The University of Manitoba

Active and Passive Sampling of Volatile Organic Compounds Using the Inside Needle Capillary Adsorption Trap (INCAT) Device

By

Shaheen Shojania

A Thesis submitted to the Faculty of Graduate Studies in partial fulfilment of

the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

April, 2000

Winnipeg, Manitoba

National Library of Canada
Acquisitions and Bibliographic Services
395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale du Canada
Acquisitions et services bibliographiques
395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-80025-3

Canada

THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

*****

COPYRIGHT PERMISSION PAGE

Active and Passive Sampling of Volatile Organic Compounds Using the Inside Needle Capillary Adsorption Trap (INCAT) Device

BY

Shaheen Shojania

A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of Manitoba in partial fulfillment of the requirements of the degree of

Master of Science

SHAHEEN SHOJANIA © 2000

Permission has been granted to the Library of The University of Manitoba to lend or sell copies of this thesis/practicum, to the National Library of Canada to microfilm this thesis/practicum and to lend or sell copies of the film, and to Dissertations Abstracts International to publish an abstract of this thesis/practicum.

The author reserves other publication rights, and neither this thesis/practicum nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

For my family

and in memory of my grandfather,

Dr. Ali Gharib.

Acknowledgements

Foremost, I would like to thank my supervisor, Dr. Art Chow, for his patience and guidance throughout my graduate studies. I gratefully acknowledge R. Oleschuk, M. E. McComb, E. Geller, and H. D. Gesser for developing the original colloidal graphite INCAT device, abandoning it for other research interests, and allowing me to pick up where they left off. I would like to express gratitude to C. Morrison and P. Marvroudis for their preliminary work on the sampling of BTEX compounds using activated carbon cloth and setting up the environmental test chamber; E. Smirnova for the use of the Varian GC; W. Buchannon for technical support in GC-MS; and K. J. Keen, H. Perreault and K. Lalbiharie, for their helpful advice.

I would like to thank L. Morton and D. Quin (RMC Kingston, ON) for providing the carbon black Saran from PVDC; J. Chatten (Columbian Chemical Co.) and K. Robinson (Mega-Carbon Co.) for information on activated carbons; K. G. Swan (Office of the Fire Commissioner for the Province of Manitoba) and W. Greenly (RCMP Forensic Laboratory Service in Winnipeg) for their time, knowledge and advice in studying arson debris; and R.Flynn and T. Spyracopoulos (School of Art, University of Manitoba) for providing and operating the kiln used in the arson study.

I would like to acknowledge the Sustainable Development Innovations Fund of the Government of Manitoba, the University of Manitoba, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. Also, I would like to acknowledge A. S. Secco for helping me obtain financial support, advice, encouragement, and endless entertainment.

Table of Contents

LIST OF ABREVIATIONS iii

LIST OF TABLES vii

LIST OF FIGURES ix

Abstract xiii

CHAPTER 1 *Background* 14

Volatile Organic Compounds in the Environment and Workplace 14
Solid Phase Extraction 19
Carbon Adsorbents 26
Analysis of Fire Debris 29
The Inside Needle Capillary Adsorption Trap 38
References 40

CHAPTER 2 *Active and Passive Sampling of BTEX Compounds with the Colloidal Graphite INCAT Device* 46

Introduction 46
Experimental 48
Active Sampling with the INCAT Device 52
Passive Sampling with the INCAT Device 53
Results 54
Active Sampling with the INCAT Device 54
Passive Sampling With The INCAT Device 60
Discussion 62
Conclusions 71

CHAPTER 3 *Qualitative Analysis of Complex Mixtures of VOCs Using the Inside Needle Capillary Adsorption Trap* **78**

Introduction **78**
Experimental **82**
Results and Discussion **87**
Conclusion **103**

CHAPTER 4 *Qualitative Analysis of Simulated Arson Debris Using an Activated Carbon INCAT Device* **107**

Introduction **107**
Experimental **112**
Results and Discussion **117**
Conclusion **129**

CHAPTER 5 *Active and Passive Sampling of VOCs in Weathered Gasoline Using the RVC-INCAT Device* **134**

Introduction **134**
Experimental **138**
Results and Discussion **142**
Conclusion **149**

CHAPTER 6 *Conclusions and Future Work with the INCAT Device* **152**

LIST OF ABREVIATIONS

ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
atten	attentuation
BET	Brunauer, Emmett, and Teller
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CCOHS	Canadian Centre for Occupational Health and Safety
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CL	ceiling limit
CLS	closed-loop-stripping
DHHS	Department of Health and Human Services
EPA	Environmental Protection Agency
FID	flame ionization detector
FRT	fire retardant treatment
GC	gas chromatograph, or gas chromatography
GC-MS	gas chromatography coupled with mass spectrometry

HAPs	hazardous air pollutants
HPD	heavy petroleum distillates
HPLC	high performance liquid chromatography
HS	headspace
HS-GC	headspace gas chromatography
i.d.	inner diameter
IDLH	immediately dangerous to life or health
INCAT	inside needle capillary adsorption trap
LC	liquid chromatography
LPD	light petroleum distillates
MAC	maximum acceptable concentration
MPD	medium petroleum distillates
MRL	minimum risk level
NIOSH	National Institute for Occupational Safety and Health
NPL	National Priorities List
o.d.	outer diameter
OFC	Office of the Fire Commissioner
OSHA	Occupational Safety and Heath Administration

OTGC	open tubular gas chromatography
P&T	purge-and-trap
PAS	personal air sampler
ppb	parts per billion ($1:10^9$)
PPI	pores per linear inch
ppm	parts per million ($1:10^6$)
PTFE	polytetrafluoroethylene
PVDC	polyvinylidene chloride
r^2	coefficient of determination
RCMP	Royal Canadian Mounted Police
R_f	response factor
RSD	elative standard deviation
R_t	retention time
RVC	reticulated vitreous carbon
SATP	standard ambient temperature and pressure
SPE	solid phase extraction
SPME	solid-phase microextraction

STEL	short term exposure limit
SVOCs	semi-volatile organic compounds
TRI	Toxic Release Inventory
TWA	total weighted average
VOCs	volatile organic compound

LIST OF TABLES

TABLE 1. Some exposure limits for benzene **17**

TABLE 2. Molecular weights (MW), order of elution, response factors (R_f), BTEX concentrations in the 70 L environmental test chamber, and internal standard used with the extraction solvent for the activated carbon SPE tube. **50**

TABLE 3. Mean amounts of BTEX compounds adsorbed, percent RSD from the mean, and the proportion adsorbed relative to the amount present, determined by repeated measurements (n=10) of an actively sampled 5 mL volume using a 26 gauge INCAT device. **55**

TABLE 4. Mean absolute passive rates of adsorption and percent RSD from the mean, for 22 gauge INCAT devices (n=3). **60**

TABLE 5. Initial slopes and absolute rates of adsorption for the 26 gauge INCAT device in active sampling of the BTEX compounds (based of the initial 5 data points in the 0 to 8 mL range). **64**

TABLE 6. Initial absolute rates of adsorption for the 26 gauge INCAT device in passive sampling of the BTEX compounds (based on the initial 6 data points in the 0 to 5.75 hour range). **66**

TABLE 7. Classification scheme for accelerants and the samples studied. **84**

TABLE 8. Means, standard deviations, and percent RSD of the response factors (R_f) and the retention times (R_t) from n=4 liquid injections of the BTEX standard. **86**

TABLE 9. Means, standard deviations, and percent RSD of the retention times and peak areas of the BTEX compounds

from n=4 trials of active sampling of 0.10 mL of the HS above Shell-Bronze gasoline. **89**

TABLE 10. Province of Manitoba 1993-1997 summary statistics for fires due to arson or suspicious origin. **107**

TABLE 11. Manitoba OFC fire investigations by cause from 1997. **109**

TABLE 12. Amount of weathering of the arson accelerants used for the analysis of simulated fire debris. **113**

TABLE 13. Means, standard deviations, and RSD values of fourteen distinct peaks in the GC profiles from active sampling of the static headspace above 88% weathered Shell-Bronze gasoline with the RVC-INCAT. **145**

TABLE 14. Coefficients of determination (r^2) for linear fits of the fourteen distinct peaks in the active and passive sampling profiles of 88% weathered Shell-Bronze gasoline with the RVC-INCAT device. **147**

LIST OF FIGURES

FIGURE 1. Schematic representation of an INCAT device **38**
FIGURE 2. The amounts of BTEX compounds determined by active sampling with a 26 gauge colloidal graphite INCAT device. **56**
FIGURE 3. (a) The amount of benzene determined by active sampling with a 26 gauge colloidal graphite INCAT device in the absence of all other BTEX compounds; (b) the Langmuir fit for benzene actively sampled in the absence of all other BTEX compounds. **57**
FIGURE 4. The amount of benzene and toluene determined from active sampling with a 26 gauge colloidal graphite INCAT device in the absence of heavier BTEX compounds. **59**
FIGURE 5. The amounts of BTEX compounds determined from passive sampling with a 26 gauge colloidal graphite INCAT device over a range of exposure times. **61**
FIGURE 6. The total amount of BTEX compounds determined from active sampling with a 26 gauge colloidal graphite INCAT device. **62**
FIGURE 7. The total amount of BTEX compounds determined from passive sampling with a 26 gauge colloidal graphite INCAT device. **67**
FIGURE 8. Plot of the effective initial adsorption rates for passive sampling against active sampling, of the BTEX compounds with a 26 gauge colloidal graphite INCAT device. **69**
FIGURE 9. Comparison of the gas chromatograms obtained from sampling a mixture of BTEX compounds (16.7% v/v of each) by: (a) direct liquid sampling (0.10 μL); (b) a Raven-15 coated INCAT (0.10 mL of HS); (c) a Saran

coated INCAT (0.10 mL of HS); and (d) a Super Sorb coated INCAT (0.10 mL of HS). **90**

FIGURE 10. GC profiles illustrating the reproducibility in HS sampling (0.10 mL) of Shell-Bronze gasoline with a Raven-15 coated INCAT device (attenuation 4). BTEX compounds correspond to the retention times and area measurements shown in Table 9 on page 89. **91**

FIGURE 11. Comparison between the GC profiles of the class 0 accelerant camp fuel, obtained from a direct liquid sample (0.10 µL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL). **93**

FIGURE 12. Comparison between the GC profiles of the class 1 accelerant Ronsonol pocket lighter fluid, obtained from a direct liquid sample (0.10 µL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL). **93**

FIGURE 13. Comparison between the GC profiles of the class 2 accelerant gasoline, obtained from a direct liquid sample (0.10 µL) and a headspace sample using a Raven-15 coated INCAT device (0.10 mL), for: (a) Shell-Bronze (octane rating 87); (b) Shell-Silver (octane rating 89); and (c) Shell-Gold (octane rating 91). **95**

FIGURE 14. Comparison between the GC profiles of the class 3 accelerant paint thinner, obtained from a direct liquid sample (0.10 mL) and a HS sample using a Raven-15 coated INCAT device (0.10 mL), for: (a) Varsol®, and (b) a generic brand of paint thinner. **96**

FIGURE 15. Comparison between the GC profiles of the class 4 accelerant kerosene, obtained from a direct liquid sample (0.10 µL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL). **97**

FIGURE 16. Comparison between the GC profiles of the class 5 accelerant diesel fuel, obtained from a direct liquid sample (0.10 µL), and a headspace sample using a Raven-15 coated INCAT device (0.10 mL). **98**

FIGURE 17. Bar chart comparison of the absolute peak areas of BTEX compounds observed from static HS sampling (0.10 mL with Raven-15 INCAT device) of the mixtures from the six classes of arson accelerants. **99**

FIGURE 18. HS-GC profiles from active sampling 10.0 mL of the static HS above: (a) an aqueous solution saturated with Shell-Bronze gasoline, attenuation 3; (b) a 1:1000 dilution of the aqueous solution saturated with Shell-Bronze gasoline, attenuation 3; (c) the 1:1000 diluted solution at attenuation 1; and (d) a blank INCAT at attenuation 1. **101**

FIGURE 19. GC profiles for comparison of (a) 88% weathered Shell-bronze grade gasoline sampled from the HS of fire debris; (b) the HS of burnt wood with no accelerant present; (c) the HS of unburnt wood with no accelerant present; and (d) a blank INCAT (no sample). All chromatograms are shown at attenuation 3 and were all obtained from the same Raven-15 INCAT device. **118**

FIGURE 20. Comparison between the HS-GC profiles of the 89% weathered class 0 accelerant, camp fuel, sampled with a Raven-15 INCAT device (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 5). **120**

FIGURE 21. Comparison between the HS-GC profiles of the 90% weathered class 1 accelerant, Ronsonol pocket lighter fluid, sampled with a Raven-15 INCAT device (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 23). **121**

FIGURE 22. Comparisons between the HS-GC profiles of three different octane grades of Shell gasoline (class 2 accelerants) from sampling (a) in the presence of burnt wood, and (b) in the absence of any fire debris. **123**

FIGURE 23. Comparisons between HS-GC profiles form two 90% weathered class 3 accelerants, Varsol® and a generic

paint thinner, sampled (a) in the presence of fire debris, and (b) in the absence of fire debris. **124**

FIGURE 24. Comparison between the HS-GC profiles of the class 4 accelerant kerosene, sampled (a) in the presence of fire debris (attenuation 3), and (b) in the absence of fire debris (attenuation 15). **125**

FIGURE 25. Comparison of the HS-GC profiles of the 91% weathered class 5 accelerant diesel fuel from sampling (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 3). **127**

FIGURE 26. Scanning electron microscope image of RVC foam material. **136**

FIGURE 27. Pattern reproducibility trials for the RVC-INCAT in active sampling of 88% weathered Shell-Bronze grade gasoline, along with a blank injection and blank sample profiles (all GC traces are shown at attenuation 16). **143**

FIGURE 28. Comparison of the HS-GC profiles of 88% weathered Shell-Bronze grade gasoline, from 15 minute passive exposure of RVC-INCAT, along with 10 mL active samples with RVC-INCAT, Raven-15 coated INCAT devices (all shown at attenuation 16). **144**

FIGURE 29. Scatterplot matrix of 14 distinct peaks in the active and passive sampling profiles of 88% weathered Shell-Bronze grade gasoline, using the RVC-INCAT device. **146**

Abstract

A new and simple method of solventless extraction of volatile organic compounds (VOCs) from air or headspace is presented. This sampling device has a carbon adsorbent contained inside a hollow stainless-steel capillary, and is called the inside needle capillary adsorption trap (INCAT). The carbon adsorbent may be in the form of a coating along the interior wall of the capillary, or as a carbonaceous foam insert. Sampling of VOCs with the INCAT device can be done actively by drawing a volume of air or headspace through the device, or passively by letting the vapour slowly diffuse into the device. In either active or passive sampling modes, the volatile analytes are adsorbed and concentrated onto the surface of the carbon inside the sampling device. The adsorbed compounds concentrated inside the device can then be thermally desorbed in the heated injection port of a gas chromatograph for separation and analysis.

To demonstrate some of the features of the INCAT sampling method, the active and passive sampling of air from an environmental chamber doped with a class of VOCs, and the static headspace complex mixtures of petroleum distillates are presented.

CHAPTER 1 *Background*

1.1 Volatile Organic Compounds in the Environment and Workplace

The development of analytical methods for the investigation of the release of hazardous substances into indoor air and the environment for public health assessments is of increasing importance. The impact of exposure to hazardous substances, in terms of human health, has created the need for determining the sources of exposure (i.e., drinking water, air, soil, food sources, etc.). The sheer number of analyses required for environmental/public health assessments implies that there is an increasing need for the development of simple and economical techniques for such investigations.

Typical air pollutants are volatile organic compounds (VOCs), sulfur dioxide, nitrogen oxides, carbon monoxide, hydrogen sulfide, and particulate matter (dispersed solids or liquids ranging in size from 0.0002 to 500 μm in diameter) [1]. Hazardous air pollutants (HAPs), or air toxics, refer to atmospheric compounds that have potentially toxic effects on both humans and the environment itself [1, 2]. In addition to the air pollutants, there are many toxic, but less volatile, compounds that are found in water and soil. As such, these compounds threaten human health via drinking water or vegetation [3].

Hydrocarbon compounds dominate most lists of hazardous substances. The 1999 National Priority List (NPL) that is distributed by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) enumerates 275 substances with known or suspected toxic effects [3] that pose the most significant potential threat to human health. Of these 275 hazardous substances, 169 are organic compounds or mixtures of organics. This list is based on the frequency of occurrence, toxicity, and potential for human exposure. Since many of these hydrocarbons are VOCs, in that they have vapour pressures greater than 0.1 mm Hg at standard temperature [4], the risk of airborne exposure is heightened. The 1991, U.S. emissions of VOCs were estimated at 16.88 million tonnes from the typical sources (i.e., transportation, fuel combustion, industrial processes, solid waste, etc.) [5, 6]. It should be noted that this estimate does not account for the release of VOCs due

to accidental sources.

Exposure to toxic substances in the workplace is ever increasing. The dependence of modern society on synthetic products has led to an increase in the numbers of possible compounds that an individual may be regularly exposed to by way of occupation, or release to the environment. This type of exposure is obviously enhanced for individuals involved in manufacturing or processing of hazardous substances, but due to isolation of indoor air and poor cleaning or ventilating of buildings, many individuals can be exposed to toxins, even though they are not in the immediate vicinity of the processing. Regulatory organizations such as the Canadian Centre for Occupational Health and Safety (CCOHS) and the National Institute for Occupational Safety and Health (NIOSH) in the United States, have set exposure limits for many identified toxic substances that are different from those set by environmental regulatory agencies. The difference in these limits lies in the fact that environmental exposure (airborne) are based on the immediate exposure to HAPs, as opposed to the long term exposure effects from lower levels of hazardous substances on an hourly or daily basis for many years.

For example, consider the VOC benzene, which is currently ranked fifth on the 1999 CERCLA NPL. The 1986 estimate for the annual production of benzene was 700 kilotonnes in Canada [7], and 5,300 kilotonnes in the United States [8]. Benzene has been labelled as a

known human *medium carcinogenic hazard* [9]; individuals who were occupationally exposed to benzene were observed to have an increased incidence of leukemia [7-9]. Short term exposures to benzene may result in drowsiness, dizziness, unconsciousness, and in convulsions or death if the exposure levels are very high (in the part-per-thousand range) [7, 9]. Chronic effects from exposure to low levels of benzene, observed in individuals with occupational exposure, showed a variety of haematological disorders (e.g., impaired immune response, and decrease in platelet count) [7]. For these reasons, recommendations for allowable levels of exposure to benzene have been imposed by the U.S. Environmental Protection Agency (EPA) for atmospheric and water levels, and NIOSH for indoor air, that have also been adopted by Health Canada. Table 1 on page 18, lists some of the current exposure limits that have been adopted by Health Canada and CCOHS, although each province may have its own permissible levels and exceptions.

TABLE 1. Some exposure limits for benzene

Concentration Limits	Regulated Levels	Regulatory Agency Source and Reference
maximum acceptable concentration in drinking water (MAC)	5 μg/L	EPA [10]
total weighted average for a 8 hr work period (TWA)	0.32 mg/m^3 (0.1 ppm)	NIOSH [11]
short-term exposure limit (STEL) for 15 min	3.2 mg/m^3 (1 ppm)	NIOSH [11]
ceiling limit (CL) not to be exceeded for an instant	80 mg/m^3 (25 ppm)	OSHA[12, 13]
odour threshold (in air)	4.9 mg/m^3 (1.5 ppm)	EPA [8]
odour threshold (in water)	2.0 mg/L	EPA [8]
immediately dangerous to life or health (IDLH)	1.6 g/m^3 (500 ppm)	NIOSH [11]

Benzene is present in gasoline at approximate levels of 1 to 2%, and it is released to the air primarily from fumes and exhaust connected with its use in gasoline [7]. Other sources of atmospheric release are from production fumes and industrial use. Additional sources of benzene in the environment are from discharges into water from industrial effluents and losses during spills. In the United States, the Toxic Release Inventory (TRI) determined that during the period of 1987 to 1992, releases of benzene to water and land directly totalled more than 900 tonnes [10]. These releases resulted primarily from petroleum refining industries, with the

greatest releases occurring in Texas.

Humans are thus exposed to hazardous VOCs via the environment, workplace, or consumer products. Consequentially, there is a need for detecting and monitoring these compounds to determine the extent of human exposure from these sources. In addition to benzene, many VOCs have severe health effects depending on the duration and levels of exposure. There is an abundance of human evidence, as well as supporting animal studies, that have shown some of these VOCs to have carcinogenic or mutagenic effects. Some VOCs will harm the immune system while others have adverse effects on tissue development [1, 2, 5, 6]. Because VOCs enter the body easily through the air, and thus pose health risks from long term exposure to even low levels (as low as 0.05 ppm) [1], simple methods of determining VOCs in ambient and indoor air are needed.

1.2 Solid Phase Extraction

Solid Phase Extraction (SPE), like any extraction method, involves the partitioning of analyte between two immiscible phases. In SPE, the immiscible phases are either solid-liquid or solid-gas, and the basis of the extraction is analogous to the principles governing liquid chromatography (LC) and gas chromatography (GC), respectively [14]. A sample of liquid or

gas is passed across or through a solid phase where the analytes distribute at the surface (interface) via physical or chemical interactions. The distribution (partitioning) of the analytes is based on varying affinities that each compound has for the solid phase material [15]. This aspect of differential affinity on the solid support allows SPE to be used as preparative method for sample 'clean-up' prior to analysis and/or concentrating the analytes for quantitative measurements. As such, SPE is a useful method for sample preparation for both GC and HPLC analysis.

The advantage of using a solid phase for the extraction procedure over conventional liquid extraction is that a guaranteed phase separation exists, and a significant reduction in the amount of solvent used. Retrieval of analytes from the solid phase can be achieved with very little solvent by choosing a solvent for which the analytes have a very high affinity. For example, in the extraction of organic pollutants in drinking water, the aqueous sample is passed through an SPE column or cartridge, and the analytes that are concentrated on the solid phase are then extracted using a small amount of organic solvent. These columns or cartridges make it very simple to collect field samples and then transport the solid form to a laboratory for analysis.

The most common mechanism employed in SPE is adsorption. There are two types of adsorption phenomena: *physical adsorption* (physisorption) and *chemical adsorption*

(chemisorption). Physical adsorption involves the same physical intermolecular forces at the interface that are involved in cohesion. These forces are essentially the Van der Waals forces that operate in any state. The Van der Waals interactions are electrostatic in nature and involve three different effects: *Keesom's orientation* effect, *Debye's induction* effect and the *London dispersion* effect [16]. The net effect of these forces is relatively weak (heat evolved is usually less than 20 kJ/mol of adsorbate) [17]. As a result, these interactions will occur readily as the adsorbate (analyte) comes into contact with the surface of the adsorbent. There may still be migration of the adsorbate molecules over the surface (into pores of the adsorbent), but the molecule is essentially removed from its original phase (liquid or gaseous) upon contact until equilibrium is reached. Hydrogen bonds are a special case these types of physical interactions. If present, the hydrogen bond will dominate the Van der Waals interactions (heat evolved is approximately 20 kJ/mol of adsorbate).

Chemical adsorptive processes involve covalent interactions between the adsorbate and adsorbent. Thus, the energy of the interaction is comparable to a chemical bond (heat evolved is of the order of 100 to 500 kJ/mol of adsorbate) [17]. The chemisorption process requires activation energy, and therefore occurs less readily than physisorption; it is often referred to as *activated adsorption* [17]. The Langmuir theory of adsorptive processes indicates that the molecules adsorbed on the surface will form a monolayer until the surface is

covered (saturation). Once the surface is covered, the chemisorptive process essentially stops but physisorption can continue to form additional layers on the existing chemisorbed layer without the strong covalent interaction between the surface and the first layer [16, 17].

Most types of SPE methods involve only physical adsorption since it allows analytes to be readily adsorbed and desorbed for analysis following the extraction. In some cases, however, where the removal of the species is important for purification or 'clean-up' purposes in sample preparation or waste removal, the covalent interactions are more desirable. However, for the most part, it is more economic and practical to use SPE materials that can be recycled so the weaker physical interactions are preferred.

The solid phase may be in the form of a membrane, foam, packed particles or fine fibrous mesh. Many of these types of materials require a wetting step in order to increase the interactions between active centres of the solid phase. Some common, commercially available materials in the form of prepacked columns and cartridges for SPE [18] are listed below:

- polymers and/or copolymers of styrene / divinylbenzene;
- porous polymers (e.g., GC column packing materials such as Tenax™ or Porapack™ [14]);
- acrylic ester polymers; and
- octyl (C_8) and octadecyl (C_{18}) reversed-phase liquid chromatographic packing

materials.

Disks or membranes of octyl or octadecyl-bonded silica particles embedded in a network of PTFE (polytetrafluoroethylene or Teflon™) fibrils have become practical alternatives to the use of columns and cartridges [18]. Both the disks and membranes have been found to have nearly the same reliability as EPA Method 525, with a dramatic reduction in extraction time [18, 19].

In the analysis of organic pollutants, it is often effective to restrict the sampling of the analytes to solid-gas extraction. This becomes particularly important in the analysis of VOCs and semi-volatile organic compounds (SVOCs), which can be extracted quite easily from the static headspace of a solid or liquid sample [14, 15, 21]. Headspace (HS) sampling is a useful step in reducing the interferences caused by complicated sample matrices. In addition, the analytes of interest may be present in relatively small amounts, and therefore obscured by other more abundant species in chromatographic analysis (this is particularly important in the analysis of volatile components in food and petroleum industries).

