equation provided the Simon.[15] The vacuum level and the size of the evacuated canister were 0.05 mm-Hg and 1000 cc respectively. The length and the diameter of the capillary column were 0.1 mm ID and 850mm length, respectively. The estimated flow rate in the capillary column with the above input parameters were 0.46cc/min. This sampling rate, according to the equation supplied was based on the assumption that the flow inside would remain stable and last for 15 hrs. The actual measured flow rate, 0.5cc/min, was very close to the estimated one. The flow rate was measured using both a GC digital mass flow meter (ALLTECH-Digital Flow Check) and a CG capillary column bubble meter (SUPELCO-0.5ml volume bubble meter). However, the rate as measured in this investigation diminished at a specific rate following an S curve polynomial curve.

To calculate the total sampling volume, flow rate was measured at different sampling intervals. The equation of the curve estimating the CSFC sampling rate is presented in Figure B-7. The area under the polynomial curve estimates the sampling volume. In contrast to the observed diminishing sampling flow rate in CSFC-evacuated canister, inlet flow rate in the CSFC-pressurized canister was uniform throughout the experiment. More empirical tests are needed to understand the behaviour of gas flow inside capillaries derived by negative pressure as opposed to positive pressure.

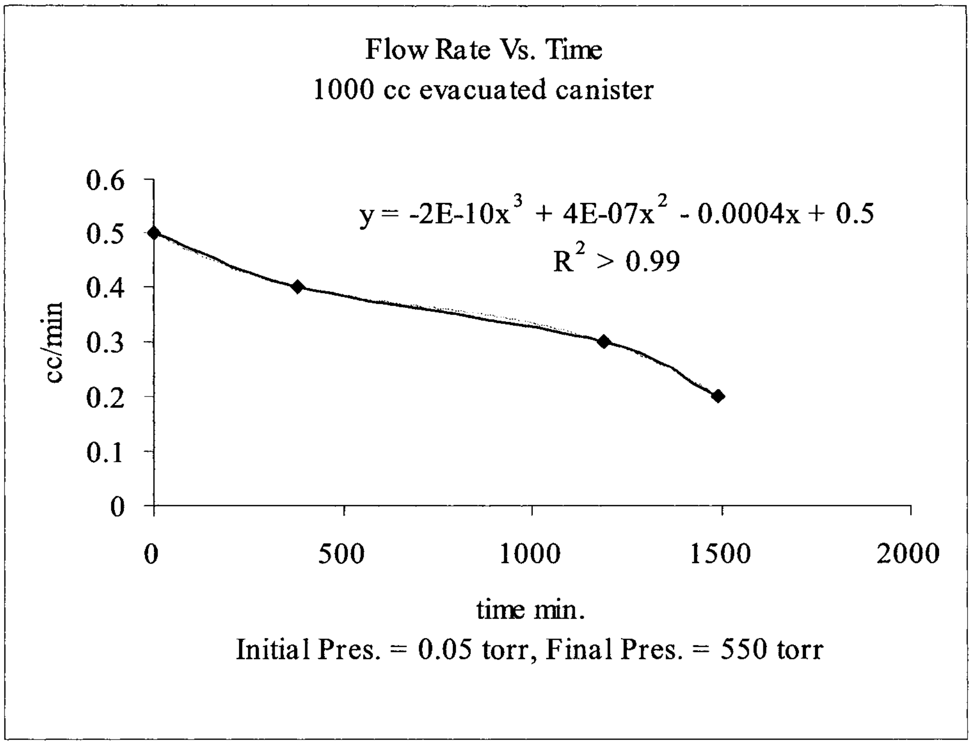


Figure B-7: CSFC-Canister sampling flow rate.