The extraction of VOCs in aqueous samples is normally done by static or dynamic headspace methods [21]. An analyte will partition between the aqueous and vapor phases to reach an equilibrium concentration in the static headspace above the liquid sample. Direct sampling of the VOCs in the absence of other compounds can then be achieved by sampling

the static headspace, rather than the aqueous mixture [21]. Thus, a portion of the separation process is achieved by sampling the headspace rather than the aqueous mixture.

Conventional HS-GC involves the injection of a volume of the static headspace directly into the GC instrument, or incorporation of the dynamic sampling methods of purge and trap (P&T) and closed loop stripping (CLS) [15]. The dynamic methods actively remove the analyte from the liquid phase and usually involve cryogenic focusing of large volumes of the headspace onto the GC column [14, 15, 21]. However, by concentrating the analytes in the static or dynamic headspace onto a solid phase, one can easily improve the sensitivity of the conventional HS-GC technique.

The method of solid-phase microextraction (SPME) [22-26] has been shown to be a useful method of sampling VOCs in the headspace of aqueous samples. In SPME, a fused silica fibre coated with an adsorbing material (e.g., poly(dimethylsiloxane)) is introduced to the headspace of an aqueous sample. The VOCs in the headspace, which are sorbed to the fibre (compounds may be both adsorbed and absorbed), are then thermally desorbed upon injection into a GC or GC-MS instrument for analysis. The SPME method has all the same advantages as conventional SPE methods with the added benefit that it is a solventless extraction.

The SPME method, like standard static HS analysis, is an equilibrium sampling

method. The VOCs that are distributed in the static headspace will then partition between the headspace and the sorbing coating of the SPME fibre. The equilibrium amount of analyte sorbed is directly proportional to its concentration in the sample and is found by the relation:

$$n = \frac{K_{fs} V_f C_o V_s}{K_{fs} V_f + V_s} \qquad \text{(EQ. 1)}$$

Where n is the mass of the sorbed analyte, V_f is the volume of the sorbent on the fiber, V_s the volume of the sample, K_{fs} is the partition (or distribution) coefficient between the sorbent and the sample matrix, and C_o is the initial concentration of the analyte in the sample [22]. In cases where $V_s >> K_{fs} V_f$, the relation in (EQ. 1) is approximated by:

$$n = K_{fs} V_f C_o \qquad \text{(EQ. 2)}$$

The implication of equation (2) is that there is no relation to the sample volume in determining the amount of the analyte. Thus, the SPME method is suited for field testing since the fiber could be used to sample the headspace of a large sample volume, as well as directly inserted into the sample matrix (e.g., well, lake, etc.). However, the amount of time for the fiber to equilibrate with the matrix (or headspace) will be highly variable, and primarily the result of mass transport of the analytes from matrix to the sorbent [26].

1.3 Carbon Adsorbents

The use of carbon as an adsorbent began in the latter part of the 18th century, although there is also mention of carbon being used medicinally in Egypt around 1550 B.C. [27]. Charcoal was reported to have been useful as a decolourising agent for many liquids (c.1785), and in the treatment of gangrenous ulcers (c.1793) for the removal of bad odours [27]. Although there were many efforts to try to incorporate charcoal in the processing of cane and beet sugar in late 19th and early part of the 20th century [16], it was not until 1915, that the usefulness of carbon as an adsorbent would truly be realized. In April of 1915, during World War I, the German army began releasing chlorine gas at the front, and the results were devastating to those lying helpless in the trenches [27]. However, since the German army themselves had no defence against the gas, they moved toward other methods of gas warfare. While Germany researched more efficient means of employing toxic vapours in warfare, the Allied Forces were able to design protective gas masks which used activated carbon to remove the toxic vapours. The efforts to market activated carbon for the sugar industry had allowed for carbon to be commercially available, and provided sufficient industrial support needed for production of new activated carbon adsorbents for gas masks [16, 28]. The fine powdered form of the early activated carbons (for removal of species from solution) was not

easily incorporated into gas masks, and as such, granular charcoal was developed for these purposes [28].

Following its application in the manufacture of gas masks during the war, rapid growth in the production of carbon adsorbents began for a wide range of application. The application to air purification was a direct consequence of the successful use of carbon in gas masks. A 1.3 cm bed of activated carbon will remove approximately 95% of odorous pollutants, including cigarette smoke from air passed across it at velocities of 0.25 m/s [28]. This efficiency, coupled with the vast number of now commercially available forms of activated carbon, has allowed for the purification of air in industrial facilities, and the reduction of many organic HAP emissions to the environment.

Activation of an organic starting material can be achieved by two approaches: chemical activation or physical activation. Chemical activation can result in a porous carbon in a single step process by treating the initial organic material with activating chemicals (e.g., zinc chloride or phosphoric acid). The chemical treatment is then followed by heating in an inert atmosphere at 600-800°C. The resulting product is washed with water or acid and dried, to yield an activated carbon material with high internal surface area.

Physical activation first involves carbonisation (pyrolysis) of a carbonaceous starting material. The pyrolysis of the starting material is done in the absence of air and other

compounds that might react with the products of pyrolysis. The resulting form is still considered to be inactive, but is referred to as 'carbonised'. Non-carbon elements are removed during pyrolytic degradation of the carbon-based starting material (wood or saw dust, coal, peat, etc.). The carbonised material is then 'activated' with steam or carbon dioxide as the material is further heated to temperatures ranging from 700-1100°C [27]. Products of chemical activation may also be further activated with steam or carbon dioxide to yield special properties on the activated product. However, the steam or carbon dioxide reaction must be performed on a material that is essentially only carbon — explaining the necessity of the initial step of carbonisation in the physical activation method.

When the carbonised material is activated by reaction with steam, carbon is removed ($C + H_2O \rightarrow CO + H_2$), which makes the internal pore structure of the amorphous carbonised material more accessible [29]. The steam or carbon dioxide treatment forms new pores by the removal of non-organised carbon, and thereby develops the macroporous structure. Further steam treatments will widen existing pores, or form new larger pores, by burn-out of walls between adjacent micropores. In either activation process — physical or chemical — the resulting product is a carbonaceous material with high internal surface area, and hence an ideal adsorbent for a wide range of compounds.

It should be noted that in addition to many activated carbons being manufactured from naturally occurring organic material, many highly adsorbing carbons are produced from simple pyrolysis of synthetic polymers without activating chemicals. One such example of this type of activation is the activated carbon referred to as Saran™, which is produced by slow carbonisation of compressed polyvinylidene chloride (PVDC) [28]. The carbonisation of PVDC yields an activated material with uniform sized pores (12-15 Å) and a very high specific internal surface area (1000 m^2/g) — much higher than from most natural polymeric starting materials [27]. However, activated carbons of even higher internal surface area may also be achieved with the natural organic starting materials by repeated steam treatment reactions and higher temperatures [28].

1.4 Analysis of Fire Debris

Much like the need for simple and economical methods for the analysis of air and water for environmental/public health assessments, there is a necessity for similar methods for application in the analysis of fire debris. The analysis of fire debris is necessary in order to identify whether a fire was *incendiary* in origin (i.e., a fire, which by virtue of physical evidence or legal decisions, has been deemed to have been deliberately set [30], and thus been

the result of the criminal act of arson). The analysis of fire debris for arson accelerants has been, and continues to be, a major problem that forensic scientists face far too regularly. The essence of this problem results from the frequency of fires that are investigated, and compiling enough evidence to not only conclude that a fire was deliberately set, but that will lead to an arrest and conviction. Since the very nature of the crime of arson has a tendency to destroy much of the physical evidence, the task of scientifically confirming a fire to be incendiary, coupled with the numbers of fires that are of suspicious origin, lead to heavy burdens on the forensic laboratories in analysing fire debris with enough certainty to satisfy a court of law. Unfortunately, the odds seem to be in favour of the arsonist, if one considers that in the United States, less than 10% of arson cases result in arrests, and of those fires that are determined to be the due to arson, only 1% result in conviction [30]. Hence, there is a 99% chance of the arsonist getting away with the crime.

Part of the reason for the low percentage of arson investigations being cleared, and an even lower percentage resulting in conviction, is due to the lack of witnesses, and the type of physical evidence to the crime (if any). For this reason, forensic scientists have had to develop sensitive techniques for detecting the presence of arson accelerants in the debris from fires. Detection of the accelerant, in conjunction with other evidence, may then confirm the suspicions of the fire investigator that a fire was incendiary in origin based on observations of

the amount of damage, spread of the fire, burn patterns, and temperatures reached during the fire [31].

Incendiary fires are most often started by 'amateurs' who rely of the use of a flammable liquid accelerant. The more proficient arsonist — the professional 'torch' — will rely on solid fuels already present at the scene for simplicity, and to minimize being seen carrying or purchasing volatile chemicals [33]. In addition, fires by more efficient arsonists usually originate in areas where there is already an accumulation of combustible material, and near a means of accidental ignition (furnace, water heater, electrical appliances, etc.). The amateur, however, will rely on the use of an accelerant, and will more than likely use more than necessary. Fortunately, this overuse of the accelerant aids the forensic scientist when analysing the debris from the fire. Unless the fire results in the total destruction of the objective (structure, vehicle, etc.), there is a chance that some of the debris along the edges of the burn pattern, will retain a residual amount of the accelerant used to start the fire. Even if residual accelerant is present in only small quantities (a μL or less) in a given sample of debris, it may be possible to isolate a GC profile, which may in turn be compared with other physical evidence obtained by the fire investigators, to conclude the fire as incendiary.

Determining which debris is most likely to retain the residual accelerant is based on the investigators' experience, and practical guidelines in evidence collection. Some of the

suggested areas for sample collection are [34]:

- lower and insulated areas within the burn pattern;
- materials made from porous plastics or synthetic fibres;
- cloth, paper, and cardboard that had indirect contact with the burn pattern;
- inside seams, cracks and tears of flooring;
- the edges of the burn pattern; and
- floor drains and bases of load-bearing columns or walls.

The fire investigator will usually have an indication of whether or not an accelerant has been used to start a fire since VOC vapours burning above the liquid accelerant tend to leave distinctive burn patterns. These ignitable liquid related burn patterns are unlike burn patterns associated with other combustible materials (solid fuels) that are found in most structure fires (that are not within an industrial or commercial site). The burn patterns from an incendiary fire are more obvious to the investigator if the fire is extinguished relatively early. Other indicators of the use of an accelerant based on the observations during and following the fire are [34]:

- unnatural fire spread (fast and in a downward direction);
- rolling flames;
- bright yellow flames accompanied by black sooty smoke;

- flames seen burning directly from the floor;
- structural damage that is inconsistent with the *fire load* (the available materials for combustion in the absence of an accelerant);
- differences in the intensity of floor burning within the burn pattern, along with puddle or trail shapes to burn pattern (corresponding to the shape of the pouring pattern of a flammable liquid);
- the appearance of gaps between wood or vinyl flooring seams within the burn pattern due to burning of a flammable liquid that has seeped between the seams;
- unusual dispersion of light on the surface of the puddles of suppression water within the burn pattern;
- an increased amount of burn damage to the bottom of objects on the floor within the burn pattern (i.e., furniture legs, boxes, etc.);
- burn patterns beneath doors and floor mouldings;
- 'rundown' burn patterns on floor joists under loose flooring, seams, or mouldings;
- localized staining underneath carpet padding, or marks from an accelerant dissolving vinyl flooring adhesive, within the burn pattern;
- mottled staining to concrete floors;
- burned flooring underneath furniture or heavy appliances (which under normal

circumstances would be expected to protect the floor);

- floor-to-ceiling wall burn patterns;
- localised areas of walls, or other vertical surfaces with clean burn above floor burn pattern (resulting from intense heat due to combustion of a flammable liquid that burned away soot deposits);
- window glass that has melted with a surface clean of soot on the fire side;
- inverted cone burn pattern on vertical surfaces within the burn pattern; and
- fire damage with no clear point of origin.

Combustion of a fuel, in the solid or liquid state, actually takes place above the surface of the fuel. When the fuel in question is heated, components of the material, or products of pyrolysis, are released into the vapour phase. If these vapours reach suitable ratios in air, then it is possible for them to be ignited by either reaching the appropriate temperature for self ignition, or by an ignition source [35]. In any case, the vapours require a proper mixture with air in order to burn. Thus, if there is too much fuel in the vapour phase, the gases may be ignited, but the oxygen required for the vapours to burn would be depleted too quickly. As a result, the fire would be extinguished until more oxygen could be made available. If there is sufficient oxygen to sustain the combustion of the vapours from a liquid fuel, then the ambient temperature will be raised, and thereby heat surrounding solid materials to the point at which

vapours or pyrolysis products may also be released and ignited [36].

If an ignitable liquid has been used to start a fire, the most common of which are gasoline and kerosene, then between the time it takes to pour the liquid and the time to ignite the vapours, much of the liquid fuel may be absorbed by materials within the target location (i.e., the liquid accelerant could be absorbed by carpet, wood, paper, etc.) [33]. Even a stack of newspapers could have gasoline poured onto it and some of the gasoline would be absorbed into the centre of the stack and therefore not have a chance to be exposed to air, or as much heat as the surface accelerant [33]. Since the stack will burn from outside to in, there is a chance that once the fire is suppressed, there will be a sufficient amount of the accelerant that has been retained by the absorbing paper for analysis.

Since the exposure to heat, and differences in absorption and evaporation rate of the components of most ignitable petroleum distillates, the residual accelerant that has been retained by some of the fire debris is not likely to closely resemble the starting fuel. For this reason, comparison to similarly weathered accelerants is required in identification of the class of ignitable liquid used to start the fire. The most common approach to extraction of the accelerant is headspace sampling of the fire debris, followed by GC or GC-MS analysis of the extract. Other non-headspace methods have also been used for certain types of sample materials. Sampling methods employed in the analysis of fire debris are [37]:

- steam distillation;
- vacuum distillation;
- solvent extraction;
- charcoal sampling; and
- swept headspace.

Headspace sampling methods (either static or dynamic) are the least interfering with the fire debris, and the least limited. Distillation and solvent extraction methods are the classical approaches to the recovery of accelerant from fire debris, and as such, are rarely used in practice today [38]. The advances in SPE devices and adsorbing materials have allowed most methods of enriched headspace and adsorbent trapping to become the modern methods of choice [38]. Headspace sensitivity is improved whenever the amount of analyte mass in the vapour phase is increased. This increase in headspace analyte mass can be achieved by simple heating of the sample container and then actively withdrawing the static headspace through a SPE device. Trapping VOC analytes with a SPE adsorbent in dynamic methods (e.g., P&T) are also effective methods of improving headspace sensitivity. The most widely used SPE adsorbent for this purpose is activated carbon. Carbon tubes or wires have been used for some time, and have shown the most versatility in the extraction of residual accelerants from fire debris. The use of a wire that has been coated with activated charcoal, *charcoal sampling*, is a

passive adsorption technique in which the coated wire is inserted through a hole in the sample container (either metal cans or glass jars) and allowed to equilibrate with the headspace. This method is similar to the method of SPME, except that it does not use a coating on a thin glass fibre, and does not require a very expensive and elaborate holder for the wire. However, the wire which has the analytes adsorbed on its carbon surface does require a specialized pyrolysis, or thermal desorption device, in order to introduce the analytes to a GC instrument for analysis. Variations of this passive method have been modified to coating of glass or plastic beads or packing the charcoal into a tube. Regardless of the form of the carbon (coated or packed), the method requires at least 12 to 15 hours to equilibrate at room temperature, or 2 hours at 50-60°C, in order to equilibrate with the headspace [36].

The more common use of carbon in SPE of accelerants, is by charcoal tubes. Activated charcoal is packed into small glass tubes, which are then inserted into a small hole in the sample container. The heated container — usually raised to 90°C and packed 1/2 to 2/3 full of debris — is then actively sampled to withdraw all of the headspace from the container through the carbon tube. The carbon tube is then flushed with a small amount of solvent (0.5 mL of pentane, diethyl ether or carbon disulfide), and a small aliquot (0.5 μL) of this extract is then injected into the GC for analysis [36]. The resulting GC profiles can then be used for comparison to other similarly obtained reference accelerants. In many cases, GC alone is not

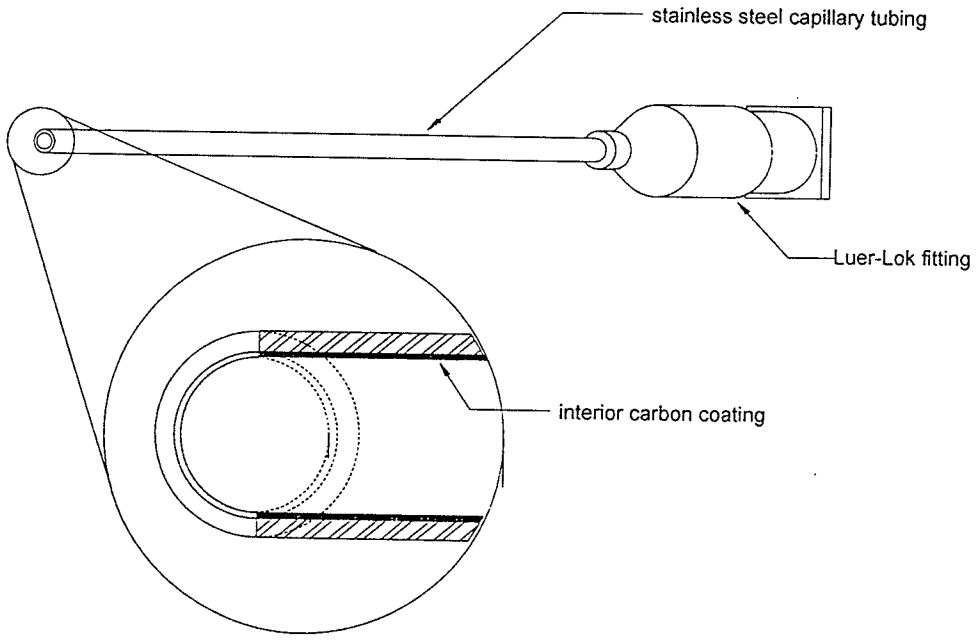
sufficient to identify the presence of an accelerant, and as such, GC-MS is required [39, 40]. The use of GC-MS is particularly important in the analysis of debris that is of synthetic origin (i.e., carpet padding, carpet, linoleum tile, etc.) which will also release some of the same VOCs that are present in accelerants, although in different ratios. These compounds must therefore be identified by GC-MS in order to determine whether their presence is consistent with the simple burning or heating of the material, or from the use of an accelerant.

1.5 The Inside Needle Capillary Adsorption Trap

A new method of solventless extraction of VOCs has been achieved using the *inside needle capillary adsorption trap* (INCAT) [41]. The INCAT device (Figure 1 on page 39) has an adsorbing carbon coating on the interior surface of a hollow stainless steel needle. Sampling can then be achieved by actively drawing a fixed volume of the gaseous mixture, or headspace of a solid or liquid sample, through the device via a syringe. For solid or liquid samples, analytes will partition between the solid or liquid, and vapour phases to reach an equilibrium concentration in the static headspace above sample. Direct sampling of the VOCs in the absence of the nonvolatile matrix can then be achieved by sampling the static headspace

rather than the solid or liquid mixture [20, 21]. The volatile analytes adsorbed and concentrated inside the device can then be thermally desorbed in the heated injection port of a GC for separation.

FIGURE 1. Schematic representation of an INCAT device



The passive sampling of VOCs in air can also be achieved by letting the vapour slowly diffuse into the INCAT device. Passive sampling of VOCs then allows for the determination of air contaminants at very low concentrations by simply extending the exposure time of the device to obtain an average concentration over the time exposed. A concentration profile of a

'sick' building may be achieved by the passive sampling method by simultaneously exposing the passive INCAT samplers at various locations within the building.

The thesis presented reports the use of the INCAT device in sampling VOCs in air and static headspace. Three main projects involving the INCAT device, as described, were undertaken:

- the active and passive sampling of the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) using colloidal graphite INCAT devices;
- the sampling of complex mixtures of VOCs using the improved, activated carbon INCAT device, for qualitative analysis; and
- the application of the INCAT to sampling fire debris.

In addition, a variation of the INCAT device, proposing a new direction for this sampling method is also introduced.

References

[1] L. W. Cantor, In *Environmental Engineer's Handbook*, 2nd Edition., D. H. F. Liu and B. G. Lipták eds., ch. 5.1, CRC Press LLC, Boca Raton (2000).

[2] *Agency for Toxic Substances and Disease Registry, Public Health Statement*, http://www.atsdr.cdc.gov/cx.html, ASTDR Science Corner (1989).

[3] *1999 CERCLA List of Priority Hazardous Substances*, http://www.atsdr.cdc.gov/99list.html, Agency for Toxic Substances and Disease Registry (2000).

[4] Hawley's Condensed Chemical Dictionary, 13th Edition, revised by R. J. Lewis Sr., John-Wiley and Sons, New York (1997).

[5] H. N. MacFarland, *Am, Ind. Assoc.*, **47**, 704 (1986).

[6] M. Tancrede, R. Nilson, L. Zeise, E. A. Crouch, *Atmos. Environ.*, **21**, 2187 (1987).

[7] Health Canada, *Guidelines for Canadian Drinking Water Quality*, http://www.hc-sc.gc.ca/ehp/ehd/bch/water_quality.htm (1999).

[8] U.S. National Library of Medicine, *Hazardous Substance Data Bank*, http://www.ccohs.ca/products/databases/samples/hsdb.html, Canadian Centre for Occupational Health and Safety (1998).

[9] *Health Effects Notebook for Hazardous Air Pollutants*, http://www.epa.gov/ttn/uatw/hapindex.html, Technology Transfer Network: Unified Air Pollutants Website, United States Environmental Protection Agency (1998).

[10] National Primary Drinking Water Regulations: Consumer Fact Sheeet, http://www.epa.gov/ogwdw000/dwh/c-voc/benzene.html, Office of Groundwater and Drinking Water, United States Environmental Protection Agency (1998).

[11] *Online NIOSH Pocket Guide to Chemical Hazards*, http://www.cdc.gov/niosh/npg/npgd0000.html, National Institute of Occupational Safety and Health (1999).

[12] ChemAdvisor® Inc., http://www.ccohs.ca/products/databases/samples/chemadvisor.html, Canadian Centre for Occupational Health and Safety (1999).

[13] D. H. F. Liu, In *Environmental Engineer's Handbook*, 2nd Edition., D. H. F. Liu and B. G. Lipták eds., ch. 5.20, CRC Press LLC, Boca Raton (2000).

[14] F. J. Debbrect, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 7, John-Wiley and Sons, New York (1995).

[15] J. M. Loeper, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 14, John-Wiley and Sons, New York (1995).

[16] M. Smìsek, and S. Cerný, *Active Carbon: Manufacture, Properties and Applications*, Elsevier, New York (1970).

[17] K. J. Laidler and J. H. Meiser, *Physical Chemistry*, 2nd Edition, Houghton Miflin Co., Boston (1995).

[18] J. A. Dean, *Analytical Chemistry Handbook*, McGraw-Hill, New York (1995).

[19] R. L. Grob, *Modern Practice of Gas Chromatography*, 3rd Edition, John Wiley and Sons, New York (1995).

[20] C. J. Koester and R. E. Clement, *Critical Reviews in Analytical Chemistry*, **24**(4), pp263-316 (1993).

[21] B. Kolb and L. S. Ettre, *Static Headspace Gas Chromatography: Theory and Practice*, ch. 7, Wiley-VCH, New York (1997).

[22] M. Chai C. L. Arthur, R. P. Belardi, K. F. Pratt and J. Pawliszyn, *Analyst*, **118** 1501 (1993).

[23] Z. Zhang and J. Pawliszyn, *Anal. Chem.*, **65**, 1843 (1993).

[24] M. Chai and J. Pawliszyn, *Environ. Sci. Tech.*, **22**, 693 (1995).

[25] P. A. Martos and J. Pawliszyn, *Anal. Chem.*, **69**, 206 (1997).

[26] Z. Zhang, M. J. Yang and J. Pawliszyn, *Anal. Chem.*, **66**, 844 (1994).

[27] J. W. Hassler, *Activated Carbon*, ch. 1, Leanoard Hill, London (1967).

[28] CRC Handbook of Tables for Applied Engineering Science, 2nd Edition, R. E. Bolz and G. L. Tuve eds, ch. 8, CRC Press, Cleaveland (1973).

[29] F. A. P. Maggs, In *Manufactured Carbon*, J. D. Pratt and T. F. West editors, ch. 4, Pergamon Press, London (1968).

[30] J. R. Hall, *The Truth About Arson*, at http://www.interfire.org/res_file/nfpaj_ar.htm, interFIRE Online (1998).

[31] G. E. Burnette Jr., *Anatomy of an Arson Case*, at http://www.interfire.org/res_file/arsnanat.htm, interFIRE online (1999).

[32] Exerpts from The Pocket Guide to Accelerant Evidence Collection, 2nd Ed., at http://www.interfire.org/res_file/aec.htm, interFIRE Online (1999).

[33] J. D. DeHaan, Kirk's Fire Investigation, 4th Ed., pp 405-411, Prentice-Hall (1997).

[34] NFPA 921Guide for Fire and Explosion Investigations, 1998 Edition, ch. 3, National Fire Protection Association, Quincy (1998).

[35] J. D. DeHaan, Kirk's Fire Investigation, 4th Ed., ch. 5, Prentice-Hall (1997).

[36] J. D. DeHaan, Kirk's Fire Investigation, 4th Ed., ch. 14 Prentice-Hall (1997).

[37] *The Lab Analysis*, In *Motive Means and Opportunity, A Guide to Fire Investigation*, American Re-Insurance Co., Claims Division, at http://www.interfire.org/res_file/mmo5a.htm (1996).

[38] Q. Ren; W. Bertsch, *J. Forensic Sci.*, **44**(3), 504 (1999).

[39] R. O. Keto, *J. Forensic Sci.*, **40**(3), 412 (1995).

[40] C. J. Lennard; V. T. Rochaix; P. Margot; K. Huber, *Science & Justice*, **35**(1), 19 (1995).

[41] M. E. McComb, R. D. Oleschuk, E. Giller and H. D. Gesser, *Talanta*, **44**, 2137 (1997).

CHAPTER 2 *Active and Passive Sampling of BTEX Compounds with the Colloidal Graphite INCAT Device*

2.1 Introduction

Evidence of human exposure to organic HAPs [1-3], especially to VOCs, indicates that new simple and economic sampling methods are needed to meet the demands of environmental and public health studies. Monitoring of these compounds is required for many occupational areas, as well as in the environment. Since human health is threatened by airborne VOCs, methods of extracting these compounds from air are needed.

The INCAT device, as described in Ch. 1.5, is a stainless-steel needle with an adsorbing layer of carbon on its interior surface. Although it had been previously demonstrated that the INCAT device is able to adsorb BTEX compounds (benzene, toluene,

ethylbenzene, and xylene) using colloidal graphite as the adsorbent [4], the reproducibility of the sampling technique was still in question. Moreover, the influence on the adsorption on colloidal graphite of other species in multicomponent systems, was yet to be determined. The preliminary study [4] essentially demonstrated that the INCAT device was able to sample VOCs, which could in turn be thermally desorbed in a heated injection port of a GC instrument for analysis. However, a more detailed study of the efficiency and reproducibility of sampling, in both active and passive modes, as well as reproducibility of making the devices, was needed.

This chapter reports the use of the colloidal graphite INCAT device in sampling BTEX compounds, as they represent an important class of organic HAPs. Sampling was performed actively for a fixed volume to determine the sampling reproducibility with the device, actively at varying volumes, and passively over varying exposure times to investigate the saturation effects with this type of carbon adsorbent. In addition, the rates of adsorption in both the active and passive modes of sampling were investigated. Quantitation of the INCAT results was based on comparison to measurements with actively sampled activated carbon SPE tubes.

2.2 Experimental

The INCAT devices used in this study were prepared from stainless steel capillary tubing (Small Parts Inc., Logansport, IN) to which a Luer-Lok was fitted. For these devices, the stainless steel capillaries were either 26 gauge (0.25 mm i.d., 0.46 mm o.d.), or 22 gauge (0.41 mm i.d., 0.71 mm o.d.). The entire length of the interior surface of the capillary was coated with a layer of colloidal graphite paint (SPI Supplies, West Chester, PA). The coated device was heated at 300°C for 20 minutes while passing helium gas through its length to dry the coating and to ensure that the capillary was not clogged. Following the drying of the carbon coating, the device was inserted into the injection port of a GC to determine if any off-gassing of residual surfactant or solvent occurred.

Gas chromatographic analysis was performed using a Hewlett Packard 5710A GC with a flame ionization detector (FID). The BTEX compounds were separated using a 2 m by 3 mm i.d., packed glass column of 5% bentone, 5% isodecylphthalate on Chromosorb W (80/ 100 mesh). Most GC columns do not resolve *para* and *meta*-xylene; this packed column was chosen since it is able to completely resolve all of the BTEX compounds [5]. The injection port temperature for the GC was 300°C, the column temperature was 90°C, and the detector temperature was 200°C. For each analysis, the thermal desorption of a sample from an

INCAT device was followed with a second desorption in the injection port of the GC to verify complete desorption.

BTEX compounds were placed into individual sample vials that were sealed with a small opening in the cap. A layer of polyethylene membrane was placed inside the vial cap to act as a semipermeable barrier. The sample vials were placed into a 70 L environmental test chamber which had dry air (9-11% relative humidity) flowing in at a rate of 32 L/hr [6]. Three fans were used to circulate the air inside the chamber, to simulate the dynamic environment of indoor air.

Analysis of the BTEX compounds was achieved using activated carbon SPE tubes (SKC Inc., Eighty Four, PA) attached to a Dräger bellows pump (BGI Inc., Waltham, MA) which reproducibly sampled a 0.5 L volume (sampled five times at 100 mL/sample) of the chamber air. The BTEX compounds were extracted from the carbon tube using 1.0 mL of CS_2 doped with an internal standard (sec-butyl benzene at 107 μg/g). The amount of BTEX compounds relative to the internal standard were obtained using the relation:

$$D_c = \frac{A}{A_{std}} \frac{D_{std}}{f} \qquad \text{(EQ. 3)}$$

D_c = the amount of BTEX found by the carbon tube,

D_{std} = the amount of internal standard in the extract,

A_{std} = the area of the standard peak in the chromatogram,

A_c = the area of a particular BTEX peak in the chromatogram,

f = the response factor for the BTEX peak of interest.

The peaks in the INCAT chromatograms can then be determined by comparison to the peaks from the carbon tube using the relation:

$$D = \frac{A}{A_c} D_c f \qquad \text{(EQ. 4)}$$

D = the amount of BTEX found by the INCAT,

A = the area of the BTEX peak of interest,

F = the fraction of the volume of SPE tube extract injected into the GC ($V_{inj}/V_{extract}$).

The results of the activated carbon SPE tube measurements of the BTEX concentrations in the test chamber are listed in Table 2 on page 51. In order to test the INCAT device, higher BTEX concentration levels (relative to environmentally significant levels) were used to determine if the device could work in both the active and passive sampling modes; to determine the effect of varying volume and exposure time when dealing with

concentration levels that might saturate the adsorbent; and to determine the usefulness of the colloidal graphite adsorbent.

TABLE 2. Molecular weights (MW), order of elution, response factors (R_f), BTEX concentrations in the 70 L environmental test chamber, and internal standard used with the extraction solvent for the activated carbon SPE tube.

Compound	MW (g/mol)	Order of Elution	R_f	Chamber Concentration [a]		
				in mg/m^3	in µmol/m^3	in ppm[b]
Benzene	78.11	1	1.48	6.89±0.07	88.2±0.9	2.19
Toluene	92.13	2	1.24	4.95±0.05	53.7±0.5	1.33
Ethylbenzene	106.16	3	1.3	2.28±0.02	21.5±0.2	0.533
p-Xylene	106.16	4	1.13	6.01±0.06	56.6±0.6	1.40
m-Xylene	106.16	5	1.12	2.50±0.03	23.7±0.2	0.588
o-Xylene	106.16	6	1.18	4.27±0.04	40.2±0.4	0.997
sec-Butylbenzene (internal standard)	134.22	7	1	absent		

[a] Chamber concentration values averaged from four activated carbon SPE tube measurements during the course of these analyses.

[b] The concentration in ppm refers to parts per million by molar volume for an ideal gas at standard ambient temperature and pressure (SATP) conditions of 298.15 K and 1.0 bar. The molar volume of a gas under these conditions is 24.79 L.

2.2.1 Active Sampling with the INCAT Device

Using the INCAT device, the reproducibility of sampling was investigated by repeated measurements ($n = 10$) of BTEX compounds within the chamber by actively sampling a 5 mL volume of the chamber air using a 10 mL glass, gas-tight syringe (Hamilton Co., Reno, NV). Samples were taken at 30 minute intervals in order to allow the chamber to return to a steady state. The temperature inside the chamber ranged from 22.0 to 24.6°C and the relative humidity was 9-11%. All of the measurements were obtained from a 26 gauge INCAT device. Active sampling was performed by drawing the volume of air through the INCAT device via the syringe, and then pushing the same volume of air back through the device into the chamber. The rate at which the sample volume was withdrawn and expelled by the syringe was approximately 4 mL/min.

In addition to the constant volume measurements of the BTEX compounds in the chamber, the effect of different sample volumes on the amount of BTEX compounds adsorbed by the device was also investigated. The time between samples in this case was 60 min, and the flow rate through the device was again 4 mL/min. All of the measurements were made using the same 26 gauge INCAT device and were performed in the same manner as the constant volume measurements. The variable volume measurements were performed with the

chamber having (*i*) all of the BTEX compounds present; (*ii*) only benzene present; and (*iii*) having benzene and toluene present.

2.2.2 Passive Sampling with the INCAT Device

Application of the INCAT device to passive sampling was investigated by preparing three needles (22 gauge) that were made from a single continuous piece of stainless steel capillary tubing, which was subsequently cut into sections. The three devices were left in the chamber for approximately 24 hours. The reproducibility of the coating process was measured relative to the passive rates of adsorption (nmol/hr).

The effect of exposure time on the INCAT device in passive sampling was investigated over a period of several days. In order to account for any instrumental drift over this time period, a toluene standard was run each day and the results of the BTEX analysis scaled relative to the toluene standard. Sampling was performed using the same 26 gauge INCAT device that was used in the active sampling experiments. The device was placed in a 3.5 mL cryogenic vial (Evergreen Scientific, Los Angeles, CA). The open end of the vial was then inserted into a small snug fitting opening on top of the chamber thus exposing the INCAT device to the chamber air.

Once the VOC sample was adsorbed inside the INCAT device (via active or passive

method), the Luer-Lok end was plugged with a piece of septum — to prevent outflow of analyte from the Luer end — and the device was inserted into the injection port of the GC instrument for thermal desorption and analysis. Since the adsorptive coating of the INCAT device is contained within a stainless-steel capillary, the heat supplied from the GC injection port is conducted readily to desorb the analytes concentrated on the carbon coating. A 60 second injection time was found to be suitable for the desorption of the BTEX compounds. A second thermal desorption injection of the device was performed to ensure that the entire sample had been desorbed in the first 60 second injection, and indicated that no carry-over occurred.

2.3 Results

2.3.1 Active Sampling with the INCAT Device

The mean amounts of BTEX compounds obtained from actively sampling 5 mL of the chamber air are presented in Table 3 on page 56. The peak areas of the BTEX compounds were quantified by comparison to the SPE tube measurements using the relationships in equations EQ. 3 on page 49, and EQ. 4 on page 50. The mean amount of each BTEX

compound was calculated based on ten sequential measurements of the chamber. The relative standard deviations from the mean amount of compound sampled (RSD) ranged from 6.3% to 9.4%. The proportional amount of each compound adsorbed relative to the amount present in the volume sampled from the chamber ranged from 16.3% to 70.7%. These results show that despite the simple manual sampling procedure, the reproducibility in sampling is still in the neighbourhood of direct liquid injections onto packed GC columns as shown by the RSD values for the mean amount of analyte adsorbed (Table 3 on page 56) all being less than 10%. The variation in the efficiency of sampling (percent adsorbed relative to amount sampled) is independent of the sampling reproducibility and is likely due to the individual affinities of the compounds for the adsorbent.

TABLE 3. Mean amounts of BTEX compounds adsorbed, percent RSD from the mean, and the proportion adsorbed relative to the amount present, determined by repeated measurements (n=10) of an actively sampled 5 mL volume using a 26 gauge INCAT device.

Compound	Mean Amount (nmol)	%RSD	Percent Adsorbed [c]
Benzene	0.072	6.3	16.3
Toluene	0.14	9.3	52.1
Ethylbenzene	0.043	8.7	40.0
p-Xylene	0.20	9.4	70.7
m-Xylene	0.059	8.0	49.8
o-Xylene	0.12	8.1	59.7

[c] The proportionate amount of the analyte adsorbed relative to the amount actually sampled from the test chamber, defined by the relation: $\text{Percent Adsorbed} = \frac{\text{moles of compound adsorbed}}{(\text{volume sampled})(\text{concentration})} \times 100$

The results of the adsorption profiles of all of the BTEX compounds actively sampled at varying volumes are presented in Figure 2 on page 57. The adsorption profiles indicated that the amount of each of the compounds determined with the INCAT device were dependent on the presence of other compounds. Active sampling of all of the BTEX simultaneously showed a distinctive trend among the heavier compounds (ethylbenzene and the xylenes) for a Langmuir-like adsorption curve [7, 8]. However, the adsorption profiles for benzene and

toluene tended to reach a maximum and then 'tail off' as the sample volume increased. This decrease in the amounts of the compounds adsorbed implies some sort of competition for space on the surface of the carbon coating. The competition for space seemed to favour the heavier compounds.

FIGURE 2. The amounts of BTEX compounds determined by active sampling with a 26 gauge colloidal graphite INCAT device.

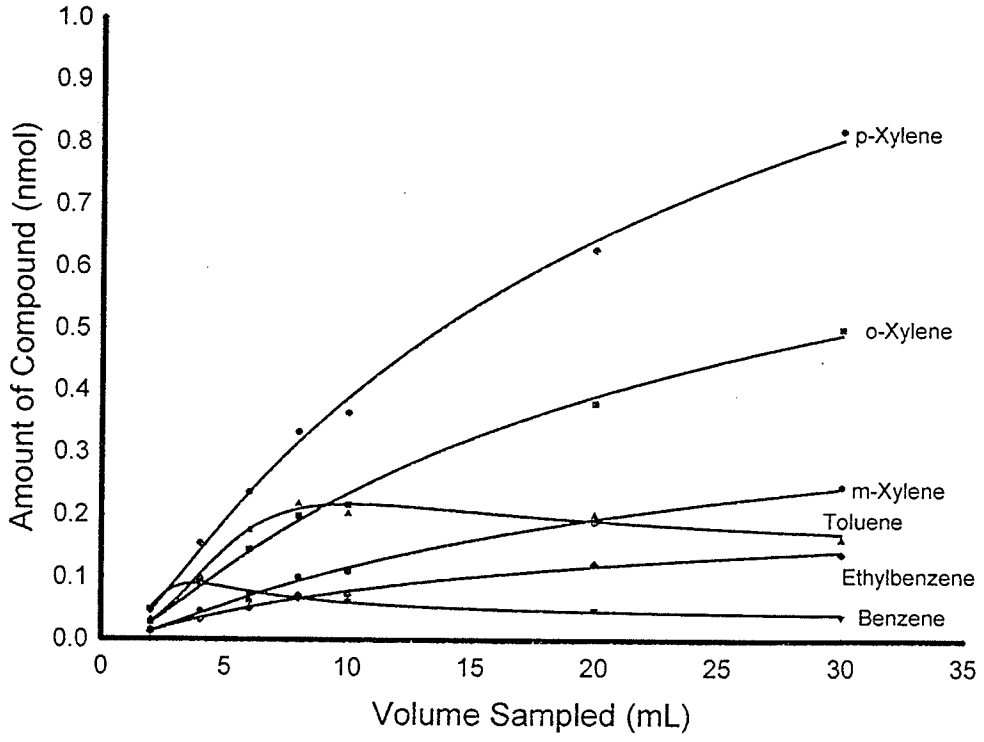
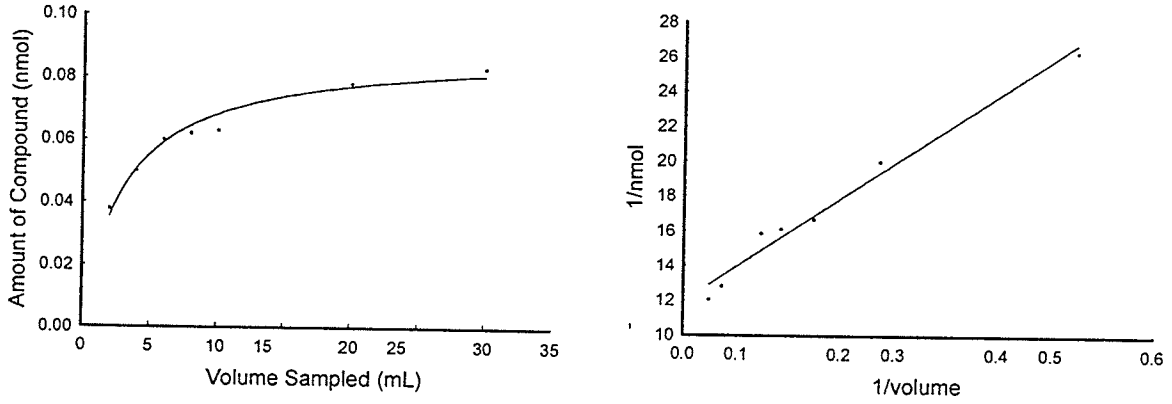


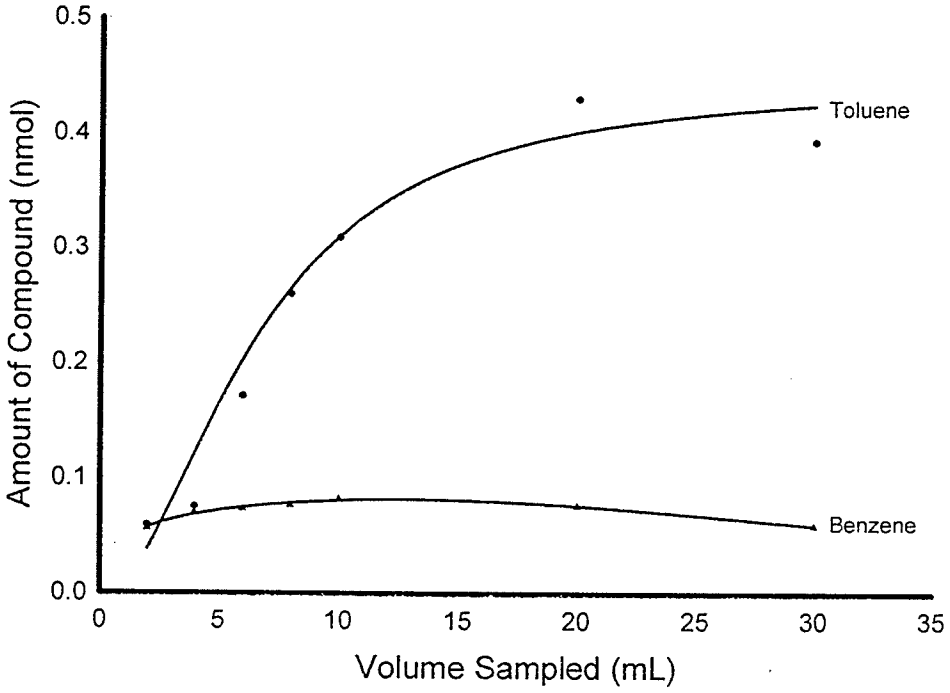
FIGURE 3. (a) The amount of benzene determined by active sampling with a 26 gauge colloidal graphite INCAT device in the absence of all other BTEX compounds; (b) the Langmuir fit for benzene actively sampled in the absence of all other BTEX compounds.



The adsorption profile of benzene, when sampled in the absence of other BTEX compounds (shown in (a) of Figure 3), demonstrates an initial rapid increase in the rate of adsorption which then decreases slightly as the interior carbon surface becomes saturated. Analysis of this single component system showed that the amount of benzene adsorbed tended to follow a Langmuir-like isotherm, i.e., the reciprocal of the amount adsorbed was directly proportional to the reciprocal of the volume sampled as indicated in (b) of Figure 3. However, the presence of an additional compound showed that there will again be a competition for space on the coating in which the heavier compound seemed to be favoured, thus disturbing the Langmuir-like behaviour. This trend was seen in the analysis of benzene and toluene sampled in the absence of the heavier compounds, shown in Figure 4 on page 60. The

constant volume active sampling results listed in Table 3 on page 56, indicate an efficiency value (percent adsorbed) of 52.1% for toluene relative to 16.3% for benzene. As such, it is not surprising that benzene is the compound affected as the capacity of the device becomes a significant factor — even in a two component system. Thus, when sampling several compounds at once, a competitive adsorption profile is likely to occur. It should also be noted, that the amount of benzene adsorbed in the absence of all other compounds from ten replicate 5 mL measurements, had a mean of 0.062±0.004 nmol and RSD of 7.2%. These constant volume results for the single component system are consistent with the multi-component system where all of the BTEX compounds were sampled. The proportional amount of benzene adsorbed relative to the amount sampled was 15.3% (the test chamber concentration of benzene was again 88.2±0.9 $\mu mol/m^3$). This low efficiency, even in the absence of other compounds, implies that benzene has a low affinity for the adsorbent regardless of the numbers of compounds in the system being sampled.

FIGURE 4. The amount of benzene and toluene determined from active sampling with a 26 gauge colloidal graphite INCAT device in the absence of heavier BTEX compounds.



2.3.2 Passive Sampling With The INCAT Device

Mean passive rates adsorption of the 22 gauge INCAT devices were determined from passive sampling with three devices for a 24 hr period. The mean passive rates of adsorption (absolute) for the three 22 gauge INCAT devices are listed in Table 4 on page 61. Since it was apparent that there existed some competition for space on the carbon coating between the various species being sampled, the mean adsorption rates serve only to show consistency in

sampling for a specific amount of time. It is likely that there would be a different set of mean adsorption rates if the devices were used to passively sample the BTEX compounds for different lengths of time. Thus, only information on the reproducibility of the carbon coating and reproducibility in passive sampling for a fixed time of exposure may be obtained from these results.

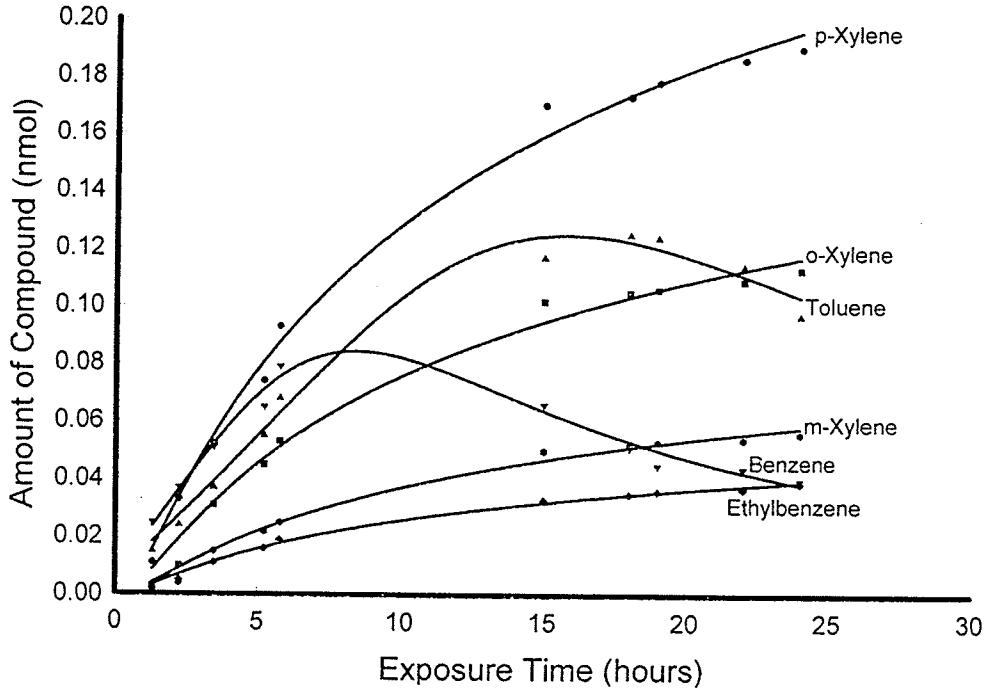
TABLE 4. Mean absolute passive rates of adsorption and percent RSD from the mean, for 22 gauge INCAT devices (n = 3).

Compound	Mean Rate (pmol/hr)	%RSD
Benzene	3.4	13
Toluene	12.4	8.6
Ethylbenzene	7.7	11
p-Xylene	46.3	10.
m-Xylene	13.9	9.5
o-Xylene	28.7	11

The adsorption profiles for the BTEX compounds, passively sampled over a range of exposure times, are shown in Figure 5 on page 62. The competitive effects observed in the active sampling of all of the BTEX compounds are again present, but are not as severe. Profiles for the passive adsorption closely resemble the active sampling adsorption profiles (in shape only but not magnitude) up to a 10 mL sample volume (Figure 2 on page 57). This

similarity suggests that similar adsorption phenomena occur, but on a slower (smaller) scale due to the slower rate of uptake in the passive mode of sampling.

FIGURE 5. The amounts of BTEX compounds determined from passive sampling with a 26 gauge colloidal graphite INCAT device over a range of exposure times.

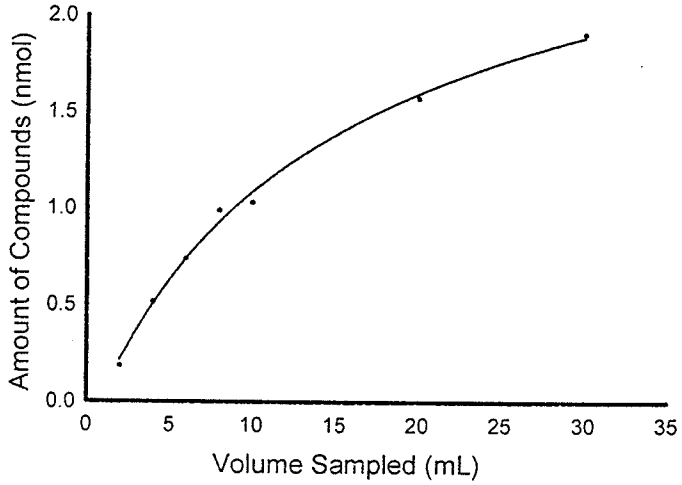


2.4 Discussion

Active sampling of the BTEX compounds over a wide volume range revealed an

inconsistency in the various adsorption profiles that was not directly related to their actual concentration. The differences in the adsorption curves suggest a preferential or competitive adsorption effect on the carbon surface. The total molar amount of compounds actively sampled with the INCAT shows a typical adsorption profile (Figure 6) similar to that of benzene sampled in the absence of the other compounds. This suggests that differences in the profiles of the individual compounds when sampled simultaneously, are the result of competition for space on the carbon surface where the individual affinities of the compounds for the adsorbent become more significant.