B.7 Sample Extraction

After sample collection, the pressure inside the partially filled canister was 550 mm-Hg. The canister was then pressurized with humidified Nitrogen to 1100 mm-Hg. Pressurization of the canister was performed to allow reverse extraction of the collected sample into a purge-and-trap concentrator. Sample extraction and analysis were performed using an extractor (Tekmar ALS 2016) connected to a purge and trap concentrator (Tekmar LSC 2000 with CarbopackB/Carboxen VOCARB 3000 trap by Supelco). The extractor was connected to a GC-MS (VARIAN Saturn) equipped with 60m/0.32mm, ID/1.8um coated fused silica capillary column (J&W Scientific). Nitrogen gas was used as the carrier gas for the purge and trap concentrator and helium gas was used as the GC carrier gas.

Purging time was 22 min and extraction flow rate was 15cc/min. The total volume of the extracted/diluted sample that is transferred to the trap was thus 330cc (22min x 15 cc/min = 330cc).

B.8 Results

An integration of the polynomial curve, Figure B-7, provides an estimate of the total sample collected during this investigation. Sampling volume, the area under the curve, from the start of the sampling (time = 0 min) to the end of sampling (t = 600 min) was:

$$\int_{0\,\text{min}}^{600\,\text{min}} -(2\times10^{-10}x^3)+(4\times10^{-7}x^2)-(0.0004x)+0.5=250cc \qquad [eq.1]$$

Due to the additional gas (N_2) that was introduced into the canister for sample extraction, a dilution factor (DF) was calculated. The DF was estimated using the following equation:

$$DF=\frac{FinalVolume}{InitialVolume}=\frac{1100torr\times\dfrac{1000cc}{760torr}}{250cc}\approx5.8 \qquad [eq.2]$$

The sampling volume, 330cc sample, was purged into a GC/MS for analysis and separation. Several VOC peaks were detected. Toluene was selected for quantification. Toluene retention time was 17.44 min with a peak area of 6910842. Peak Area of 100 ng net toluene used as an external standard was 1863071. The mass of toluene in the collected sample was thus 371ng of net toluene. Using equation 3 below and applying appropriate conversion units, the concentration of toluene in the sample collected can be estimated. The estimated concentration was thus 6.5 ng/cc.

$$Concentration(ng/cc) = \frac{Total\ VOC\ in\ ng}{Total\ Vol.\ Extracted\ by\ the\ Trap\ in\ cc.} \times DF \quad [eq.3]$$

After determining the concentrations of toluene, a mass balance equation for a well-mixed chamber at STP conditions was used to calculate the steady state VOC emission rate from the painted surface. With an inlet flow rate of 0.5cc/min, the air change rate in the cell of the FLEC was almost 1 ACH (air change per hour). Applying equation 4 below with a FLEC volume of 0.000035 m^3, ACH of 1, and a surface area of 0.01767m^2, toluene emission rate was calculated at 0.012 $mg/m^2.hr$.

$$ER(mg/m^2hr) = \frac{Cell\ Vol.(m^3) \times ACH \times VOC\ Concentration(mg/m^3)}{Sample\ Surface\ Area(m^2)} \quad [eq.4]$$

B.9 Discussion

The sampling setup presented, a double canister system, has never been attempted elsewhere. It demonstrated the possibility of performing material emission sampling without a sampling pump. Sample duration lasted for 10 hrs without any electrical or battery sources. Sampling duration could be extended to days or weeks depending on canister size, capillary length and capillary diameter.

However, before using the capillary-canister sampling method as a sampling method for surface emission sampling these issues need to be addressed first:

1. Empirically, there seems to be a difference between the flow in a capillary due to differential pressure that is based on a pressurized canister, and the flow in a capillary due differential pressure that is based on a depressurized canister (evacuated canister). More research is needed in this area.
2. Canister evacuation and cleaning is an involved operation that needs specialized and dedicated tools and expertise.
3. Valves that were tested for pressure leaks do not necessary mean that their use would be valid in a vacuum application.
4. Self-locking quick-connects, a trade mark of Swagelok, are not appropriate for evacuated canisters. Not only the self-locking mechanism of a quick-connect system depends on a positive pressure to maintain seal, the mere action of pushing the two parts of a quick connect system generates a leak enough to raise the pressure in an evacuated canister from 0.05 torr (mm-Hg) to 1 torr (mm-Hg).
5. Pressure gauges commonly used in laboratories mostly likely do come with a partial vacuum gauge. These however could only indicate the presence of a vacuum and not the level of it. Special vacuum-only gauges are indeed needed to read the level of vacuum inside a canister.
6. The original design of the capillary-canister configuration, as developed by Simon et al., had several connections, each increasing the likelihood of a leak. A new configuration was designed and proposed with only a single connection rendering the capillary-canister assembly less prone to leaks.
7. Sampling flow rate in a capillary-canister system is not constant and tends to exhibit a polynomial S-curve decay. The rate constant of this decay curve could only be determined empirically.