FIGURE 6. The total amount of BTEX compounds determined from active sampling with a 26 gauge colloidal graphite INCAT device.



The competition for space on the adsorbing surface of the INCAT device becomes

significant only as the coating is nearing saturation. Therefore, looking more closely at the initial regions of the active and passive sampling results may be prudent. The initial rates of adsorption for the active samples are found in Table 5 on page 65. Considering the molar amount of each compound obtained with the device in the actively sampled range of 0 to 8 mL, it appears that the adsorption of each compound, with exception of benzene, was approximately linear. The coefficient of determination for the linear relationship was at least 97% for all compounds other than benzene. Benzene was not included as it reached its maximum and then began to decrease within the initial range of volume sampled. The best fit line for benzene could not be determined to same degree of certainty as the other compounds since too few data points were collected prior to the 5 mL sample. An estimate of the slope and adsorption rate based on the initial three data points is included in Table 5 on page 65 for comparison. The coefficient of determination for the linear fit for benzene has been omitted since it is the result of only three data points and is therefore misleadingly high.

TABLE 5. Initial slopes and absolute rates of adsorption for the 26 gauge INCAT device in active sampling of the BTEX compounds (based of the initial 5 data points in the 0 to 8 mL range).

Compound	Initial Slope (nmol/mL)	Coefficient of Determination (r^2)	Initial Rate of Adsorption (nmol/hr)[f]
Benzene [e]	0.023		5.5
Toluene	0.029	0.985	7.0
Ethylbenzene	0.0091	0.991	2.2
p-Xylene	0.043	0.988	10.
m-Xylene	0.013	0.976	3.1
o-Xylene	0.026	0.989	6.2

[e] The values determined for benzene are based on only the first 3 data points since the profile becomes clearly curved after sampling 4 mL of chamber air. Thus, the values are only included for the purpose of an approximate comparison and cannot be considered as relevant as the values for the other compounds. It is for this reason that the r^2 value for benzene has been omitted since it was based on only 3 points it is deceivingly high.

[f] The active rates of adsorption were determined by the relation:

Initial Adsorption Rate = (initial slope in nmol/mL)(flow rate through the INCAT of 4 mL/min)

In addition to the molar amounts of each compound adsorbed (except benzene), having an initial linear relationship with the sample volume, the slopes of these linear fits to the initial region of the data, were in order of increasing chamber concentration (see Table 2 on page 51). The rates of adsorption of the BTEX compounds, listed in Table 5 on page 65, are obtained from the initial slopes and the flow rate at which they were actively sampled. The

sampling efficiencies of each compound with this type of carbon surface (or affinities for the adsorbent) are reflected by the initial slopes and rates of adsorption. Differences in the amount of each compound adsorbed, relative to the amount sampled from the chamber (listed in Table 3 on page 56), also reflect the individual affinities of the BTEX compounds for the adsorbent.

In comparison, analysis of the BTEX compounds by passive sampling resulted in the same linear trends being observed in the initial region of sampling (0 to 5.75 hours of exposure). The initial slopes, or passive rates of adsorption, are listed in Table 6 on page 67. For each compound, the coefficient of determination for the linear relationship (r^2) was greater than 95%. Although the curvilinear shape to the benzene profile is present in the initial passive sampling data, it is not as extreme as observed in the active data. As such, benzene can be included in the analysis to the same degree of certainty as the other compounds.

The initial rates of adsorption listed in Table 1.6 are not meant to be compared with the mean passive rates of adsorption found in Table 4 on page 61. The mean adsorption rates listed in Table 1.4 resulted from sampling with three INCAT devices (22 gauge) over a 24 hour period, whereas Table 6 on page 67 lists the initial adsorption rates for a single INCAT device (26 gauge) exposed for up to 5.75 hours. Even if the devices used in the two analyses were the same size (gauge), and had the same surface area of adsorbent, the periods of

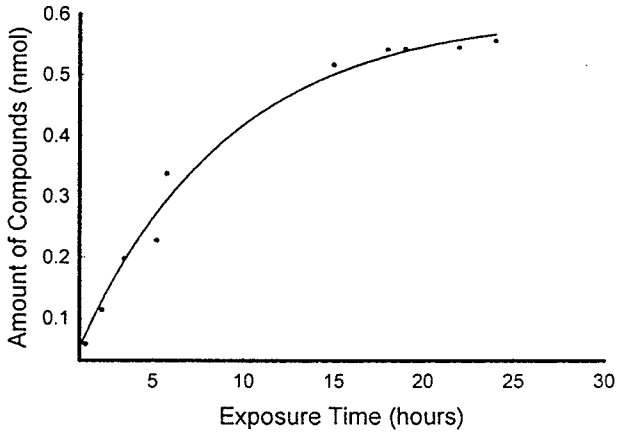
sampling would not be the same and are unlikely to result in equivalent passive adsorption rates.

TABLE 6. Initial absolute rates of adsorption for the 26 gauge INCAT device in passive sampling of the BTEX compounds (based on the initial 6 data points in the 0 to 5.75 hour range).

Compound	Initial Adsorption Rate [g] (nmol/hr)	Coefficient of Determination (r^2)
Benzene	0.013	0.977
Toluene	0.011	0.991
Ethylbenzene	0.0034	0.981
p-Xylene	0.016	0.984
m-Xylene	0.0048	0.950
o-Xylene	0.0099	0.960

[g] The initial rates of adsorption are the initial slopes of the adsorption profiles in Figure 6 on page 63.

FIGURE 7. The total amount of BTEX compounds determined from passive sampling with a 26 gauge colloidal graphite INCAT device.

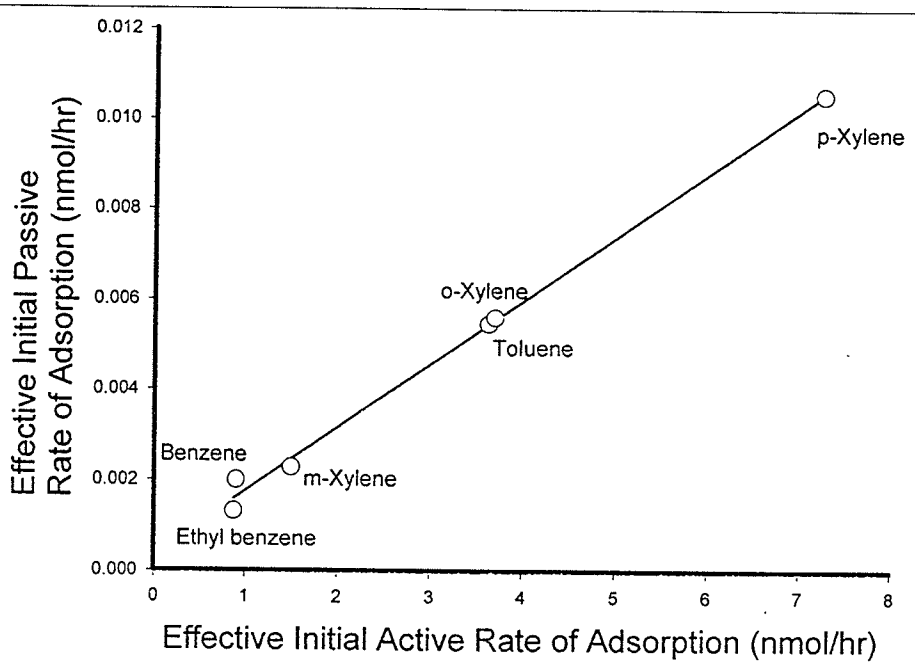


Passive sampling the BTEX compounds over the entire range of exposure times, showed that the amounts of benzene and toluene both reached a maximum, but were still obtained in high amounts relative to the heavier compounds being sampled. Ethylbenzene is consistently adsorbed to a lesser degree than all of the other compounds. This observation is similar to what is seen in the initial portion of the active sampling curve of all of the BTEX compounds (Figure 2 on page 57). Similarity between the passive sampling profiles and the initial portion of the active sampling profiles (up to 10 mL) suggests consistency of the adsorbing material. Again, the shape profile for the total amount of compounds adsorbed in Figure 7 on page 68 shows a typical Type I BET adsorption profile [9], as observed in the active sampling. The correlation coefficient (r) between the active and passive initial rates of

adsorption (Table 5 on page 65, and Table 6 on page 67) was calculated to be 0.930, indicating reasonable agreement between the independent sets of results. The correlation coefficient between the active and passive sampling rates is even greater, $r = 0.999$, when the benzene point is excluded due to the higher error associated with its initial active rate of adsorption. Moreover, if the efficiency of adsorption of the individual analytes is taken into account, the initial rates of adsorption in the passive and active sampling modes show very good agreement. The proportional amount of each compound adsorbed (listed as the percent adsorbed in Table 3 on page 56) may be considered as the efficiency for sampling the individual species in the initial linear region of the adsorption profiles. Then, the passive and active rates of adsorption may be scaled to account for the variation in the individual affinities of the analytes for the adsorbent. Figure 8 on page 70 shows the 'effective' initial active and passive rates of adsorption plotted against each other, with the best fit line through the data. The coefficient of determination for the linear fit through the data in Figure 8 was calculated to be $r^2 = 0.996$ with the benzene point included, and $r^2 = 0.999$ with the benzene point excluded. The result of this correlation is that the INCAT device can serve as both a passive or active sampler for these VOCs. Direct correlation between the rate of adsorption (active and passive) and the analyte partition coefficient was poor. The lack of correlation between the adsorption rates and partition coefficients is likely due to the influence of the individual

efficiency or affinity factors for the compounds.

FIGURE 8. Plot of the effective initial adsorption rates for passive sampling against active sampling, of the BTEX compounds with a 26 gauge colloidal graphite INCAT device.



Active sampling a 10 mL volume takes only 5 minutes, with the flow rate through the device of 4 mL/min (to draw through and expel the sample volume). Therefore, one can obtain relatively the same amounts of the compounds in 5 minutes of active sampling as one does in 24 hours of passive sampling with this device. If the rate of actively drawing the air through the INCAT is reduced, then the same sample volume would be sampled over a longer period. As such, the analytes in the sample volume would have more time to interact with the

adsorbing coating and increase the amount adsorbed, thus raising the sensitivity of analysis. In addition, longer periods of exposure for passive sampling may be better for situations where VOC levels vary with time, allowing an integrating effect averaged over time.

2.5 Conclusions

BTEX compounds were chosen as an indicator of the effectiveness of the INCAT device to act as a representative set of VOCs that occur frequently in urban environments and pose particular occupational hazards [1]. BTEX compounds are found in gasoline and automobile exhaust, in tobacco smoke, and in commercial or industrial solvents. Thus, the potential for human exposure to these compounds is quite high, especially for individuals in occupations involving the use of these compounds. Furthermore, the severe impact of the BTEX compounds on human and animal health has been observed and documented. Benzene is listed as the fifth compound in the top twenty hazardous substances by the Agency for Toxic Substances and Disease Registry (ATSDR) of the US Department of Health and Human Services (DHHS) [1]. Benzene has been found to cause leukemia and to have adverse effects on blood production and the immune system. It is because of this level of impact on humans that passive monitors for VOCs in certain occupational areas are particularly

necessary.

The reproducibility of the INCAT device in measuring the BTEX compounds sampled actively at a fixed volume showed a variation in sampling error ranging from 6.3-9.3% for the different compounds when sampled simultaneously. The sampling error for the individual analytes all being less than 10%, implies that the consistency in sampling is very good, despite the fact that the active samples were performed manually. Variation between the sampling errors is likely due to the influences of the individual analytes on each other resulting from the high levels that the BTEX compounds are present in the test chamber. The reproducibility of the coating surface, determined from passive sampling of three INCAT devices for a fixed amount of time, showed relative standard deviations from the mean adsorption rate ranging from 8.6-12.9% for the different compounds. Again, the variation in the sampling error was perhaps due to the effect of the compounds on each other, leading to different adsorption profiles when sampling a mixture as opposed to a single component. The variation in the adsorption profile for benzene and toluene appeared dependent on other compounds present. This variation implies that a specific calibration would be required for quantitative analysis or that measurements would have to be restricted to the range in which the adsorption is essentially linear. Although these analyses were performed using a packed column, the INCAT has been used with capillary columns with a split injection system. The use of a

packed column was to resolve all of the BTEX compounds.

The adsorption profiles for both active and passive sampling suggested competitive effects between the lighter and heavier compounds. These effects become more pronounced as the carbon coating inside the device nears saturation at which point the individual affinities for the surface become more evident. Since the competitive effects were observed in the passive sampling mode as well, it was concluded that an adsorbing coating with a higher surface area to raise the capacity of the device was needed. Colloidal graphite reached to capacity too quickly with the BTEX concentrations at such levels. It should be noted that some concentration levels in the test chamber are much higher than what the minimum risk levels (MRL) are for indoor air (e.g., the test chamber concentration for benzene is approximately 2.2 ppm and the MRL is 0.05 ppm) [10].

In general, it can be concluded that most of the shortcomings of the INCAT sampling methods are directly related to the use of colloidal graphite for the adsorbing coating. The colloidal graphite was chosen only because it was commercially available and of reasonable consistency to easily coat the interior surface of the capillary. The principal concept is that 'a carbon coating material' on the interior of the device can be used to adsorb VOCs, either actively or passively, and that the device may then be inserted into a GC or GC-MS instrument for the thermal desorption of the analytes. The simplicity of the INCAT sampling

method is related to:

- the INCAT device being relatively robust and may therefore be used many times before the adsorbing coating begins to degrade; sampling is achieved in solventless extraction process;
- the active sampling of analytes can be achieved for indoor air;
- the passive sampling can be done for any amount of time and in various locations of a site (a 'sick' building) to obtain a profile of VOCs; and
- the device is technically simple for sampling and injecting.

The INCAT device is analogous to the activated carbon SPE air sampler used to measure the test chamber concentrations in these analyses. Rather than containing loosely packed adsorbent particles that allow air flow, as with the activated carbon SPE tubes, the INCAT has an adsorbing coating on the interior surface of capillary. However, the fact that the adsorbent is present in the device much like a GC capillary column, analyte partitioning between air and the adsorbent should not be confused with analyte partitioning in open tubular gas chromatography (OTGC). OTGC involves a 'sample plug' being transported through the column via an inert carrier gas. The INCAT device in the active sampling mode, involves the continuous flow of analytes that are uniformly distributed throughout the air volume sampled. Although both systems are flow/velocity dependent, the partitioning of the analytes between

the air and the INCAT adsorbent is not likely to occur in the same manner as in OTGC. The dependence on analyte velocity, in active sampling with the INCAT device, is related to whether the analyte has sufficient time to interact with the carbon adsorbent, and the presence of sufficient numbers of adsorption sites. Physical adsorption interactions are relatively weak, but occur readily when the adsorbate comes into contact with the adsorbent. As such, the proximity to an adsorbing site and the speed at which the analyte moves through the device, are two variables that will affect analyte adsorption. The effect of these variables would then be more significant as the adsorbing surface nears its capacity.

The passive adsorption rates partially involve the diffusion coefficient of the analytes through air. As with SPME, the sampling rate will depend on the rate of analyte mass transport through a matrix (air in this study) to the adsorbent. However, in the environmental chamber used here, the air is being constantly circulated via fans and clean air is being blown in (32 L/hr). Therefore, the environmental chamber is not a static headspace where the diffusion of the analyte would be an important variable.

This chapter describes a new method of sampling VOCs using a particular adsorbing coating in the device. The use of carbon coatings with greater surface areas should reduce the problem of the competitive effects for space by raising the level at which the interior carbon coating becomes saturated. Competitive effects and variation in sampling efficiencies for the

different compounds are the result of the low capacity of the graphite adsorbent, not with the sampling method. In summary, these results show that the INCAT device may be used to sample BTEX compounds from air in both the active and passive modes.

References

[1] *Agency for Toxic Substances and Disease Registry, Public Health Statement*, at http://www.atsdr.cdc.gov/cx.html, ASTDR Science Corner (1989).

[2] H. N. MacFarland, *Am. Ind. Assoc.*, 47, 704 (1986).

[3] M. Tancrede, R. Nilson, L. Zeise, E. A. Crouch, *Atmos. Environ.*, 21, 2187 (1987).

[4] M. E. McComb, R. D. Oleschuk, E. Giller and H. D. Gesser, *Talanta*, 44, 2137 (1997).

[5] S. F. Spencer, *Anal. Chem.*, 35, 592, (1963).

[6] S. Shojania, R. D. Oleschuk, M. E. McComb, H. D. Gesser and A. Chow, *Talanta*, **50**, 193 (1999).

[7] D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, p. 80-96, Wiley, New York (1984).

[8] V. Ponec, Z. Knor, S. Cerny, *Adsorption on Solids*, p. 326-332, Butterworths, London (1974).

[9] S. J. Gregg and K. S. Sing, *Adsorption Surface Area and Porosity*, ch. 1, Academic Press, London (1967).

[10] *Minimal Risk Levels (MRLs) for Hazardous Substances*, Agency for Toxic Substances and Disease Registry, Division of Toxicology, at http://www.atsdr.cdc.gov/mrls.html (1998).

CHAPTER 3

Qualitative Analysis of Complex Mixtures of VOCs Using the Inside Needle Capillary Adsorption Trap

3.1 Introduction

Pattern recognition, or *fingerprint* analysis, is employed in the qualitative analysis of complex mixtures. Source identification of a sample can be determined by comparing a characteristic chromatogram of the sample to libraries of complex mixture chromatograms [1]. In such analyses, the identification of the individual components is not necessary. The characteristic profile or *fingerprint* of the chromatogram allows for positive identification of the material. Fingerprint analysis by gas chromatography has been by itself sufficient for source identification of complex petroleum distillates in both forensic and environmental applications [1]. For example, identification of arson accelerants can be achieved by comparing the chromatograms of the static headspace above fire debris, with those of

similarly obtained commercial reference accelerants (e.g., kerosene, gasoline, etc.). Environmental investigations of point source pollution may also be achieved by fingerprint analysis [2]. Identification of the source of a spill may be possible by chromatographic comparison of a sample from the contaminated site with waste or products from suspected source points.

In the analysis of complex mixtures, such as petroleum distillates, the use of HS-GC may often simplify the analysis by reducing the number of peaks in the chromatogram. Moreover, distinctive differences between samples may be observed based on the levels of VOCs [2, 3]. The VOCs in some liquid samples may be present in relatively low concentrations, and thus be obscured by the more abundant nonvolatile components in the chromatogram. The VOCs that are part of these complex mixtures will partition between the liquid and vapor phases. If the sample is placed in a gas-tight container, an equilibrium between the liquid and vapor phases will be established. Most petroleum distillates contain many VOCs in characteristic proportions. Thus, a profile of the peaks from the static headspace of the sample will also serve as fingerprint of the sample.

Headspace sampling (static or dynamic) is advantageous over direct liquid sampling of complex mixtures of VOCs in cases when a liquid sample is not always available, or when the analytes are in a liquid matrix that would complicate GC analysis. The sampling of

headspace is then advantageous for samples that would require solvent extraction (i.e., contaminated soil, water, foods, packaging materials, arson debris, etc.). Conventional methods for HS-GC usually involve cryogenic focusing of large volumes of the static headspace onto the GC column [2]. Samples often require heating to increase the amount of analyte mass in the static headspace [3] However, depending on the nature of the mixture, thermal degradation of the sample may result upon heating of the sample, thereby producing compounds that may obscure the analysis.

SPE methods have been used to concentrate headspace components, which are then solvent desorbed from the solid phase [2, 4]. A sample of the headspace is actively drawn through small packed columns or cartridges containing the solid phase adsorbent. The adsorbed analytes are then solvent desorbed, and a fraction of the solvent extract is introduced into the GC for analysis. Extraction of the analytes from the static headspace onto the solid phase avoids the necessity of cryogenic focusing of large headspace volumes, but usually requires a solvent extraction step. In some cases, there may be additional sample preparation steps required for the cartridges themselves.

The SPME method has been applied to the analysis of a variety of complex mixtures of VOCs [5-9]. The SPME method uses a small fused silica fibre that is coated with a liquid phase sorbent. The coated fibre is introduced into the static headspace and allowed to reach

equilibrium with the VOCs that are present. The headspace analytes are then concentrated onto the fibre coating. The SPME device is then inserted into a GC or GC coupled to a mass spectrometer (GC-MS) system to thermally desorb the analytes directly onto the column. Thus, the SPME method is a solventless extraction technique.

The INCAT device (Figure 1 on page 39) as described in Ch. 1 and 2, has an adsorbing carbon coating on the interior surface of a hollow stainless-steel needle [10, 11]. This device is able to sample the static headspace of a sample both actively and passively. In the active sampling procedure, an aliquot of the static headspace volume is drawn through the device via a syringe. The volatile analytes are then adsorbed and concentrated inside the device. The INCAT device can then be inserted into a heated injection port of a GC to thermally desorb the analytes directly onto the GC column for separation. The concentration of analytes inside the INCAT device avoids the necessity for cryogenic focusing of large sample volumes onto the GC column — a method employed in most HS-GC analyses [3].

Other methods designed to increase headspace sensitivity, such as CLS and P&T methods, require larger headspace sample volumes for cryogenic focussing onto the GC column. The use of extraction devices, such as SPE cartridges or SPME fibres, increases the sensitivity of headspace sampling. The INCAT device can be used in a similar manner without a solvent extraction step, and with no time required by the headspace analytes to reach

equilibrium. To demonstrate these features, a simple application to qualitative analysis of samples of the six classes of accelerants [1] has been performed. The chromatograms of the static headspace of the six classes of accelerants, according to the ASTM forensic classification scheme [12], were obtained from active sampling with the INCAT device and compared to the chromatograms obtained from direct liquid injection of the samples. Samples included the following: light petroleum distillates (pocket lighter fluid), gasolines, medium petroleum distillates (paint thinner), kerosene, heavy petroleum distillates (diesel fuel), and unclassified accelerants (camp fuel). The BTEX compounds present were used as target analytes to compare the different classes. In addition, aqueous samples with low levels of gasoline components were examined to determine the sensitivity of the technique and simulate environmentally significant levels.

3.2 Experimental

The INCAT devices used in this study were prepared from 50.8 mm long, 26 gauge (0.46 mm nominal o.d.; 0.25 mm nominal i.d.) hypodermic needles with metal Luer-Lok hub (Hamilton Co., Reno, NV). The needles were coated with one of three types of activated carbon blacks: Raven-15 (Columbian Carbon Co., New York, NY), Super Sorb (Amoco

Research Corp., Chicago, IL), and Saran from poly(vinylidene chloride) (RMC, Kingston, ON). The carbon blacks were suspended in 1.0% w/w solution of Silwet surfactant (Union Carbide, Danbury, CT) in isopropanol (Fisher Scientific Co., Fair Lawn, NJ). The needles were coated using a syringe to draw a 1 mL volume of the carbon black suspension through the length of the needle which was then pushed out. The coated devices were baked for one hour at 300°C while passing helium gas through the length of the needle to ensure that no clogging occurred and to remove the suspension solvent. Once ready, the INCAT device was plugged with a small piece of septum at the Luer-Lok end, and inserted into the injection port of a GC to determine if any off-gassing occurred.

Direct liquid sampling and static headspace sampling (via the INCAT device) was performed on the samples listed in Table 7 on page 85. For each sample, 2 mL of the liquid was placed in a 40 mL GC vial sealed with a screw-top septum-containing cap for headspace sampling. A separate sample, with 2 mL in a 4 mL GC vial sealed with screw-top septum-containing cap, was prepared for direct liquid sampling. Active sampling of the headspace with the INCAT device was performed by drawing 0.10 mL of the headspace through the device at an approximate rate of 0.35 mL/min, with a 0.50 mL gas-tight syringe (Hamilton Co., Reno, NV). The withdrawn headspace volume was then pushed out the device at the same rate. Thus, the 0.10 mL sample was allowed to pass over the coating twice. The Luer-

Lok end of the INCAT device was then plugged with a small piece of septum. Subsequently, the INCAT device was immediately inserted into the injection port of the GC for thermal desorption.

Gas chromatography was performed using a Varian Star 3400 CX series GC (Varian Instrument Group, Walnut Creek, CA) with FID. The samples were separated on a 15 m DB-1 megabore column (J&W Scientific Inc., Folsom, CA) of 100% dimethylpolysiloxane (0.53 mm i.d., 5.00 μm film thickness). Analytes were thermally desorbed from the INCAT device in the heated injection port (210°C) of the GC for two minutes. The initial column temperature was held at 30°C for the two minute injection time. The temperature of the column was ramped to 195°C at a rate of 8°C/min and held for five minutes. The column was then heated to a final temperature of 200°C at a rate of 20°C/min, and held at this temperature for two minutes. The detector temperature was 200°C. The entire run time for the separation was 30 minutes. A second thermal desorption injection of the device was performed to ensure that the entire sample had been desorbed in the first two minute injection, and indicated that no carry-over occurred.

TABLE 7. Classification scheme for accelerants and the samples studied.