The complex procedure involved for canister preparation and vacuuming, the need for pre and post analysis of canisters for quality control, and the empirical validation needed for each capillary column before use, and other limitations as outlined above, deemed the capillary-canister sampling method impractical, at this stage, as a sampling alternative for the Kappa. In line with the objective of this research, any approach for sampling surface emissions from interior finishes and furnishing should be simple and practical. The capillary-canister sampling method did not pass the requirements of simplicity and practicality, let alone the much involved and the much higher costs of sampling with and the analyses of evacuated canisters.

Endnotes

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[1] Simon, P & Farant, JP 1997, 'Capillary Sampling Flow Controller', US patent #5,621,180, Canadian patent # 2 175 843.

[2] Mendell, MJ 1993, 'Non-specific Symptoms in Office Workers: A Review and Summary of the Epidemiologic Literature', Indoor Air, Vol.3, pp. 226-236.

[3] Brown, SK et al. 1994, 'Concentrations of Volatile Organic Compounds in Indoor Air: A Review", Indoor Air, Vol. 4, pp. 123-134.

[4] Wallace, L et al. 1990, 'Total organic concentrations in 2500 personal, indoor and outdoor air samples collected in the USA EPA Team studies'. In: Walkinshaw, DS (ed.), Proceedings of Indoor Air '90, Ottawa, Vol. 2, pp. 639-644.

[5] Wolkoff, P 1995, 'Volatile Organic Compounds-Sources, Measurements, Emissions, and the Impact on Indoor Air Quality', Indoor Air - Supplement No 3.

[6] CHEMTEC refers to this product as a "FLEC test-plate for carpet", while the authors used it as a base chamber for the FLEC Cell. The plate exhibited an excellent sealing effect when used with the FLEC Cell.

[7] USEPA 1997, 'Compendium Method TO-15: Determination of Volatile Organic Compounds In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)', 2nd ed., Center for Environmental Research Information Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH, USA.

[8] Teledyne Hastings Model 2002™, viewed 13 August 2005, http://www.teledyne-hi.com/products/pv-2002.htm

[9] Viewed 13 August 2005, http://www.sisweb.com/vacuum/sis/exfilter.htm

[10] Viewed 13 August 2005, http://www.varianinc.com/cgi-bin/nav?products/vacuum/pumps/scroll/tri300/index&cid=IMHKJMKLFO

[11] Viewed 13 August 2005, http://www.restek.com/advantage/adv_2003_01_13.asp

[12] Viewed 13 August 2005, http://www.swagelok.com/

[13] Viewed 13 August 2005, http://www.varianinc.com/image/vimage/docs/products/vacuum/valves/shared/valves-catalog.pdf

[14] Viewed 13 August 2005, http://www.swagelok.com/results/dyn/group_VALVES/tp_128

[15] Simon, P 1997, Long-Term Integrated Sampling to Characterize Airborne VOCs in Indoor and Outdoor Environments, Ph.D. Thesis, Department of Occupational Health, McGill University, Canada.

Appendix C
Passive Badge Sampling

This appendix presents few examples, applications and limitations of diffusive badge sampling in non-industrial microenvironments. It reviews field investigations that have used passive badges in their sampling campaigns. Basic fundamentals of passive diffusion sampling are reviewed. The appendix also presents the preliminary results of few experiment conducted to examine the potential application of diffusive badges in the Kappa sampler. The Kappa is a novel in-situ surface emission sampler that was developed for emission sampling of VOCs from interior finishes and furnishings. According to the initial results obtained, passive diffusive badges are not suitable for general non-industrial IAQ sampling, let alone surface emission sampling. The low indoor air velocities present in non-industrial indoor settings are not applicable for passive diffusive sampling.

The background impurities observed in several blanks in different batches of passive diffusive badges was also a problem that limited the application of passive diffusive badges in sampling low level indoor VOCs. Diffusive badge sampling is however appropriate for industrial environments, indoors of outdoors, where concentrations and air velocities are at levels that are relatively higher than those found in non-industrial microenvironments. As a rule of thumb, the use of a passive diffusive badge is only appropriate in an environment where the concentration of a VOC is > 1ppm and the indoor air velocity in that microenvironment is >20cm/s. Such levels are hardly encountered in non-industrial indoors. Even if indoor air velocities were increased during sampling, the level of impurities found in new, unused and off-the-shelf passive badges raises major concerns in the application of passive diffusive badges in sampling low level (ppb) VOCs in non-industrial indoor environments.

Each passive diffusive badge is designed with a critical range of face velocities that should not be used outside, especially below, the prescribed range. According to the literature on passive diffusive badges, changes in air velocities influence the diffusive sampling rate. Decline in uptake rates, the sampling rate in diffusive badges, are more pronounced at the lower air velocity range, < 20 cm/s, than at the higher range, >20cm/s, by several folds.[1] Most commonly used diffusive badges require a minimum critical face velocity of 15-20 cm/s.[2] This critical and "minimum" face velocity that is required in passive diffusive badges is to limit the starvation effect in the diffusive transport mechanism.

Higher air velocities and turbulences maintain the continuity of a positive concentration gradient between the air outside the badge and the still air inside the badge.[3] Air velocities in offices and homes are usually < 10cm/s. These low levels of air velocities limit the continuity of VOC transport from a not-that-high concentration gradient found indoors to the lower concentration gradients. In other words, molecules of VOCs near the exterior surface of a diffusive badge cannot be steadily renewed once they enter into the diffusive chamber of the badge. A complimentary driving force is required to maintain a constant mass transport throughout the diffusive sampling process.[4]

The diffusive transport process could be summarized as: (1) the VOCs in the bulk indoor air enters into the boundary film near the exterior inlet of the badge (known as the anti-convective membrane); (2) permeation into the diffusive membrane; (3) diffusion through the diffusive chamber; (4) molecular diffusion through a thin film of still air into the pore spaces between carbon particles of the sampling medium, activated carbon felt or granules; and finally (5) resting onto the surfaces of carbon particles.

To facilitate such multidimensional transport process, an external complimentary driving force is needed. This force is provided by the turbulent, in terms of air velocity, and mixed, in terms of distribution of concentration, conditions present in most industrial microenvironments. To this end, passive sampling is no doubt appropriate for sampling VOCs in indoor industrial settings. The range of air velocities are >20cm/s. However, when it comes to non-industrial indoor environments such as in offices and homes, the average air velocities are hardly above 10cm/s. According to ASHRAE, a 20cm/s air velocity in an indoor office environment contributes to the dissatisfaction of occupants.[5]

Studies indicate that among the three major environmental parameters that influence the performance of passive diffusive sampling, air velocity, relative humidity; and temperature, the former is considered the most influential in passive diffusive sampling.[6] In a field validation study, three different passive diffusive badges (AT, 3M, and SKC) were used to capture VOCs in an indoor microenvironment with indoor air velocities ranging from 4cm/s to 14cm/s.[7] Although the study might have overlooked the influence of the lower than recommended air velocity in diffusive sampling, it concluded that all three types of passive diffusive badges failed the National Institute for Occupational Health and Safety standard recommended CV value of < 25% at a mean VOC level of < 1ppm. The study however mentioned that the presence of "unique non-homogenous atmospheres" could have influenced the results.