Class	Class	Samples Studied
0	Unclassified	Escort Camp Fuel (Imperial Oil Ltd., Toronto, ON)
1	Light Petroleum Distillates (LPD)	Ronsonol pocket lighter fluid (Ronsonol Corporation of Canada, Mississauga, ON)
2	Gasoline	Shell octane rated gasolines: Bronze 87, Silver 89 and Gold 91 (Shell Canada Ltd, Calgary, AB)
3	Medium Petroleum Distillates (MPD)	Varsol® (Imperial Oil Ltd., Toronto, ON), generic paint thinner (Canadian Tire Corporation Ltd., Toronto, ON)
4	Kerosene	Kerosene (Reochem Inc., Toronto, ON)
5	Heavy Petroleum Distillates (HPD)	Shell diesel fuel (Shell Canada Ltd, Calgary, AB)

To estimate the sensitivity of the INCAT sampling method, and to demonstrate its usefulness in characterizing environmentally significant concentrations of VOCs, four aqueous solutions, each saturated with one of the three Shell gasolines or diesel, were prepared, and an aliquot of the saturated aqueous Shell Bronze solution was further diluted by a factor of 1000 with water. Initially, samples prepared with 2 mL of the aqueous solution in 40 mL vials were used, and 0.10 mL of the static headspace was actively sampled by the INCAT device. However, the chromatogram obtained for the saturated solution showed poor peak intensity. A second set of samples was prepared with 5 mL of the aqueous solution in 40 mL GC vials, and 10.0 mL of the headspace was actively sampled using a gas-tight syringe

(Hamilton Co., Reno, NV). The rate of sampling with this 10.0 mL syringe was approximately 2.5 mL/min. The withdrawn volume was pushed out of the INCAT device at the same rate at which it was actively removed from the headspace, allowing the headspace sample volume to pass over the coating twice. The larger headspace volume for the aqueous gasoline solutions, improved the sensitivity of the sampling method.

The retention times and response factors were determined for the BTEX compounds by repeated (n=4) 0.10 µL liquid injections of the BTEX standard. The mean, standard deviation, and percent RSD from the mean of the retention times and response factors for each of the BTEX compounds are listed in Table 8. The *meta* and *para* xylenes were not resolved as two distinct peaks with the DB-1 column.

TABLE 8. Means, standard deviations, and percent RSD of the response factors (R_f) and the retention times (R_t) from n = 4 liquid injections of the BTEX standard.

Compound	Mean R_f	Std. dev. R_f	%RSD R_f	Mean R_t	Std. dev. R_t	%RSD R_t
Benzene	1.109	0.014	1.28	6.264	0.013	0.204
Toluene	1.02	0.003	0.282	8.972	0.004	0.05
Ethylbenzene	1.048	0.011	1.086	11.29	0.004	0.035
m, p-Xylene	0.954	0.002	0.201	11.58	0.005	0.043
o-Xylene	0.948	0.004	0.393	12.07	0.008	0.064

3.3 Results and Discussion

These experiments were designed to determine if the adsorptive coating of the INCAT device would improve the headspace sensitivity in direct gas sampling. Previously reported INCAT devices [10, 11] (Ch. 2) were made with a colloidal graphite coating as the carbon adsorbent. However, graphite has a very low surface area, and hence a low capacity which gave a variation in the relative amounts of adsorbed compounds as the device reached capacity [11]. In order to improve the capacity of the devices, activated carbon coatings have been incorporated. Other methods designed to increase headspace sensitivity, such as CLS and P&T methods, require larger headspace sample volumes for cryogenic focussing onto the GC column [3]. The use of extraction devices, like SPE cartridges or SPME fibres, increases

the sensitivity of the headspace sampling. The INCAT device can be used in a similar manner, without a solvent extraction step, and with no time required to reach equilibrium with the headspace. To demonstrate these features, a simple application to qualitative analysis of the six classes of accelerants [1] has been performed.

The static headspace of the BTEX standard was actively sampled using INCAT devices with three different coatings. The chromatograms obtained for the liquid injection and the injection of INCAT sampled headspace of the standard are shown in Figure 9 on page 91. The Raven-15 coated INCAT (Figure 9(b)) showed the best adsorption of the compounds. Using the change in mass from the uncoated needle and the internal surface area of the capillary, the coating contained 0.40 mg carbon. The Saran and Super Sorb (Figure 9(c) and (d)) coatings contained 0.11 mg carbon and 0.24 mg carbon, respectively. The differences in the amount of carbon resulting from the coating process, are likely due to the differences in the grain sizes among the three carbon blacks. To reduce the variation in the amount of carbon in each needle, it is necessary to have a uniform grain size for the different carbon blacks. The Raven-15 INCAT device was chosen for the remaining headspace samples due to the larger amount of carbon on the interior surface of the needle. It should also be noted that the tailing in the benzene peaks in (b), (c) and (d) of Figure 9 on page 91 are the result of benzene diffusing onto the column during the two minute injection. The initial column temperature

during the injection was held at 30°C, but lower temperatures would be required to focus benzene at the top of the column for the entire injection time. Shorter injection times for the INCAT device at higher desorption temperatures would reduce the tailing of benzene. In addition, a lower initial column temperature would prevent benzene from moving through the column until the entire sample had been desorbed from the device. Thus, all of the analytes would be focussed at the top of the column until the temperature program begins upon completion of the injection. The lowering of the initial column temperature, coupled with an increase in the injection port temperature (reducing the desorption time) would then improve the chromatographic resolution. The entire sample would be desorbed before any of the analytes begin to diffuse onto the column — then all analytes would enter the column as a small 'sample plug', as in a normal liquid sample introduction.

TABLE 9. Means, standard deviations, and percent RSD of the retention times and peak areas of the BTEX compounds from n = 4 trials of active sampling of 0.10 mL of the HS above Shell-Bronze gasoline.

Compound	Mean R_t	Std. Dev. R_t	%RSD R_t	Mean Peak Area	Std. Dev. Area	%RSD Area
Benzene	6.26	0.02	0.258	2732	317	11.6
Toluene	8.969	0.007	0.073	5389	603	11.2
Ethylbenzene	11.292	0.005	0.040	432.5	28.7	6.64
p, m-Xylene	11.574	0.005	0.044	1691	148	8.72
o-Xylene	12.067	0.007	0.058	529.8	58.4	11.0

To show that the INCAT device can be used to yield a reproducible fingerprint of a complex mixture, the Shell-Bronze gasoline was sampled four times. The chromatograms shown in Figure 10 on page 92 were obtained from a 0.10 mL active sampled volume of the static headspace above 2 mL of gasoline in 40 mL containers, for four separate Shell-Bronze gasoline samples. The BTEX peaks in the four chromatograms were used to measure the consistency of the sampling method. Table 9 lists the mean retention times and peak areas of the BTEX compounds for the four trials of the Shell-Bronze gasoline using active sampling of the headspace with the Raven-15 INCAT device. The RSD for the BTEX peak areas ranged from 6.6 to 11.6%. There is a strong indication of preferential adsorption of aromatic compounds found in the headspace over lighter and more volatile compounds which are in

high concentrations in gasoline. Although the presence of these lighter gasoline components is noticeable in the headspace chromatograms, the peak areas are not as high as expected.

FIGURE 9. Comparison of the gas chromatograms obtained from sampling a mixture of BTEX compounds (16.7% v/v of each) by: (a) direct liquid sampling (0.10 μL); (b) a Raven-15 coated INCAT (0.10 mL of HS); (c) a Saran coated INCAT (0.10 mL of HS); and (d) a Super Sorb coated INCAT (0.10 mL of HS).

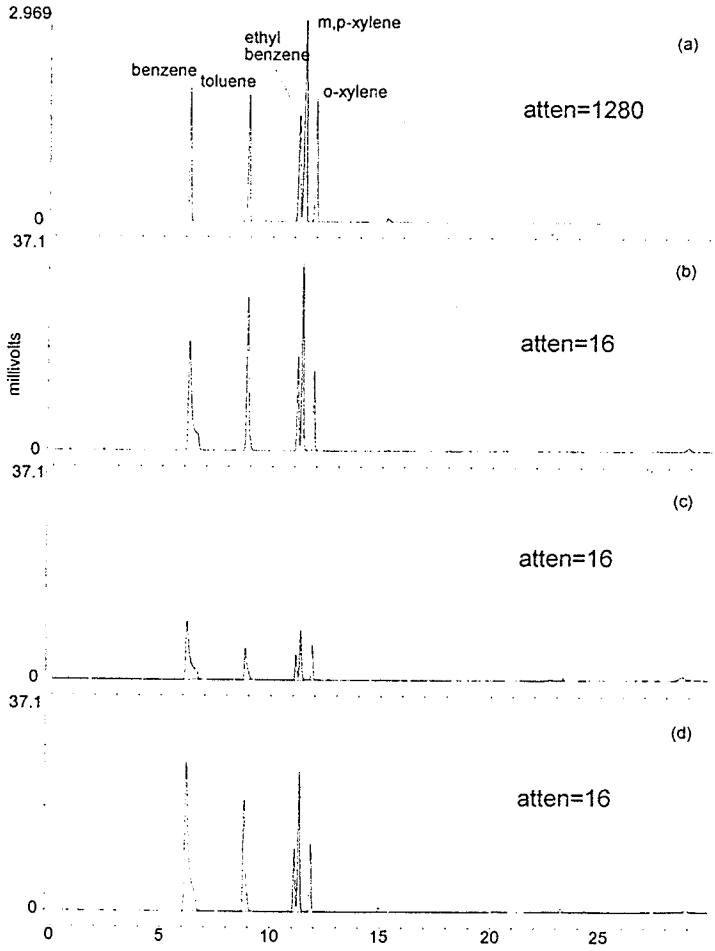


FIGURE 10. GC profiles illustrating the reproducibility in HS sampling (0.10 mL) of Shell-Bronze gasoline with a Raven-15 coated INCAT device (attenuation 4). BTEX compounds correspond to the retention times and area measurements shown in Table 9 on page 90.

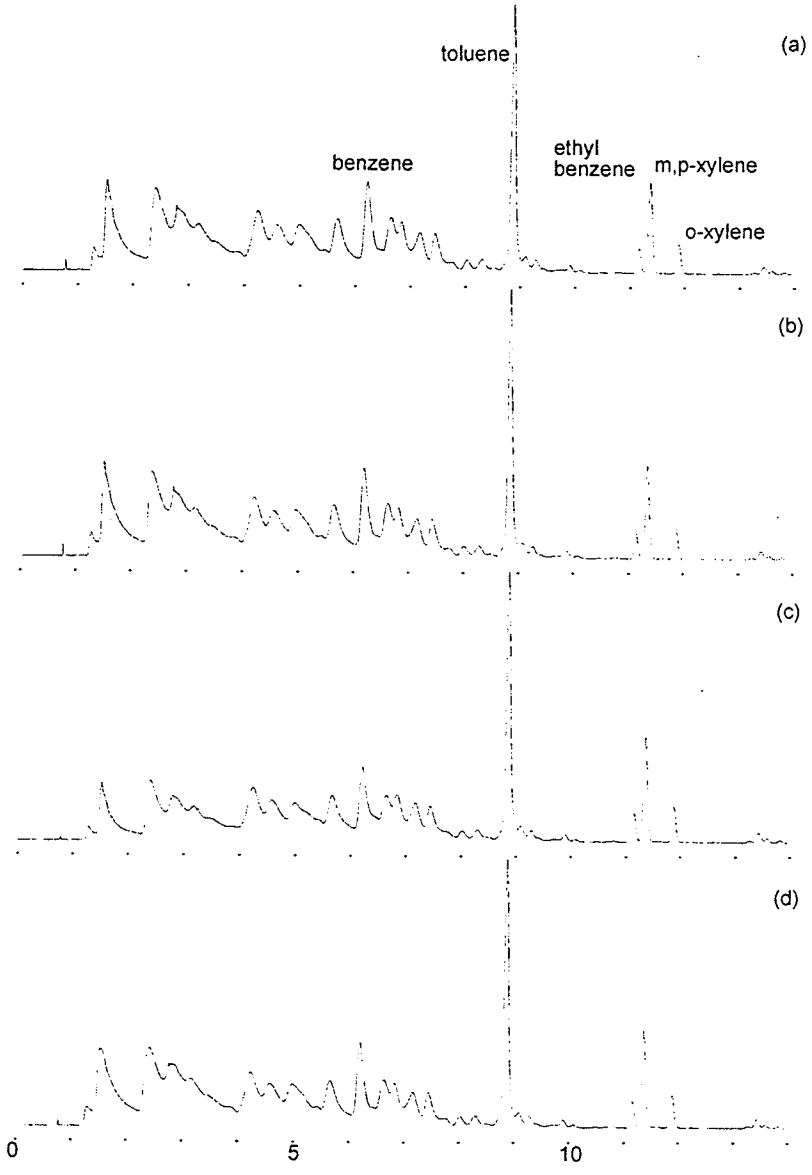


Figure 11 to Figure 16 show direct comparisons between chromatograms obtained using the INCAT to actively sample the headspace and direct liquid sampling for the samples from each class of arson accelerants. The chromatograms have been normalized to percentage of the full scale for qualitative comparison of the fingerprints. The chromatograms obtained for classes 0 and 1 (camp fuel and pocket lighter fluid, Figure 11 and Figure 12 on page 94) show only subtle differences between their respective liquid and headspace peak profiles. According to the liquid sample chromatograms (Figure 11(a) and 12(a)), these mixtures are not very complex in terms of numbers of components (relative to gasoline), and show only low levels of a few BTEX compounds to be present. The similarity between the profiles obtained for the liquid and INCAT headspace sampling suggest that in cases where a liquid sample is not available, the INCAT headspace sampling method can produce a characteristic peak profile of the sample for fingerprint identification.

FIGURE 11. Comparison between the GC profiles of the class 0 accelerant camp fuel, obtained from a direct liquid sample (0.10 μL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL).

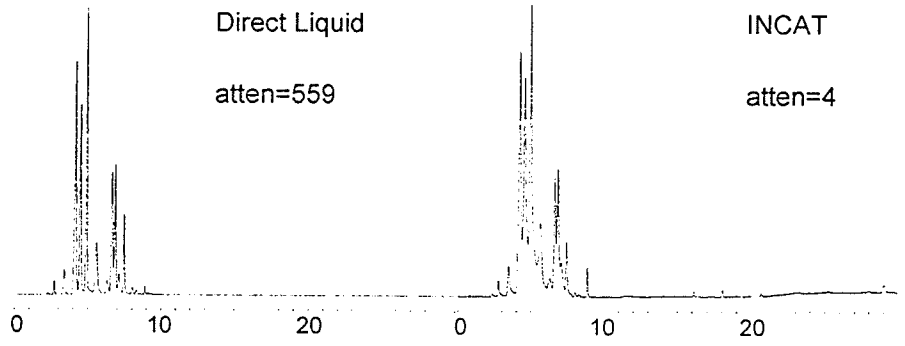
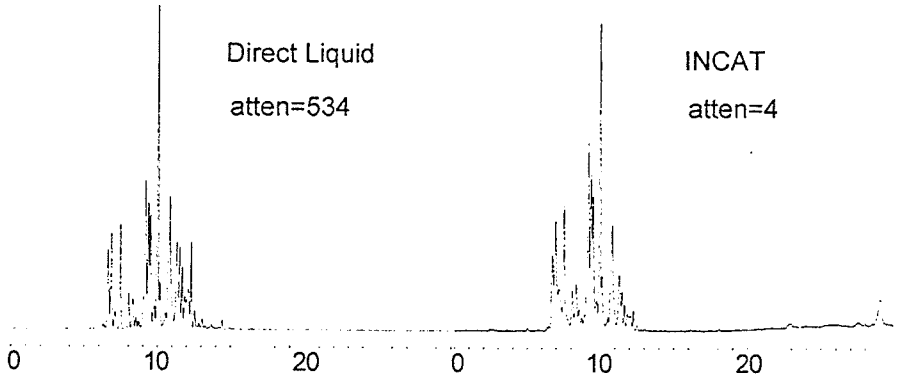


FIGURE 12. Comparison between the GC profiles of the class 1 accelerant Ronsonol pocket lighter fluid, obtained from a direct liquid sample (0.10 μL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL).



The liquid and headspace sample chromatograms for the different grades of gasoline shown in Figure 13 on page 96, again indicates the preferential adsorption for aromatic compounds on the coating inside the device. From these chromatograms, it is clear that the

lighter components, appearing at shorter retention times, are not as abundant as expected in the headspace sample. BTEX compounds are more abundant than lighter and more volatile compounds when the INCAT device is used. This indicates that the Raven-15 coating has a greater affinity for the aromatic species in the headspace. The presence of BTEX compounds in headspace samples at different levels allows for differentiation of gasolines rated with specific octane numbers, from other classes of accelerants and from each other. However, it is likely that the differences in the relative amounts of BTEX compounds may be too subtle to positively identify a particular brand of gasoline among samples with the same octane rating. In such situations, the monitoring of a few more characteristic peaks would be required to positively identify the manufacturer of the gasoline.

The chromatograms obtained for the two paint thinner samples — the class 3 accelerants (Figure on page 96) — show very similar amounts of BTEX components. The presence of BTEX components in this case is sufficient to positively identify the two samples as class 3 accelerants. However, Varsol® and the generic brand of paint thinner could not be differentiated on the basis of BTEX compounds alone. There are a few characteristic peaks in both the initial and final regions of the headspace chromatograms, that do allow distinction between the samples.

FIGURE 13. Comparison between the GC profiles of the class 2 accelerant gasoline, obtained from a direct liquid sample (0.10 μL) and a headspace sample using a Raven-15 coated INCAT device (0.10 mL), for: (a) Shell-Bronze (octane rating 87); (b) Shell-Silver (octane rating 89); and (c) Shell-Gold (octane rating 91).

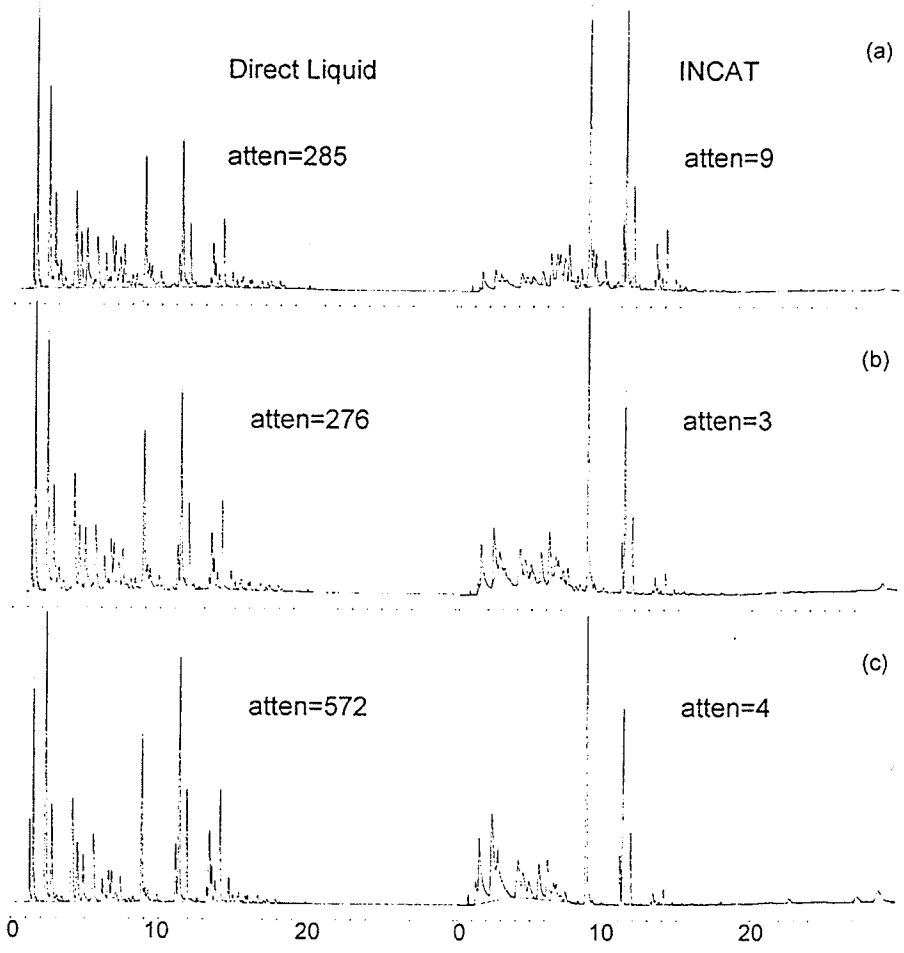


FIGURE 14. Comparison between the GC profiles of the class 3 accelerant paint thinner, obtained from a direct liquid sample (0.10 μL) and a HS sample using a Raven-15 coated INCAT device (0.10 mL), for: (a) Varsol®, and (b) a generic brand of paint thinner.

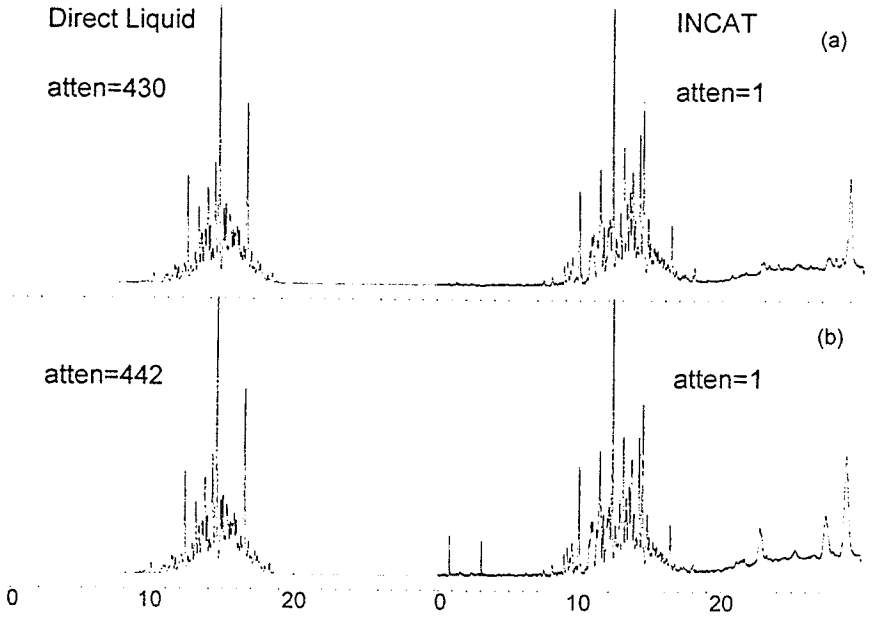
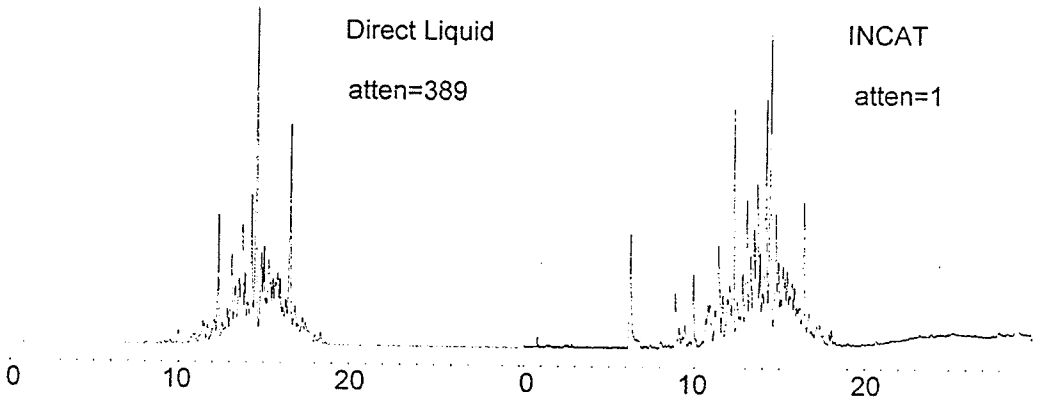


Figure 15 on page 98 shows the chromatograms obtained from direct liquid and headspace sampling of the class 4 accelerant, kerosene. As with the class 0 and 1 accelerants, the chromatograms obtained for the liquid and headspace samples are very similar. The chromatograms can be distinguished based only of the differences in the relative amounts of a few peaks, one of which is the obvious benzene peak. The relative amounts of BTEX compounds in the headspace are present at characteristic levels relative to the other classes of accelerants. Therefore, the BTEX compounds can be used to distinguish kerosene from the

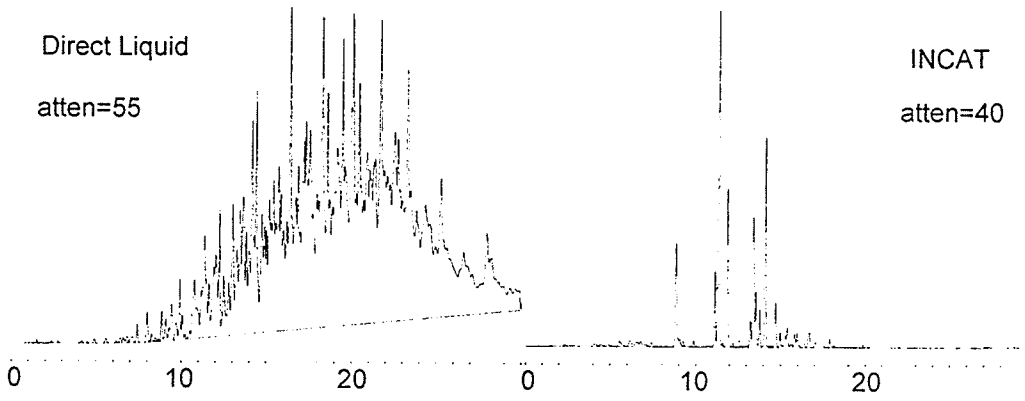
other classes. In addition, the similarity between the two chromatograms of Figure 15 once again illustrates how the INCAT device would be useful for sampling the headspace when a liquid sample is not available.

FIGURE 15. Comparison between the GC profiles of the class 4 accelerant kerosene, obtained from a direct liquid sample (0.10 μL), and a HS sample using a Raven-15 coated INCAT device (0.10 mL).



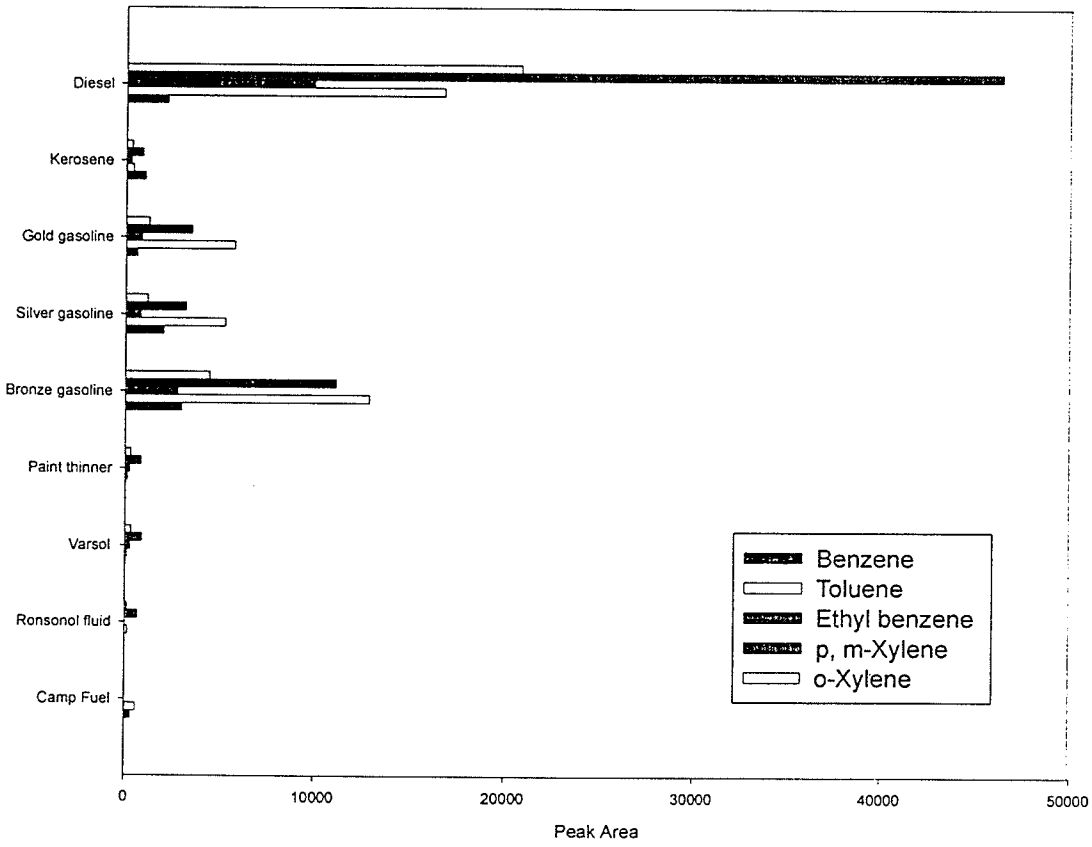
The chromatograms obtained from the liquid versus INCAT headspace sampling of diesel fuel (Figure 16 on page 99), a class 5 accelerant, show the most noticeable difference in the peak profiles. All of the BTEX compounds are present, and most are in greater amounts relative to their levels in gasoline samples. Only benzene is less abundant in diesel fuel than in the Bronze grade of gasoline, which contained the highest levels of BTEX compounds relative to accelerants from classes 0 to 4.

FIGURE 16. Comparison between the GC profiles of the class 5 accelerant diesel fuel, obtained from a direct liquid sample (0.10 μL), and a headspace sample using a Raven-15 coated INCAT device (0.10 mL).



The bar chart shown in Figure 17 on page 100, represents the data for the absolute peak areas of BTEX compounds observed in the six classes of accelerants. From the relative amounts of BTEX compounds in representative samples for each class, it is possible to discriminate between the classes of accelerants. To distinguish between different brands of a sample within a specific class (e.g., Varsol® and the generic paint thinner), it would be necessary to monitor additional peaks. Since the aromatic components in these samples tend to be preferentially adsorbed by the Raven-15 adsorbent, it would be useful to identify a few more characteristic aromatic compounds by GC-MS.

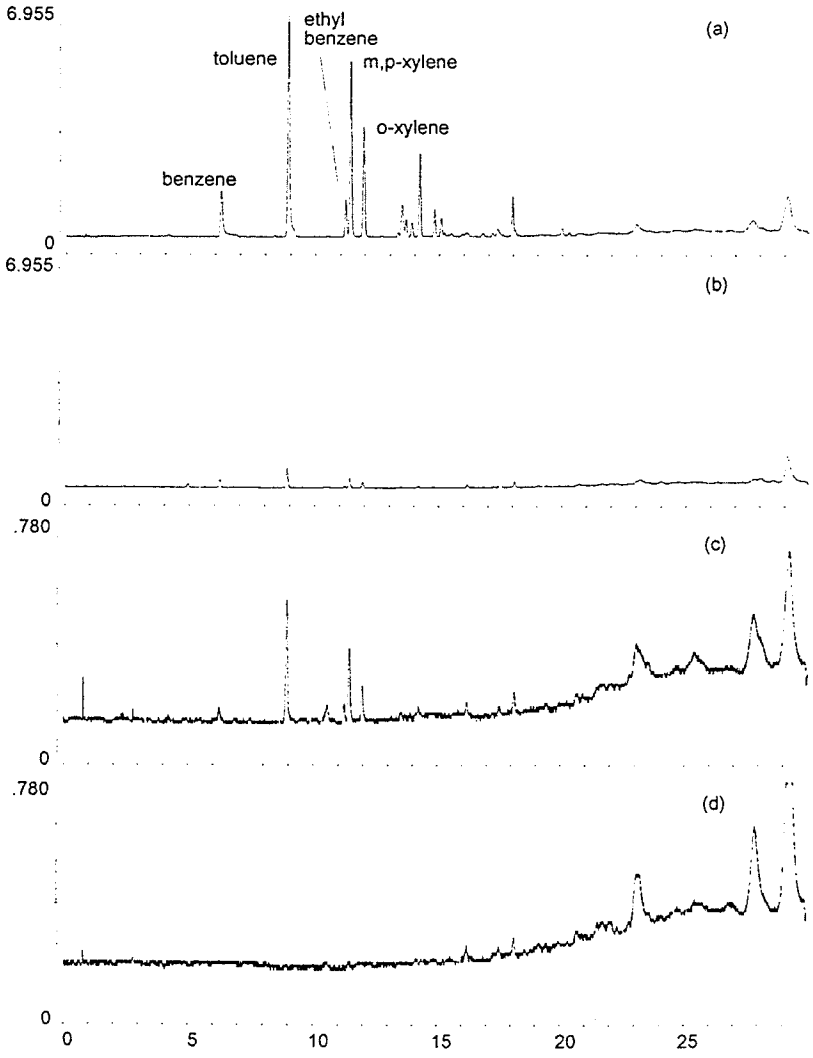
FIGURE 17. Bar chart comparison of the absolute peak areas of BTEX compounds observed from static HS sampling (0.10 mL with Raven-15 INCAT device) of the mixtures from the six classes of arson accelerants.



The chromatograms in Figure 18 on page 102 were obtained with the INCAT device by active sampling of the static headspace of the aqueous solution saturated with Shell-Bronze gasoline (Figure 18(a)), the 1:1000 diluted solution of the latter (Figure 18(b) and (c)), and a blank (Figure 18(d)). The aqueous solution saturated with gasoline (Figure 18(a)) shows all of

the BTEX compounds, as well as some of the other VOCs. This profile is not comparable to that of the Bronze gasoline, shown in Figure 10 on page 92 and Figure 13 on page 96, due to the different solubilities of the various components in water. The diluted aqueous gasoline solution chromatograms (Figure 18(b) and (c)) are also shown to contain all of the BTEX compounds. The remaining peaks ($R_t \geq 20$) are likely to be the result of irreversible adsorption of some of the adsorbates which may gradually lead to the formation of a tar on the adsorbing surface [13] — which is slowly decomposing upon repeated use of the INCAT sampler. A more thorough cleaning step may be required to reduce the amount of tar buildup, such as passing a reactive gas through the device during the cleaning run, or a periodic longer baking period. It should be noted that during the course of these experiments, the Raven-15 INCAT device was used for more than 60 manual injections, and is still being used. It is not surprising then that there may be a gradual buildup of these irreversibly adsorbed compounds — the effects of which became more prevalent in the background with increased use of the device

FIGURE 18. HS-GC profiles from active sampling 10.0 mL of the static HS above: (a) an aqueous solution saturated with Shell-Bronze gasoline, attenuation 3; (b) a 1:1000 dilution of the aqueous solution saturated with Shell-Bronze gasoline, attenuation 3; (c) the 1:1000 diluted solution at attenuation 1; and (d) a blank INCAT at attenuation 1.



In order to estimate the amounts of the BTEX compounds present (an upper bound

estimate), the solubilities of each of pure BTEX compounds in water can be used. Thus, the 1:1000 diluted solution is estimated to contain (w/v): 1.78 ppm of benzene, 0.515 ppm of toluene, 0.152 ppm of ethylbenzene, 0.198 ppm of p-xylene, 0.200 ppm of m-xylene, and 0.175 ppm of o-xylene. The other species present in gasoline will, however, affect the solubilities of the individual components. Pure benzene has a water solubility in the pure phase of 1780 ppm, but in the presence of the other components of gasoline, its solubility is reduced to 65 ppm [14]. Thus, the upper bound estimate of the BTEX levels in the 1:1000 diluted solution of saturated aqueous gasoline is very generous. The INCAT device, when sampling at room temperature and sampling less than a third of the headspace volume (10.0 mL out of 35.0 mL of headspace), enabled detection of 65 ppb of benzene in the 1:1000 diluted solution. The limit of detection could still be reduced further by increasing the volume of the headspace that is actively sampled, or by heating the sample to increase the headspace concentration of the VOCs prior to sampling.

3.4 Conclusion

Static headspace sampling of complex mixtures is extremely useful for fingerprint identification of mixtures when liquid samples are not available. Sampling of the headspace

above samples can be achieved without solvent extraction The INCAT device can be used to sample the headspace of a sample and concentrate the analytes inside the device. Thermal desorption of the analytes from the INCAT directly into the GC, simplifies the extraction and analysis procedure.

The INCAT device has been shown to enable reproducible GC fingerprints of complex mixtures of VOCs, with an average RSD of 9.8%. Using the INCAT device, the distinction between different classes of accelerants has been achieved using only five target peaks corresponding to BTEX compounds. The INCAT device provides a novel approach the characterization of complex mixtures for fingerprint analysis. Concentration of the headspace analytes inside the device allows for larger volumes of the headspace to be sampled without requiring cryogenic focussing. The INCAT sampling technique thus provides a sensitive alternative to the conventional methods of direct headspace sampling, like CLS and P&T methods. Moreover, the solventless extraction aspect of active sampling with the INCAT device, simplifies the sampling method without requiring time to reach an equilibrium with the headspace analytes.

References

[1] F. J. Debbrect, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 7, John-Wiley and Sons, New York (1995).

[2] J. M. Loeper, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 14, John-Wiley and Sons, New York (1995).

[3] B. Kolb and L. S. Ettre, *Static Headspace Gas Chromatography: Theory and Practice*, ch.8, Wiley-VCH, New York (1997).

[4] K. Robards, P. R. Haddad and P. E. Jackson, *Principles and Practice of Modern Chromatographic Methods*, ch. 8, Academic Press, London (1994).

[5] C. L. Arthur and J. Pawliszyn. *Anal. Chem.*, **62**, 2145 (1990).

[6] D. Louch, S. Motlagh and J. Pawliszyn. *Anal. Chem.*, **64**, 1187 (1992).

[7] C. L.Arthur, L. Killam, K. D. Buchholz, D. Potter, M. Chai, Z. Zhang and J. Pawliszyn. *Environmental Lab*, **11**, 10 (1992).

[8] Z. Zhang and J. Pawliszyn. *Anal. Chem.*, **65**, 1843 (1993).

[9] C. L. Arthur, M. Chai and J. Pawliszyn. *J. Microcol. Sep.*, **5**, 51 (1993).

[10] M. E. McComb, R. D. Oleschuk, E. Giller and H. D. Gesser. *Talanta*, **44**, 2137 (1997).

[11] S. Shojania, R. D. Oleschuk, M. E. McComb, H. D. Gesser and A. Chow, *Talanta*, **50**, 193 (1999).

[12] T. A. Brettel, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 13, John-Wiley and Sons, New York (1995).

[13] J. W. Hassler, *Purification with Activated Carbon*, pp 65-68, Chemical Publishing Co., Inc., New York (1974).

[14] B. Bauman. EPA OUST National Conference, Charlotte, NC, March 1997.

CHAPTER 4

Qualitative Analysis of Simulated Arson Debris Using an Activated Carbon INCAT Device

4.1 Introduction

It has been estimated that 15% of all fires across Canada are the result of arson, with an additional 25 to 30% undetermined in the cause [1]. In the absence of the actual numbers of fires, these percentages do not truly reflect the severity of this sort of crime, nor the damage or cost that results from them. If we consider, for example the province of Manitoba, then the frequency of incendiary fires can be put into perspective. The values listed in Table 10 are the Manitoba fire loss statistics due to arson or suspicious fires for the period of 1993 to 1997 [2]. The numbers of arsons or suspicious fires listed in Table 10 includes fires resulting from vandalism and juvenile fire setting.

TABLE 10. Province of Manitoba 1993-1997 summary statistics for fires due to arson or suspicious origin [2].

Year	No. of Fires Labelled as Arson or Suspicious	Percent of Total No. of Fires	Cost of Property Damage Due to Arson or Suspicious Fires	Total No. of Fires	Total Cost of Property Damage
1993	2009	35	16.5 million	5746	52.3 million
1994	2555	37	20.8 million	6963	67.9 million
1995	2041	35	11.6 million	5839	50.5 million
1996	1668	32	21.2 million	5164	69.6 million
1997	1756	35	19.3 million	5018	68.0 million
Mean	**2006**	**35**	**17.9 million**	**5746**	**61.7 million**

Fortunately, not all fires are in need of in-depth investigation since the cause may be obvious (to police). However, in instances where a fire requires in-depth investigation, it is referred to the Office of the Fire Commissioner (OFC) which must determine or classify the cause of the fire. It is these investigations that necessitate the use of forensic analysis to confirm or rule out the fire as incendiary. Fires that are referred to the OFC for investigation occur under the following circumstances [3]:

- fires resulting in fatalities;
- fires resulting in serious injury;
- fires initiated by, or resulting in explosions;

- any fire of suspicious origin in which the cause cannot be positively determined;
- any structure fire where the cause is not positively determined; and
- any fire which the Fire Chief considers to be a major loss within the community.

All fires that are referred to the OFC for investigation must be categorized as one of the following: incendiary (arson), accidental, undetermined accidental, or undetermined suspicious. In 1997, of the 5746 fires that occurred in Manitoba (Table 10 on page 108), 355 fires [2] (see Table 11 on page 110) were referred to the OFC for investigation (equivalent to one investigation every 24.7 hours). Any fire that is investigated requires many samples of debris — as outlined in Ch. 1.4 — along with multiple trials of any given sample. As such, these numbers of analyses occupy a significant amount of time on the part of the forensic analysts who try to positively determine the cause of the fire. Within Manitoba, there is only one forensic facility, the RCMP Forensic Laboratory. Only four forensic analysts within the chemistry division are charged with the responsibility of analysing fire debris [4], a sundry of other forensic obligations including recovering and comparing all non-biological trace evidence for any criminal investigation (paint, footwear, glass, fibres, textiles, insulation, soil, explosive debris, and commercial products) [5]. Even with automation of GC injections, the amount of time associated with sample preparation for the analysis of fire debris still occupies a large percentage of the analyst's time. As such, any methods that might decrease the amount

of time required to prepare or analyse fire debris would aid in the overall cost resulting from fire investigation.

TABLE 11. Manitoba OFC fire investigations by cause from 1997.

	Province of Manitoba		City of Winnipeg	
Conclusion	Investigations	Percent of Total (Manitoba)	Investigations	Percent of Total (Winnipeg)
Accidental	128	36	82	37
Arson	149	42	109	50
Suspicious	60	17	24	11
Undetermined	18	5	4	2
Total	**355**	**100**	**219**	**100**

In Ch. 3, it was demonstrated that the activated carbon INCAT device could be used to obtain GC fingerprints that allowed discrimination between the six classes of arson accelerants, based only on the five peaks associated with the BTEX compounds. In this chapter, the same commercial petroleum distillates from the six classes of accelerants are sampled from simulated fire debris. Simulation of the fire debris was achieved by weathering the petroleum distillates to account for loss of analyte due to burning or exposure to high temperature. The nine commercial products that might be used as arson accelerants were weathered to 88-95% of their original mass (i.e., percent of analyte mass lost). A small aliquot of the weathered accelerant (see Table 12 on page 114) was then sampled in the presence of

burnt wood to determine if the INCAT device was able to adsorb VOC analytes from the weathered accelerants above any background produced by the burning or pyrolysing of wood [4].

As it was discussed in Ch. 1.4, the sample container (one-quart or one-gallon untreated paint cans, or glass jars) filled 1/2 to 2/3 full of fire debris, is usually heated to increase the analyte mass in the static headspace [6]. The entire static headspace is then actively drawn through some sort of activated carbon SPE tube (the common approach). In this study, no heating of samples was done in order to first determine whether the INCAT device could be used to easily obtain a GC fingerprint of the accelerant under normal temperatures. In addition, the INCAT device was used to obtain a GC fingerprints of the liquid accelerants in smaller sample containers — hence, a smaller static headspace volume — and sampling only a fraction of the headspace (25% of the available headspace). The sampling of the liquid accelerant in smaller sample containers was also done in the absence of fire debris to determine the difference in fingerprints when burnt material is present (i.e., differences in background VOCs, and in component ratios due to sorption by the fire debris).

4.2 Experimental

The INCAT devices used in this study were fabricated from 26 gauge (0.25 mm i.d., 0.46 mm o.d.) stainless steel capillary tubing (Small Parts Inc., Logansport, IN). A single continuous length of capillary (30.0 cm) was coated and subsequently cut into six 5.0 cm segments. Raven-15 activated carbon paint was drawn through the entire length of the 30.0 cm capillary, until 6 mL of paint had passed through. The paint was drawn through the capillary via a vacuum line with a trap attached to obtain the paint after it passed through the capillary. The Raven-15 paint was made from a 15% (w/w) suspension of the Raven-15 carbon black (Columbian Carbon Co., New York, NY) in 8.0% (w/w) solution of Silwet L-7604 surfactant (Union Carbide, Danbury, CT) in isopropanol (Fisher Scientific Co., Fair Lawn, NJ). Once coated, the entire length of capillary was baked at 300°C for six hours while passing helium gas through the capillary. The capillary was then cut into 5.0 cm segments, and each fitted with Luer-Lok ends to yield six INCAT devices with 2.06±0.03 mg of carbon per cm^2 along the interior wall of the capillary. Of these six INCAT devices, only two were used in this study: one to sample the simulated arson samples, and one to sample weathered accelerants in the absence of burnt material.

The weathered accelerants were prepared from the commercial samples listed in

Table 7. Weighed amounts of each sample were heated in a sand bath to a boil. The boiling sample was heated until approximately 90% of the volume had been evaporated. The samples were then allowed to cool to room temperature and weighed to determine the final mass after the loss from vaporization. Table 12 lists the accelerants used in this study, and the amount of weathering (percent loss by weight) to each sample.

In order to simulate the characteristic GC profile for accelerants which might be found in arson debris, burnt material needed to be included with the weathered accelerants. In this manner, the headspace of the sample container would contain VOCs that are released from the fire debris, as well as those from residual accelerant. The fire debris for this study was chosen to be a 'hardwood' that would release only low levels of VOCs to the headspace.

The burnt wood samples were prepared by heating wood blocks ($2\times4\times15$ cm^3) in a kiln. The pieces of wood were all cut from a single untreated oak plank, i.e., no paint, stain or fire retardant treatment (FRT). The oak blocks were distributed in the centre of the kiln, and were surrounded by insulating bricks in order to prevent direct contact between the wood and the propane flame from the kiln's burner. The temperature inside the kiln was raised gradually for 43 min, at which point the wood self-ignited at approximately 300°C [7]. The wood was allowed to burn for a few minutes in order to ensure that all of the blocks had in fact ignited. The burning samples were then cooled with minimal amounts of water, and then placed in

sealed 1.0 L mason jars, with two blocks per jar (approximately 25% of the jar volume). The lids of the jars had a small hole that was covered with Magic™ Tape (Scotch™, St. Paul, MN). The purpose of this hole was to allow the INCAT device to pierce the tape and sample the headspace of the mason jar. Once the INCAT was withdrawn from the container, the hole was resealed with tape. The lids of the mason jars were all fitted with a rubber seal to prevent loss of analyte.

TABLE 12. Amount of weathering of the arson accelerants used for the analysis of simulated fire debris.

Class No.	Sample	Amount Weathered (%)
0	Camp Fuel	89
1	Ronsonol	90
2	Shell Bronze Gasoline	88
2	Shell Silver Gasoline	95
2	Shell Gold Gasoline	94
3	Varsol®	90
3	Generic Paint Thinner	90
4	Kerosene	91
5	Shell Diesel	90

In each of the jars, a small piece (3.0×3.0 cm^2) of Kimwipe® tissue (Kimberly-Clark Corp., Rosewell, CA) was placed, and a single 1.0 μL drop of a weathered accelerant (from the samples listed in Table 12) was absorbed by the tissue. In addition, there were two sample

jars — one with two blocks of burnt wood, and one with two blocks of the unburnt wood — that contained the Kimwipe® tissue, but with no accelerant. These two jars were prepared as sample blanks, so that the background levels of VOCs released from both the burnt and unburnt material could be observed.

For comparative purposes, 1.0 μL of each accelerant was placed on a 3.0×3.0 cm^2 Kimwipe® inside 40 mL sealed GC vials with septa. A blank sample with the Kimwipe® tissue and no accelerant was also prepared. The purpose of these samples was to determine how much the presence of the fire debris would affect the characteristic HS-GC profile of the accelerant, and to see if the accelerants can be differentiated by comparison to headspace samples of similarly weathered accelerants in the absence of fire debris. Even though both sets of samples (those with fire debris and those without) have the accelerants present with the same level of weathering, and both have been absorbed by the Kimwipe®, it is unlikely that the headspace concentrations of the VOCs are present in the same proportions. Different proportions of the individual components of each VOC mixture would likely result because the equilibrium concentration in the headspace of the mason jars with fire debris will involve sorption of the analytes by the debris itself.

Headspace sampling of the mason jars with accelerant and fire debris was performed

using a mechanical personal air sampler (PAS-3000, Spectrex Corp., Redwood City, CA), to actively draw 500 mL of the headspace volume through the INCAT device (100 mL/min for 5 min). Hence, half of the volume of the mason jar was removed. The sampling of the GC vials containing only accelerant and Kimwipe®, was done manually via a gas-tight syringe (Hamilton Co., Reno, NV), and sampling 10 mL of the headspace at a rate of 10 mL/min. It should be noted that active sampling of the headspace for both sets of samples — the mason jars with accelerant, Kimwipe® and fire debris, and the GC vials with only accelerant and Kimwipe® — were done at room temperature, and the sample containers were not heated at all (to increase the amount of headspace analyte) prior to sampling. For each sample studied, once the headspace sample had been drawn through the INCAT, the Luer-Lok end of the INCAT device was plugged with a small piece of septum, and the device was immediately inserted into the injection port of the GC for thermal desorption.

Gas chromatography was performed using the same instrumentation and column type, as described in Ch. 3.2 (on page 84). Analytes were thermally desorbed from the INCAT device in the heated injection port (300°C) of the GC for two minutes. The initial column temperature was held at 30°C for the two minute injection time. The temperature of the column was ramped to 200°C at a rate of 8°C/min and held for five minutes. The column was

then heated to a final temperature of 250°C at a rate of 20°C/min, and held at this temperature for five minutes. The detector temperature was 300°C, and the entire run time for the separation was 36 minutes. A second thermal desorption injection of the device was performed to ensure that the entire sample had been desorbed in the first two minute injection and indicated that no carry-over occurred.

4.3 Results and Discussion

These experiments were designed to determine if the activated carbon INCAT device was able to obtain sufficient analyte from the static headspace of weathered (residual) accelerants, for the purpose of obtaining a GC fingerprint. The previous study (Ch. 3) had already demonstrated that the Raven-15 activated carbon INCAT devices were able to obtain reproducible fingerprint chromatograms of complex mixtures of VOCs. However, in this study, although the samples of accelerants are the same as those previously studied, the resulting chromatograms were expected to differ greatly. The weathering of the accelerants, resulting from burning or exposure to intense heat, reduces the amount and number of components in the mixture. As a result, only the compounds present in the largest quantities, or those which are less volatile, are likely to be present in any detectable quantity.