Measuring air velocities at levels below 10cm/s requires special measuring devices. The standard hot-wire anemometer that is used in most indoor air velocity measurement studies could only measure air velocities that are above 8cm/s.[8] Reporting values below 5cm/s is no doubt erroneous unless specialized and sophisticated velocity measuring instruments are used. The comparative and validation studies conducted by OSHA – Occupational Health and Safety Administration – for passive diffusive badges are performed in laboratory conditions with air velocities above, and in many cases, twice that of 20cm/s. According to OSHA, variations in uptake rates of a passive diffusive badge for a particular VOC at a face velocity of 20 cm/s should not be used as estimated variations in filed studies. OSHA uses a face velocity of 40 cm/s to determine, validate and compare uptake rates in passive diffusive badges.[9]

Regardless of the above limitations in the use of passive badges in non-industrial microenvironments, there are many IAQ studies that have used passive badges to report indoor VOC concentrations. Table C.1 presents few of these studies. Some studies took into consideration the limitations mentioned above, while others overlooked these limitations.

Table C-1: VOC concentrations in homes and offices using passive badge sampling.

Reference	**Number of sites**	**Location**	**Species monitored**	**VOC (μgm^{-3})**
Fellin and Otson, (1994)	754 homes	Canada	26 VOCs	Benzene (5.5); *d*-limonene (20.8); Toluene (39.7)
Ilgen *et al.*, (2001a; 2001b)	114 homes	Germany	BTEX*1	Ethylbenzene (2.8); Benzene (2.9); Xylene (9.4); Toluene (28)
Wolkoff *et al.*, (1991)	Twin apartments	Denmark	21 VOCs	Benzene (3.2); Toluene (16)
Schneider *et al.*, (2001)	405 homes	Germany	BTEX*1	Benzene (2.7)*2 Xylene (6.1) Toluene (38.5)
Shields *et al.*, (1996)	70 offices	United States	31 VOCs	Ethylbenzene (2.1)*3 n-undecane (10.7)
Weschler *et al.*, (1990)	4 office buildings	United States	36 VOCs	Toluene (14.5) *d*-limonene (39.6)

*1 Benzene, Toluene, Ethylbenzene, Xylene.
*2 Median concentrations reported.
*3 Geometric means reported.

In this experiment, two different types of passive badges, 3M and SKC, and active charcoal tubes were compared for blanks impurities. A GC-FID was used for sample analysis. In both types of badges impurities were observed in the chromatograms while active charcoal tubes had non what so ever.

Figures C-1 and C-2 illustrates the impurities observed in terms of chromatographic peaks. Based on the analytical system used, an FID response of less than 5000 was considered insignificant. For charcoal tubes, no peaks were reordered above the 5000 FID response limit, hence no data is shown. Sources of impurities in both passive badges could be attributed to the batch, manufacturing, handling and production processes.

Some impurities observed in the SKC blank badges were found to be from a component of the SKC badge itself. In each SKC sampling kit an O-ring is supplied by the manufacturer. The O-ring is used to seal the badge during solvent extraction. The solvent, CS_2, may have reacted with the O-ring polymer during extraction and hence producing the impurities. Upon further investigation it was concluded that the type of the O-ring supplied by SKC was made from a polymer that was not suitable for solvents such as CS_2. Once the O-ring was replaced with a Teflon-based O-ring, few impurities disappeared. To confirm this finding, both types of O-rings, the old and the new, were immersed into CS_2 and the solutions injected into the GC-FID. Chromatographic results mapped the source of the two impurities to the original SKC O-ring. Figure C.3 presents the results of the mapping. The alternative Teflon-based O-ring sample produced no single peak; hence no response is shown in the Figure. However, the sources of other peaks could not be identified. With the observed impurities and the limitations of air velocities, the use of passive badge sampling method was considered inappropriate for in-situ surface emission sampling.