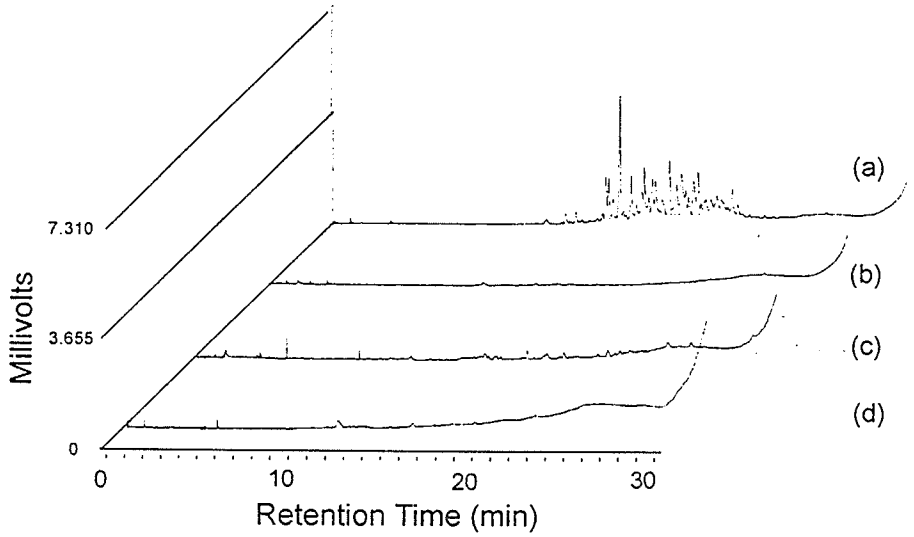
In the previous chapter, accelerants studied were sampled from the headspace above 2 mL of the liquid sample inside 40 mL GC vials. Although these same 40 mL GC vials were used in this study, only 1.0 μL of the liquid was present, and the liquid was absorbed by the Kimwipe® tissue. Hence, the equilibrium established would not simply be between the liquid and vapour phase. Rather, the equilibrium would be between the absorbed liquid on the Kimwipe® and the vapour phase. This difference in equilibrium, coupled with the fact that 88-95% of the components were lost from the sample, implies that the sampling is not likely to produce the same fingerprint for the headspace as in the samples in Ch. 3.

The inclusion of burnt wood for this study was to determine whether detectable HS-GC fingerprints above small quantities of weathered accelerants, were possible in the presence of burnt material that might introduce pyrolysis products to the background. In addition, burnt wood was included into the samples to observe differences in the headspace profile when a sorbing material, such as burnt or charred wood, is present. Since the charring of wood produces a highly adsorbing carbonaceous product, and the wood itself is an absorbing material, an equilibrium concentration between the headspace and the carbonised wood will result, thereby altering the ratios of the components in the headspace.

The four profiles shown in Figure 19 on page 119 are of the blank desorption of the INCAT device (no headspace sampling), along with the profiles from INCAT sampling of

unburnt wood (no accelerant), burnt wood without accelerant, and burnt wood with an accelerant. All of these profiles are shown at attenuation 3, and demonstrate that there is no significant interference from the background produced by desorption of the INCAT device, or volatile products from the pyrolysis of the wood. In fact, the burnt wood sample shows less background interference than the unburnt sample.

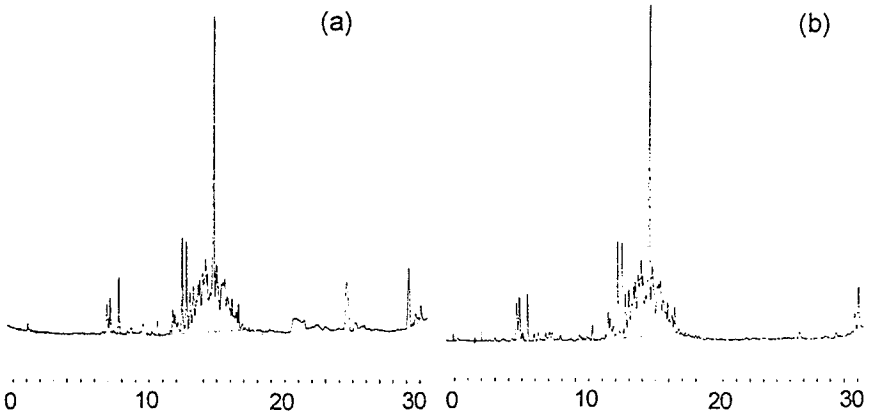
FIGURE 19. GC profiles for comparison of (a) 88% weathered Shell-bronze grade gasoline sampled from the HS of fire debris; (b) the HS of burnt wood with no accelerant present; (c) the HS of unburnt wood with no accelerant present; and (d) a blank INCAT (no sample). All chromatograms are shown at attenuation 3 and were all obtained from the same Raven-15 INCAT device.



Figures 20-25, show the direct comparisons between the headspace profiles — shown normalized to percent of full scale — of the examples from the six classes of accelerants

actively sampled in the presence of burnt wood, and in controlled samples in the absence of fire debris. Recall that the sampling of the accelerants in the presence of burnt wood was done from 1.0 L mason jars, packed 1/4 full of fire debris, and with 500 mL of headspace sampled. The profiles of the accelerants in the absence of the fire debris were sampled from 40 mL GC vials. Both sample containers contained only 1.0 μL of the liquid accelerant absorbed on a small piece of Kimwipe® tissue. It should be noted that although the retention times have been included into these figures, they can only be used to compare the samples from a given group (i.e., all of the samples from the mason jars, or all of the samples from the GC vials). The fire debris samples were all collected on the same day, but the samples of the weathered accelerants in the absence of fire debris were collected several weeks later, and therefore the instrumental conditions cannot be considered to be identical to due electronic drift and slight deviations in the carrier gas flow rate.

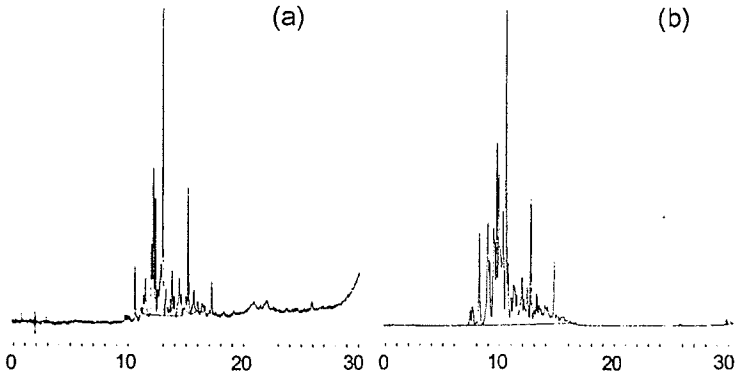
FIGURE 20. Comparison between the HS-GC profiles of the 89% weathered class 0 accelerant, camp fuel, sampled with a Raven-15 INCAT device (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 5).



The profiles for the headspace chromatograms of the 89% weathered camp fuel (Figure 20), a class 0 accelerant, are observed to be more complex in the weathered state than in the unweathered state shown in Ch. 3 (Figure 11 on page 94). The INCAT samples of the weathered accelerant in both cases (in the presence or absence of burnt wood), show more peaks than observed in the unweathered sample. There are approximately 25 peaks seen observed in both (a) and (b) of Figure 20, although some are incompletely resolved split peaks. However, both the direct liquid and INCAT sample of the unweathered accelerant in Figure 11 show only 14 distinct peaks, although additional peaks might be resolved by modification of the GC temperature program. Many components observed in the profile of the

weathered samples would have been present in very small proportions in the unweathered samples, and thus obscured by the more abundant compounds in the GC profile. Nevertheless, the weathered sample demonstrates that even with the majority of the lighter components lost from the weathering of the accelerant, there are still sufficient components present at detectable levels to obtain a GC pattern indicating the presence of the accelerant in the headspace.

FIGURE 21. Comparison between the HS-GC profiles of the 90% weathered class 1 accelerant, Ronsonol pocket lighter fluid, sampled with a Raven-15 INCAT device (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 23).



The 90% weathered class 1 accelerant, Ronsonol pocket lighter fluid, shows very similar profiles (Figure 21) to that obtained from the unweathered sample in Ch. 3 (Figure 12 on page 94). The similarity between the weathered and unweathered headspace profiles is demonstrable only in the numbers of observed peaks, as the relative proportions differ. A few

additional small peaks appear in the weathered Ronsonol profiles, in part due to slight modification of the GC temperature program in these samples compared to those from Ch. 3, but also because these components are present at very low levels in the unweathered sample, and thus obscured in the unweathered GC profile. The similarity in the profiles between the weathered and unweathered samples would likely allow simple identification of this accelerant from sample fire debris — in that the same components are apparent, only in different relative proportions.

The headspace samples of the three samples of Shell gasoline (class 2 accelerants), show much more complex profiles than observed in the unweathered samples in Figure 13 on page 96. The weathered sample profiles — from sampling in the presence and in the absence of fire debris — show very few peaks in the initial portion of the profile (R_t<10 min in the fire debris sample, and R_t<8 min in the control sample). Both the direct liquid and INCAT samples in Figure 13 showed significant numbers of compounds present in the initial region, which have clearly been lost due to the weathering of the accelerants. However, despite the loss of the characteristic and abundant lighter components used for increasing the combustion properties of gasoline, the weathered gasoline profiles in Figure 22 indicate that there are still many detectable peaks among the three grades of gasoline to provide a characteristic profile for qualitative comparison. In addition, the differences in the relative proportions of the

components between the fire debris samples and the controls, indicate the importance for comparison of true fire debris samples to similarly weathered accelerants in the presence of burnt material. The relative proportions of the gasoline components are clearly affected by the sorption of analyte onto the fire debris itself.

FIGURE 22. Comparisons between the HS-GC profiles of three different octane grades of Shell gasoline (class 2 accelerants) from sampling (a) in the presence of burnt wood, and (b) in the absence of any fire debris.

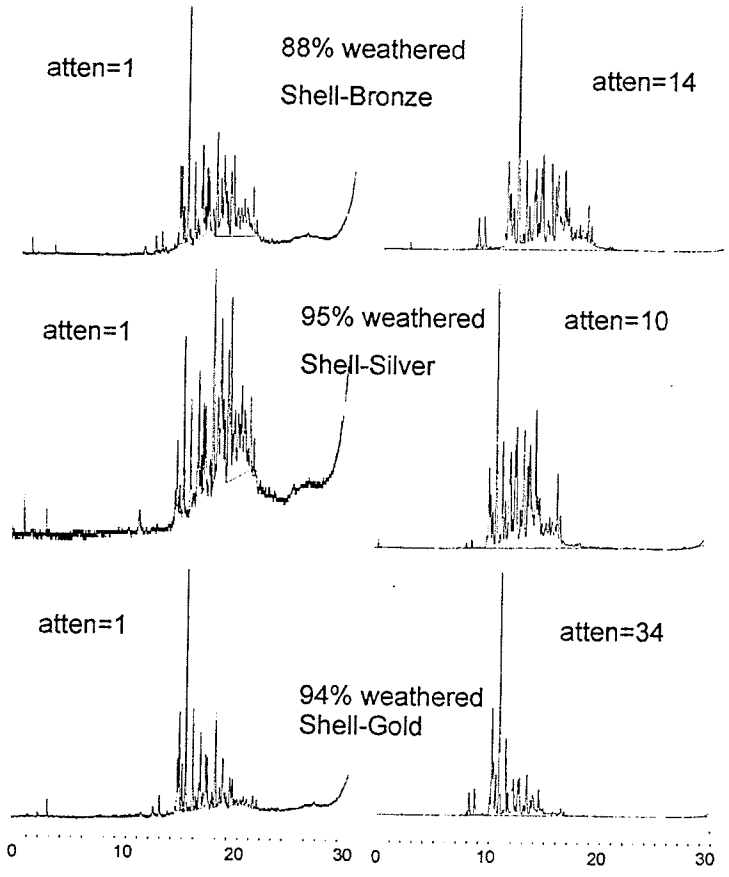
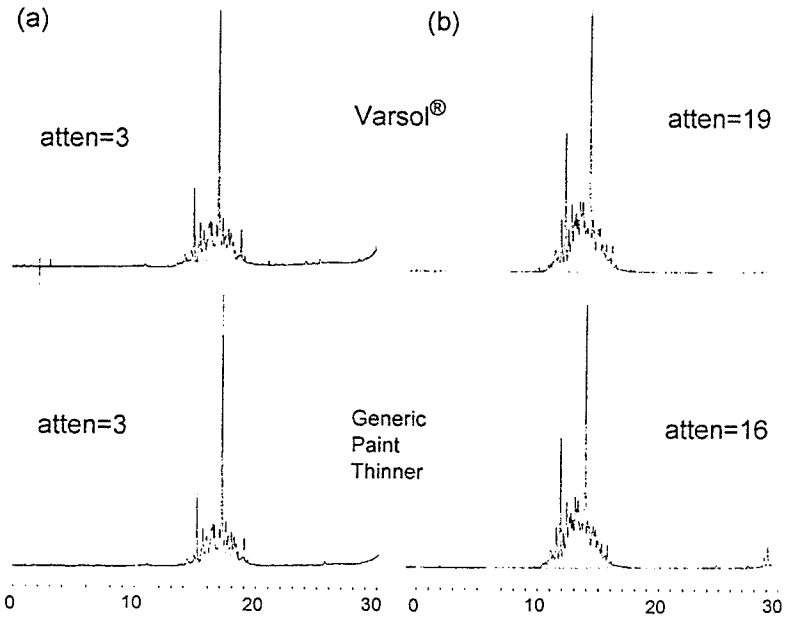


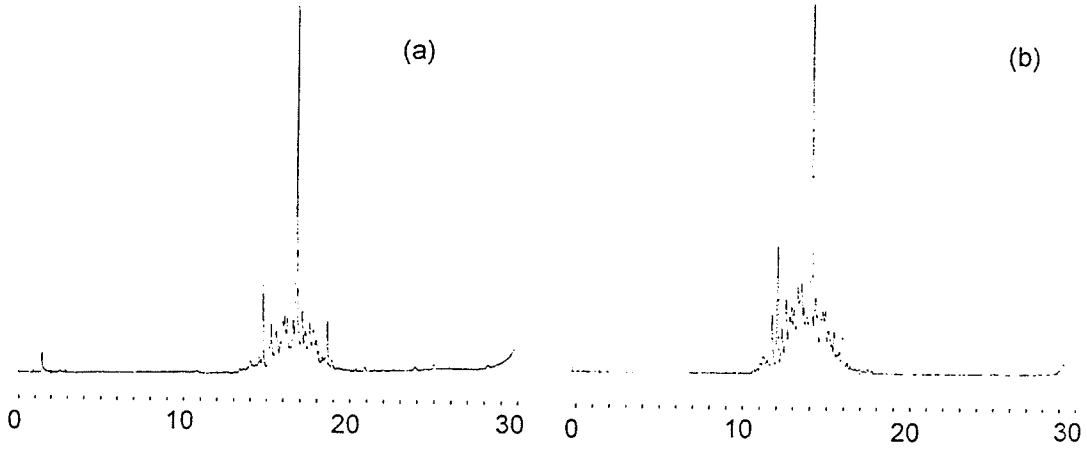
FIGURE 23. Comparisons between HS-GC profiles form two 90% weathered class 3 accelerants, Varsol® and a generic paint thinner, sampled (a) in the presence of fire debris, and (b) in the absence of fire debris.



The weathered class 3 accelerants, Varsol® and the generic paint thinner (both 90% weathered), display virtually identical profiles between the two samples from fire debris (Figure 23), although the profiles do differ in relative proportions of the components from their respective control samples. However, the differences between the profiles of the fire debris samples, and the control samples are not so significant. Identification of the class of accelerant is therefore possible from simple comparison to the control. The fact that the two types of paint thinner give almost identical profiles is not surprising since the profiles

obtained from the unweathered samples in Ch. 3 (Figure on page 96) showed almost identical profiles as well. In fact, the only way to distinguish the two paint thinners was by a few peaks in the initial and final regions of the chromatograms, which are not present in the weathered samples chromatograms.

FIGURE 24. Comparison between the HS-GC profiles of the class 4 accelerant kerosene, sampled (a) in the presence of fire debris (attenuation 3), and (b) in the absence of fire debris (attenuation 15).



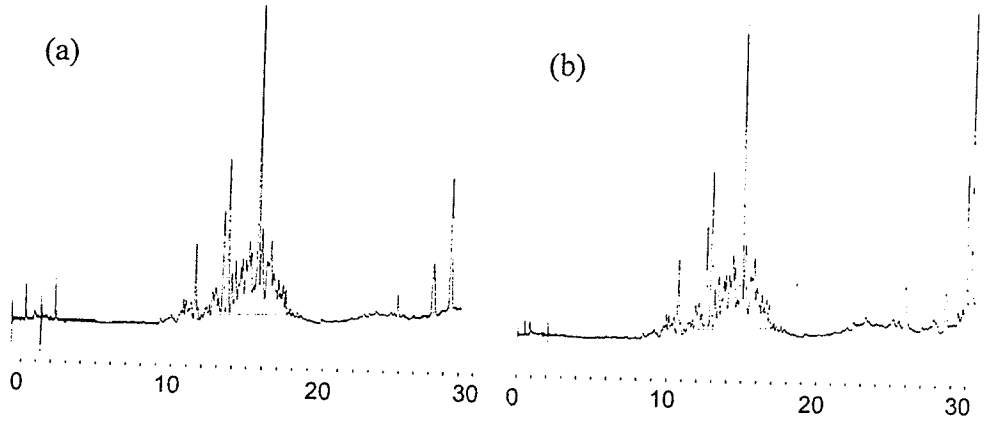
The profiles obtained from the headspace sampling of the 91% weathered class 4 accelerant kerosene (Figure 24), show remarkable similarity to the profiles of the two weathered paint thinner samples (Figure 23 on page 125). This similarity was also found between the unweathered profiles of kerosene (Figure 15 on page 98) and the paint thinners (Figure on page 96) as well, although discrimination between those samples was possible

based on the presence of the BTEX compounds, which are not apparent in these weathered samples. The discrimination between the weathered samples was, in fact, mostly based on the differences in the relative proportions of benzene and toluene, which were both quite apparent in kerosene, but not in the paint thinner samples. The similarity between the profiles is found in the fire debris samples as well as the controls. Thus, it is not likely that sampling from different fire debris material would make discrimination between these accelerants any easier. Since the unweathered profiles from Ch. 3 indicated that the three accelerants had essentially the same components in similar proportions (with exception to the BTEX compounds), it is unlikely that discrimination between these classes would be any easier by charcoal tube sampling. Nevertheless, it is clear that despite difficulty in distinguishing between the class 3 and 4 accelerants, it is clear that the sampling method obtained a sufficient profile to detect the presence of the accelerants in the headspace.

The profiles obtained from headspace sampling of 90% weathered diesel fuel (Figure 25 on page 128), a class 5 accelerant, show very similar traces. There are only a few peaks that differ in the relative proportions between the fire debris and the control samples. The control sample also was relatively weak in comparison to the other control samples (shown at attenuation 3) which is likely due to the weathered sample having very few volatile compounds. The low levels of VOCs in the weathered diesel sample profile was somewhat

expected, since the weathering of the diesel sample produced a very viscous fluid that was not very odorous in comparison to the other weathered samples. However, despite the low levels of VOCs in the weathered diesel fuel, there are still sufficient detectable levels of enough components to obtain a reasonable fingerprint of the accelerant that is distinguishable from the other classes of accelerants.

FIGURE 25. Comparison of the HS-GC profiles of the 91% weathered class 5 accelerant diesel fuel from sampling (a) in the presence of fire debris (attenuation 1), and (b) in the absence of fire debris (attenuation 3).



4.4 Conclusion

The INCAT device had previously been shown to be able to obtain reproducible GC profiles of complex mixtures of VOCs for fingerprint analysis (Ch. 3). In this chapter, the INCAT has been used to obtain fingerprint profiles of weathered accelerants from fire debris. These headspace profiles were obtained from sampling 500 mL of the static headspace above 1.0 μL of the weathered liquid accelerant when absorbed by tissue. All of the headspace sampling with the INCAT device was done actively and at room temperature. The fact that these GC fingerprints were obtained without heating of the fire debris — to increase the amount of analyte mass in the headspace — implies that lower levels of residual accelerant could be used and still obtain a profile of the accelerant.

The comparisons to the control samples of the weathered accelerant actively sampled in the absence of fire debris, demonstrates the importance of comparison sampling in arson analysis. Comparison sampling — to debris outside the burn pattern — is necessary in order to determine that the detected VOCs are not from the debris itself (particularly important if the debris is a synthetic material). Moreover, comparison of the fire debris samples, to standard reference weathered accelerants in the presence of similar debris, is required to account for differences in the relative proportions of analytes resulting from sorption by the debris itself.

Most of the headspace profiles collected in this study showed differences in the profiles that were the result of some analytes being more readily sorbed by the debris than others. In addition to some of the compounds from the residual accelerant being sorbed more than others, there must also, in general, be a significant amount of sorption by the debris to account for the fact that all of the control samples were obtained in greater amounts than in the fire debris samples (as seen from the differences in attenuation scales for the samples). The control samples produced profiles with much greater peak areas from sampling the same amount of accelerant used with the fire debris — although sampling from 40 mL GC vials, as opposed to 1.0 L mason jars, and only 1/4 of the available headspace volume. This difference in headspace sample volume implies that the INCAT device can, in general, be used for sampling of low levels of VOCs when a liquid sample is not available.

Fingerprint identification in the headspace sampling of complex mixtures of VOCs is a useful technique for simplifying chromatograms. However, for situations in which a liquid sample is not available, headspace sampling becomes more of a necessity than a simplifying technique. Such is the case with the analysis of fire debris, where not only is the sampling for accelerants being from solid debris, but in most cases from sorbing material which may release only very low levels of the accelerant components into the headspace. For most types of solid fire debris, the use of a solvent extraction to obtain the residual accelerant would be

impractical. For one, this would require the use of a lot of organic solvent which is both costly and environmentally unsound. In addition, the solvents would likely extract more compounds from the debris material than would be released to the headspace, and thus creating more background interference.

In order to avoid the use of solvents to extract these organic mixtures for analysis, headspace sampling techniques are used. Direct gas sampling of the headspace is not a very sensitive method, and, as such, dynamic methods such as CLS and P&T were developed to increase the headspace sensitivity [8, 9]. However, the dynamic methods are more complicated and require additional equipment for GC analysis. SPE methods, like charcoal tube sampling, have proven to be a very useful method for increasing the headspace sensitivity in either static or dynamic sampling modes and require much less solvent than required in a solvent extraction directly from the debris. The INCAT sampling method provides an alternative sampling technique which has the advantages of other SPE methods, but without requiring any solvent to introduce the analytes to a GC. The fact that the adsorbing coating inside the INCAT device is activated carbon implies that it is essentially the same as the charcoal tube sampling method with regard to its adsorbing ability. Any activated carbon that is used in granular form for charcoal tubes, could be obtained in carbon black form to yield an INCAT device with the same adsorbing abilities. The performance of the INCAT

device would be even further improved by using more narrow capillaries, which would reduce the amount of space inside the device where there is no adsorbent. The capillaries used to make the INCAT device for this study were 26 gauge, and were chosen because it was easier to coat capillaries of that inner diameter. A better vacuum system would allow the same carbon paint to be drawn through a smaller diameter capillary, producing a device with improved adsorption efficiency, and allowing faster active sampling rates.

References

[1] J. Taylor, In Red Flags, *Arson and Fraud Indicators*, *Can. Assoc.of Fire Investigators Journal*, March 1999.

[2] Manitoba Fire Loss Statistics, Office of the Fire Commisioner, Manitoba Labour, at http:// www.firecomm.gov.mb.ca (1999).

[3] Fire Investigations, Office of the Fire Commisioner, Manitoba Labour, at http://www.fire-comm.gov.mb.ca/OFCcontentb5.html (1999).

[4] W. Greenly, RCMP Forensic Laboratory, Chemistry Division, Personal Communication (1999).

[5] Forensic Laboratory Services Directorate, RCMP-GRC Forensic laboratory Service, at http://www.rcmp-grc.gc.ca/html/labs.htm (2000).

[6] Excerpts from The Pocket Guide to Accelerant Evidence Collection, 2nd Ed., at http:// www.interfire.org/res_file/aec.htm, interFIRE Online (1999).

[7] N. Schultz, *Fire and Flammability Handbook*, pp45-46, Van Nostrand Reinhold Co., New York (1985).

[8] J. M. Loeper, In *Modern Practice of Gas Chromatography*, Third Edition, R. L. Grob ed., ch. 14, John-Wiley and Sons, New York (1995).

[9] B. Kolb and L. S. Ettre, *Static Headspace Gas Chromatography: Theory and Practice*, ch.8, Wiley-VCH, New York (1997).

CHAPTER 5 *Active and Passive Sampling of VOCs in Weathered Gasoline Using the RVC-INCAT Device*

5.1 Introduction

The efficiency of active sampling, with any form of SPE device, will involve the flow rate through the sampling device. This dependence on the flow rate is due to the analytes in the sample volume being drawn through the device, requiring sufficient time to interact with the adsorbent. Although any single organic molecule of reasonable size should be adsorbed as it comes into contact with an active site on the adsorbent, the molecule needs to get into close proximity to the adsorbent. In addition, the rate of diffusion of the adsorbate into the pores of the adsorbent will also vary between adsorbents. Thus, even though an activated carbon has a very high specific internal surface area, the adsorbates may not readily migrate into the pores

of the internal surface to allow exposed active sites on the external surface for additional analytes. As such, even if the adsorbent is not saturated, at a given instant there may be very few exposed active sites at the external surface depending on this rate of migration of the adsorbates into the internal pore structure. The migration of these adsorbed compounds is allowed since the analytes are physically adsorbed onto the solid phase adsorbents used in SPE sampling methods. The physical interactions (as described in Ch. 1.2) between the adsorbate and adsorbent are relatively weak, and thus allow migration of the molecules on the adsorbent.