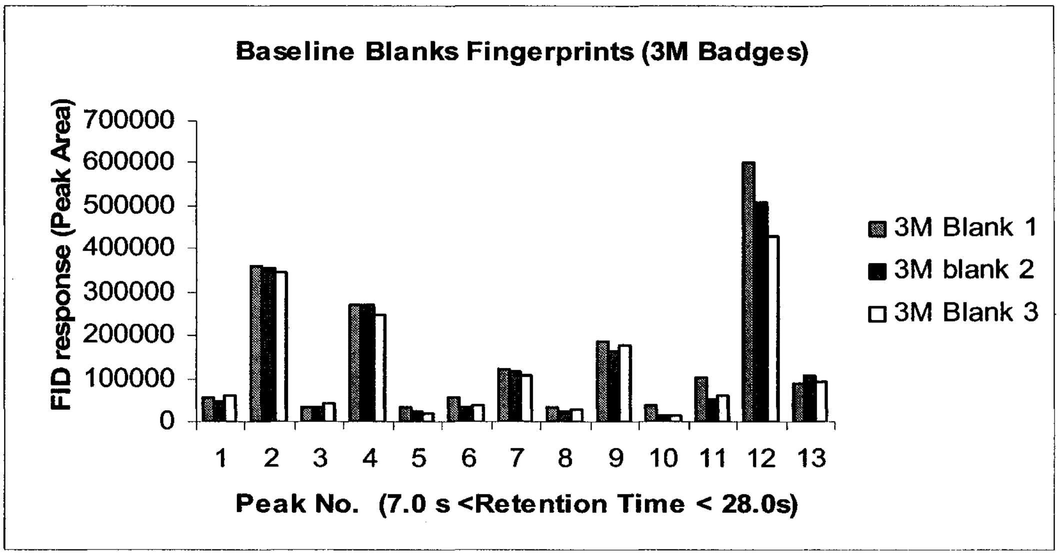

Figure C-1: 3M OVM 3500 blank impurities (FID response > 5000 is significant).

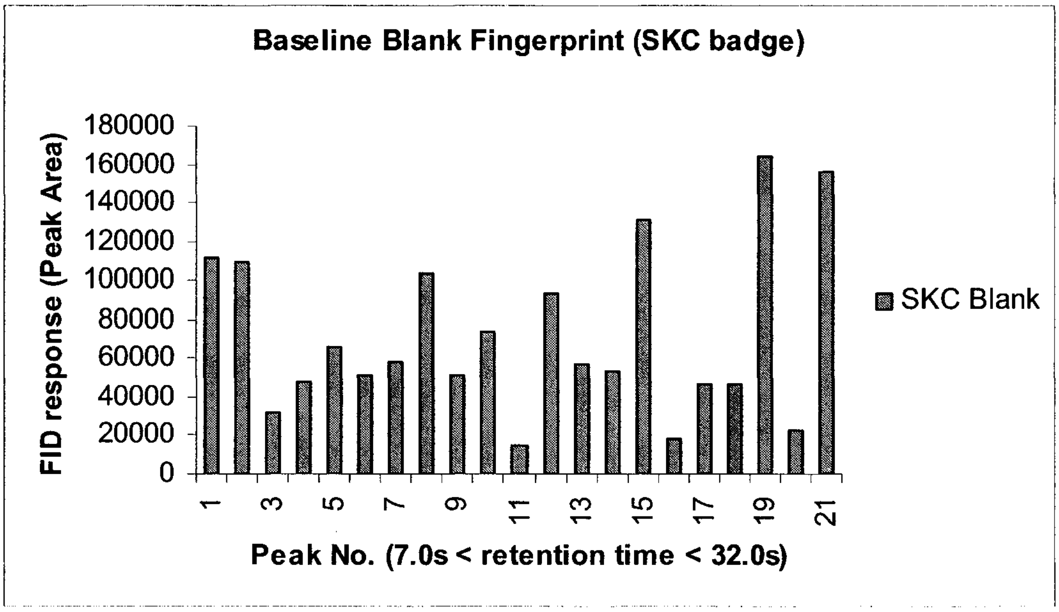

Figure C-2: SKC blank impurities (FID response > 5000 is significant).

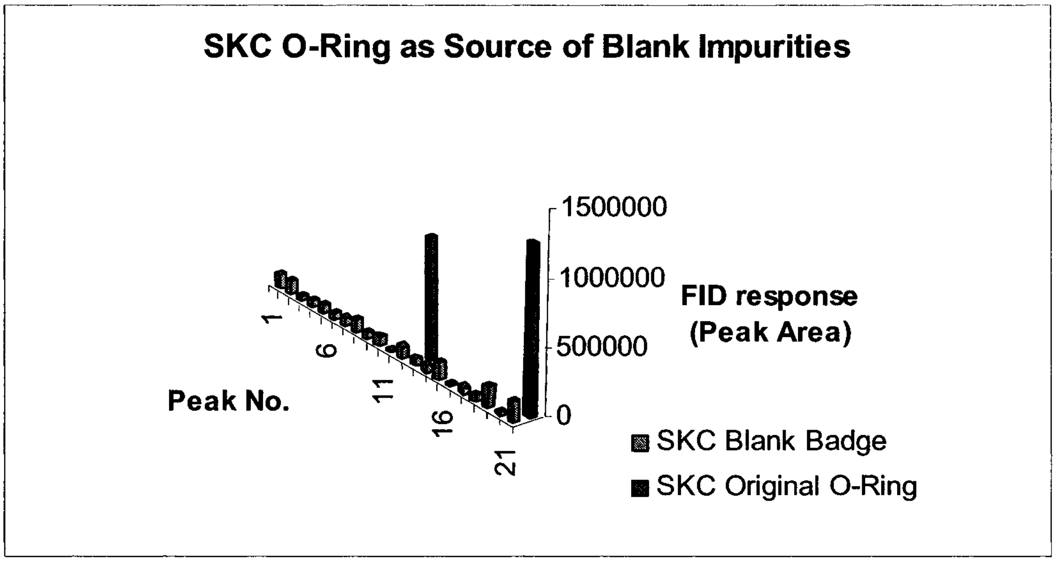

Figure C-3: SKC blank and O-Ring impurities.
(O-Ring impurities are peaks # 13 and 21, see Figure C-2)

Endnotes

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[1] Crump, DR 1999, 'Application of Diffusive Samplers', In: Salthammer, T (ed.), Organic Indoor Air Pollutants – Occurrence, Measurement, Evaluation, pp. 57-71.

[2] OSHA 1998, 'Method 111: Toluene', Analytical Methods Manual Vol. 4, U.S. Department of Labor, Occupational Safety and Health Administration; Directorate for Technical Support, Salt Lake Technical Center, Salt Lake City, UT, USA.

[3] Pozzoli, L & Cottica, D 1987, 'An Overview of the Effects of Temperature, Pressure, Humidity Storage and Face Velocity', In: Berlin, A et al. (eds.), Diffusive Sampling: An Alternative to Workplace Air Monitoring, Royal Society of Chemistry, London, pp. 119-130.

[4] Tompkins, FC & Goldsmith, RL 1977, 'A New Personal Dosimeter for the Monitoring of Industrial Pollutants', Am. Ind. Hyg. Assoc. J., Vol. 38, pp. 371-377.

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[6] Pozzoli, L & Cottica, D 1987, 'An Overview of the Effects of Temperature, Pressure, Humidity Storage and Face Velocity', In: Berlin, A et al. (eds.), Diffusive Sampling: An Alternative to Workplace Air Monitoring, Royal Society of Chemistry, London, pp. 119-130.

[7] Charron, KA et al. 1998, 'Field Validation for Passive Monitors for the Determination of Employee Exposure to Methylene Chloride in Pharmaceutical Production Facilities', American Industrial Hygiene Journal, Vol. 59, pp.353-358.

[8] Zhang, JS 1991, 'A Fundamental Study of Two-Dimensional Room Ventilation Flows under Isothermal and Non-isothermal Conditions', Ph.D. Thesis, University of Illinois at Urbana-Champaign, USA.

[9] OSHA 1998, 'Method 111: Toluene', Analytical Methods Manual Vol. 4, U.S. Department of Labor, Occupational Safety and Health Administration; Directorate for Technical Support, Salt Lake Technical Center, Salt Lake City, UT, USA.