To improve the sampling efficiency with SPE devices, packed particles, foams or fibrous mesh are used for sampling vapour phase analytes. These types of devices allow greater opportunity for the vapour phase being actively sampled, to interact with the adsorbent. However, even with these devices, the active sampling flow rate must still allow sufficient time for the migration of analytes into the internal adsorbing sites. The most efficient sampling of any SPE device is in the passive mode in which the rate of diffusion of the analyte mass through air is the only variable. The slower the active sampling flow rate, the closer one reaches this passive diffusion rate and therefore, the greater the efficiency in adsorption.

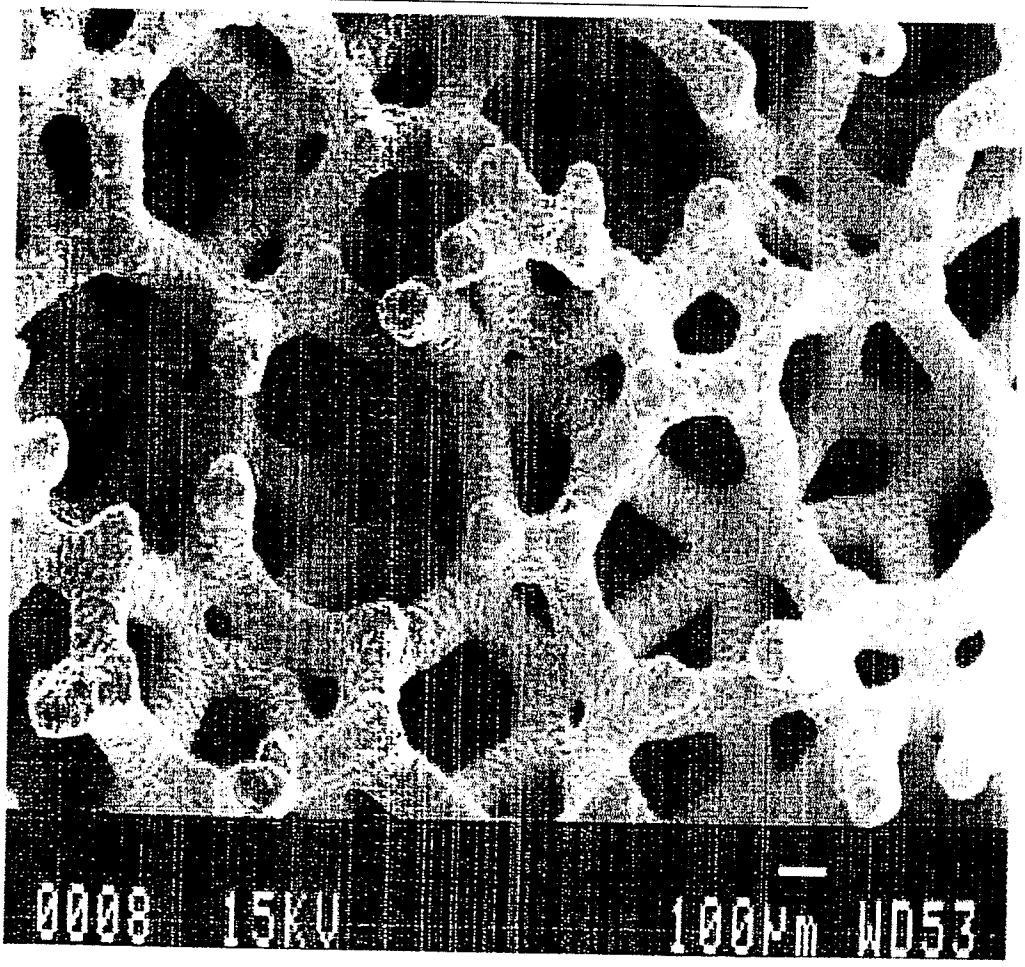
As it was suggested in Ch. 4.4, decreasing the inner diameter of the capillaries used in

making the INCAT device, would reduce the void volume of the device. Reducing the void volume allows less space for the analytes to flow through where there is no adsorbent. This reduction in void volume is the reason for packing granular carbon used in the charcoal tube sampling described in Ch. 1.4. When the carbon granules are closely packed, such that there are only small spaces between the granules, there is an increased chance of interaction between vapour phase analytes and the adsorbents. Unfortunately, it is difficult to achieve this same level of reduction in void volume with coated capillaries of practical dimensions. The alternative to reducing the capillary diameter, then is to have the adsorbent inside the device in such a way that it is not just along the interior wall of the capillary. Incorporating small carbon granules or foam into the INCAT would allow greater opportunity for the solid phase adsorbent to interact with the vapour phase analytes.

Reticulated vitreous carbon (RVC) is an open pore (cell) form of amorphous carbon [1]. This carbonaceous material is essentially a network of glass-like ligaments which form the open cell structure. RVC in general has a high surface to mass ratio, but not as high as activated carbon blacks or granular charcoal. Although this type of carbon foam has a high void volume (97%) allowing air flow [2], due to its network structure (see Figure 26 on page 137), there is an increased amount of material along its cross sectional area for adsorption sites. Since the coated INCAT devices have essentially a ring shaped cross-

sectional area, analytes near the centre of the ring may never have the opportunity to get into close enough proximity to interact with the adsorbent. However, with a network or mesh like cross-section — as with the RVC foam — there is greater chance of analyte interaction across any given cross-sectional segment.

FIGURE 26. Scanning electron microscope image of RVC foam material [1].



In this chapter, an introductory examination of the use of RVC as an adsorbent for the INCAT device is presented. To assess whether RVC can be used to increase the efficiency of the INCAT sampling method, a simple test of the reproducibility of active sampling with the RVC-INCAT has been performed. Samples of weathered gasoline — used in the arson study of Ch. 4 — were actively sampled to determine whether a reproducible fingerprint chromatogram could be obtained using this type of INCAT. In addition, an example of the RVC-INCAT used in the passive mode is shown for the same gasoline sample.

5.2 Experimental

A new form of the INCAT device was developed in an effort to simplify the fabrication and use of this type of sampler. Rather than coating the interior surface of the capillary with activated carbon, the new INCAT has an insert of RVC foam (Energy Research and Generation Inc., Oakland, CA) placed inside the capillary. The first of these RVC-INCAT devices were made using 22 gauge (0.41 mm i.d., 0.71 mm o.d.) capillaries and RVC foam with 100 PPI (pores per linear inch), or 3.9 pores per millimetre. However, since the diameter inside the capillary is 0.41 mm, only 1.6 pores can fit across the diameter of the capillary. Hence, the carbonaceous skeleton of the foam did not have enough structural support to allow

a continuous piece of the RVC foam to be inserted. As a result, these early RVC-INCAT devices had only a small amount of the RVC foam at the tip of the capillary. Nevertheless, the devices still worked in both active and passive modes of sampling. However, such a small amount of RVC adsorbent was not sufficient for use with the INCAT since it lacked the structural strength to be a durable component of this kind of sampler.

The obvious remedy to the problem of being unable to get a continuous piece of the foam inserted through the entire length of the column, is to simply increase the diameter of the capillary being used for the INCAT device. However, increasing the size of the capillary can result in problems when thermally desorbing the analytes in the injection port of the GC, the most important of which is that most injection ports can only allow needles of a certain size to go into the injection port sleeve. In addition, if the needle that goes through the septum of the injection port is too large, the hole made by the needle will deform the septum so much that it will not sustain the column back pressure — leading to a drop in the column back pressure and loss of analyte once the needle is withdrawn from the injection port. Even when using the 22 gauge INCAT devices, it was usually observed that septa were only good for a few injections before they needed to be replaced, so increasing the diameter of the device would

require a specialized septum-less injection port such as a Jade™ Valve injection kit (Alltech Associates, Deerfield, IL).

To overcome the problem of the capillary being too large for the injection port sleeve and avoid the purchase of the Jade™ Valve, an adapter was fitted to the top of the injection port, which effectively increased the length and diameter of the injection port (9.5 cm long, 5.0 mm i.d., 6.0 mm o.d.). With this adapter, a 20 gauge stainless steel capillary (0.89 mm o.d., 0.58 mm i.d.) with an RVC insert fitted through the entire length of the device (4.7 cm), could be used to sample, and thermally desorb analytes onto a GC column. To test this new RVC-INCAT device, five 40 mL GC vials were prepared with a 1.0 μL droplet of 88% weathered Shell Bronze grade gasoline on a 3.0×3.0 cm^2 Kimwipe®. Four of these GC vials were sampled actively, and the last vial was sampled passively for 15 min. The actively sampled vial had 10 mL of the headspace drawn through the INCAT manually via a gas-tight syringe (Hamilton Co., Reno, NV) at 600 mL/min. The passive sample was obtained by plugging the Luer-Lok end of the INCAT device, and puncturing the septum of the GC vial with the INCAT to expose the device to the headspace for 15 min. In both active and passive sampling methods, once the analyte had been adsorbed inside the INCAT onto the carbonaceous foam, a small piece of septum was used to plug the Luer-Lok end of the

INCAT, and the device was then inserted into the adapted injection port of the GC for thermal desorption and separation.

Gas chromatography was performed using the same instrumentation and column type, as described in Ch. 3.2 (on page 84). Analytes were thermally desorbed from the INCAT device in the heated adapted injection port (300°C) of the GC (the adapter was encased with insulating material to maintain the injection port temperature). Unlike the injection of the carbon-coated INCAT, the RVC-INCAT was left in the adapted injection port for the entire run of the GC. The reason for leaving the device in the adapted injection port was that once removed, there would be an immediate loss of column back pressure. By leaving the INCAT in the adapted injection port for the duration of the separation, the column back pressure was maintained. The initial column temperature was still held at 30°C for two minutes so that all of the analyte could sufficiently desorb and accumulate at the top of the column and then enter the column as a small sample plug when the temperature program began. It should be noted that it had been previously determined that two minutes was sufficient time for desorption of the analytes from the RVC-INCAT, otherwise, there would be severe band broadening, and/or multiple sample plugs entering the column. For headspace sampling of VOCs at higher concentration levels than these weathered gasoline samples, it may be necessary to increase

the initial column temperature hold time in order to allow the complete desorption of the analyte prior to the initiation of the GC temperature program.

Following the initial column temperature hold time for the desorption process, the temperature of the column was ramped to 200°C at a rate of 8°C/min and held for five minutes. The column was then heated to a final temperature of 250°C at a rate of 20°C/min, and held at this temperature for five minutes. The detector temperature was 300°C. The entire run time for the separation was 36 minutes. Once the sample run was complete and the column had returned to 30°C, a second run was done to ensure that all of the analyte had been desorbed in the first sample run, and indicated that no carry-over occurred.

5.3 Results and Discussion

The four trials of active sampling the static headspace above weathered accelerant absorbed by tissue, show very consistent GC profiles. The profiles shown in Figure 27 on page 144, are of the four active sampling trials with the RVC-INCAT, of the static headspace above 88% weathered Shell-Bronze grade of gasoline. The GC patterns are shown along with the profiles of a blank desorption injection of the RVC-INCAT (no headspace sample), and

the profile of a blank sample (10 mL headspace sample with no accelerant).

The profile obtained from passive sampling of the equivalent sample of the weathered gasoline is shown in Figure 28 on page 145. This profile is again shown along with the blank injection of the RVC-INCAT, blank sample, but also with one of the active sampling trials, and with a Raven-15 active sample. The passive profile was obtained from a 15 minute exposure of the RVC-INCAT device to the static headspace of the sample. This profile shows very good agreement with the profiles obtained from active sampling with this type of INCAT device. However, the profile obtained from active sampling with the Raven-15 activated carbon-coated INCAT device used in Ch. 4, achieves a similar profile, but obtains larger amounts of analyte in terms of the peak areas (but of the same order of magnitude). The coated INCAT devices were actively sampled at 10 mL/min, but the RVC-INCAT profiles were obtained from actively sampling at 600 mL/min. The difference in active sampling rate may account for the difference in the peak areas between active Raven-15 and active RVC samples, but differences in overall surface areas may also account for the differences in peak areas. Table 13 on page 146, lists fourteen distinct peaks from the profiles that were used to compare the reproducibility of the fingerprints obtained from the RVC-INCAT. Included in the table are the means, standard deviations, and percent RSD from the mean, of the fourteen peaks. The peak areas were normalised to percent of the total area of the fourteen peaks.

FIGURE 27. Pattern reproducibility trials for the RVC-INCAT in active sampling of 88% weathered Shell-Bronze grade gasoline, along with a blank injection and blank sample profiles (all GC traces are shown at attenuation 16).

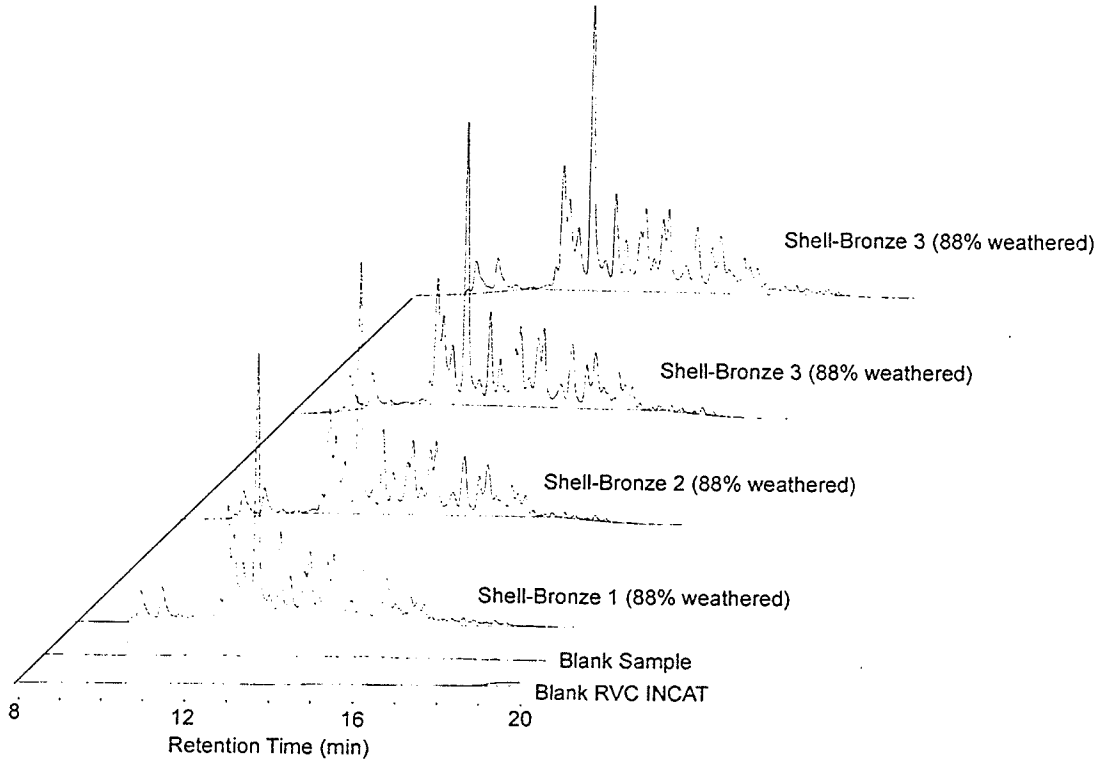
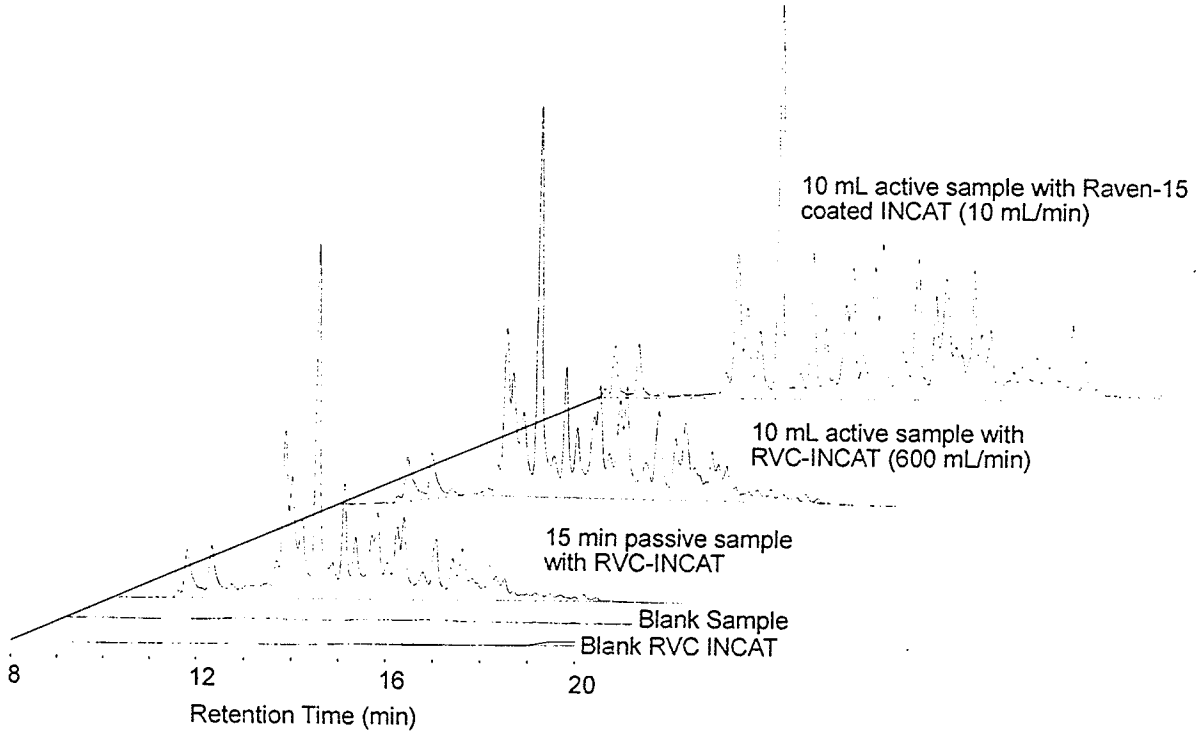


FIGURE 28. Comparison of the HS-GC profiles of 88% weathered Shell-Bronze grade gasoline, from 15 minute passive exposure of RVC-INCAT, along with 10 mL active samples with RVC-INCAT, Raven-15 coated INCAT devices (all shown at attenuation 16).



The similarity between the profiles obtained from active sampling and the passive exposure of the RVC-INCAT devices can be seen by the scatterplot matrix shown in Figure 29 on page 147. The narrow pattern of the scatterplots indicate the linear relationship between the active sampling trials and the passive trial.

TABLE 13. Means, standard deviations, and RSD values of fourteen distinct peaks in the GC profiles from active sampling of the static headspace above 88% weathered Shell-Bronze gasoline with the RVC-INCAT.

Peak Number	Mean R_t (min)	Mean Percent Relative Peak Area	Standard Deviation	%RSD
1	9.51	3.81	0.28	7.5
2	10.01	3.67	0.58	16.
3	11.52	9.64	0.28	2.9
4	11.70	7.42	0.24	3.2
5	11.92	6.17	0.22	3.5
6	12.24	22.3	0.88	3.9
7	12.81	7.21	0.19	2.6
8	13.06	4.62	0.26	5.6
9	13.40	4.76	0.09	1.9
10	13.52	6.48	0.26	4.1
11	13.94	5.73	0.25	4.3
12	14.08	6.34	0.27	4.3
13	14.76	6.44	0.22	3.5
14	15.32	5.39	0.34	6.3

FIGURE 29. Scatterplot matrix of 14 distinct peaks in the active and passive sampling profiles of 88% weathered Shell-Bronze grade gasoline, using the RVC-INCAT device.

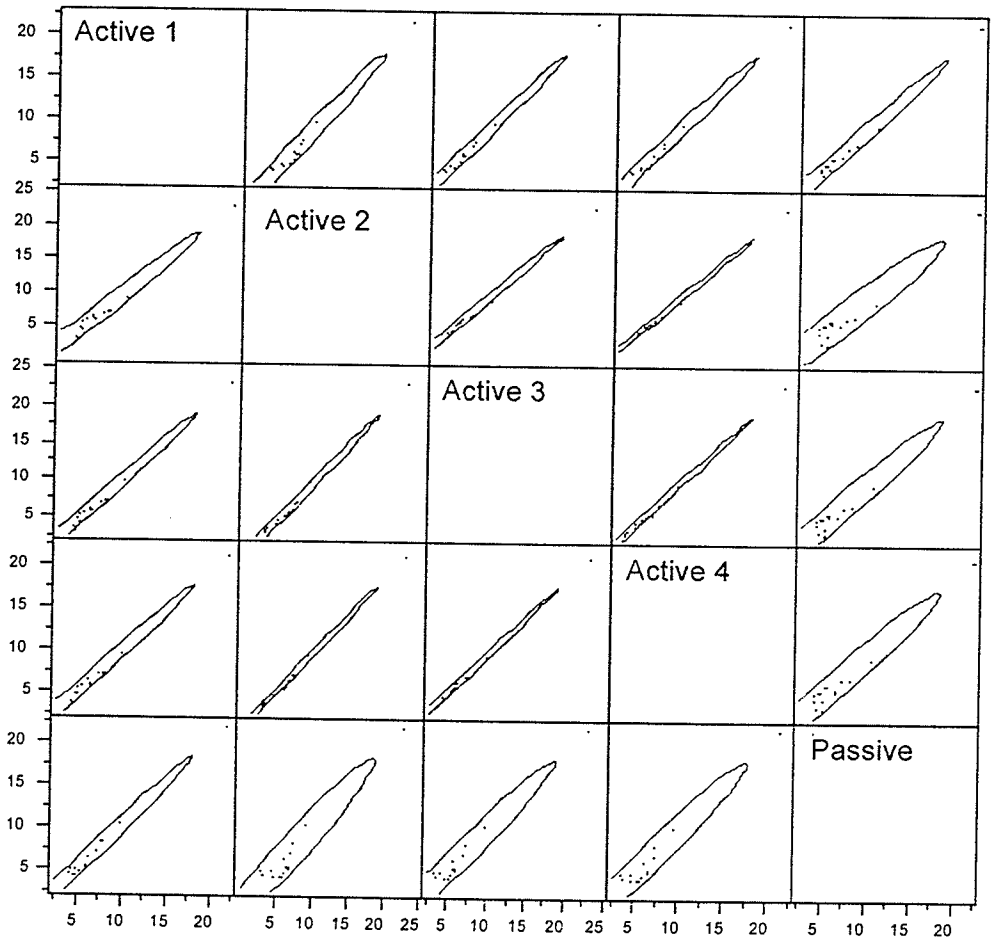


TABLE 14. Coefficients of determination (r^2) for linear fits of the fourteen distinct peaks in the active and passive sampling profiles of 88% weathered Shell-Bronze gasoline with the RVC-INCAT device.

Trial	Active 1	Active 2	Active 3	Active 4	Passive
Active 1		0.982	0.992	0.990	0.988
Active 2	0.982		0.996	0.997	0.945
Active 3	0.992	0.996		0.998	0.969
Active 4	0.990	0.997	0.998		0.962
Passive	0.988	0.945	0.969	0.962	

The coefficients of determination, listed in Table 14, are from the calculation of the least squares best fit straight line through the data. These values indicate that a very high degree of linear relationship exists between the normalised data from all of the profiles (active and passive). The r^2 values for the linear fits between the active sampling trials and the passive trial are slightly lower than those between just the active trials. The lower r^2 values for passive versus active samples may be accounted for by small deviations in the passive diffusion rates of some analytes, that may not be observed when the analytes are actively brought into contact with the adsorbent. Nevertheless, the active data still correlates well with the data from 15 min passive exposure of this INCAT device ($r^2 > 94\%$).

5.4 Conclusion

The RVC-INCAT device has been shown to yield reproducible fingerprints of complex mixtures of VOCs. The fact that the device was tested with weathered gasoline, as opposed to unweathered gasoline, implies that this sampling device would prove even more useful for samples with more volatile analytes — as with the activated carbon-coated INCAT device used in Ch. 3 for sampling the unweathered petroleum distillates. The RVC device would obviously be improved greatly by increasing the surface area of the adsorbing foam. Since RVC is simply a carbonaceous structure, it would be very easy to activate the material by the steam or CO_2 methods described in Ch. 1.3. However, these activating processes result in the loss of carbon from the material to open the existing pores (or create new pores). As such, the resulting foam may not have the structural rigidity to be durable inside INCAT devices of these dimensions. Therefore, RVC foam with greater numbers of pores per unit of length may be necessary to have enough carbon ligament structure to support the RVC insert inside the device. Additional pores per unit length in the carbon network in general would improve the adsorptive ability of this type of device, since it would increase the amount of external surface available for analyte interaction. However, for the device to be a more versatile sampler of air or headspace, a greater internal surface area resulting from activating

the carbon foam would be needed.

The fact that the RVC-INCAT sampler, in either active or passive mode, was able to obtain GC profiles comparable to the Raven-15 INCAT device used in Ch. 4, implies the importance of the effective surface area of the carbon ligaments in the RVC foam. The Raven-15 carbon black used to make the coating for the INCAT device has a surface area of approximately 126 m^2/g [3]. However, much of this surface area is the result of the internal pore structure of the carbon grain. The RVC foam, however, has a surface area of approximately 0.19 m^2/g [2] — approximately 650 times less than the Raven-15 carbon — but since this carbonaceous foam is not activated, the surface area of the material is primarily external ligament surface (as opposed to internal ligament pore surface). Thus, an increase in the number of ligaments in the foam structure (pores per unit of length) would still allow air flow though the RVC, and have more external surface sites for contact with analytes.

The fact that the 15 min passive exposure of the RVC foam produced a profile for the weathered gasoline sample that was equivalent in terms of the peak areas, to the profiles obtained from passive sampling at 600 mL/min, implies that this INCAT device could be used to sample low levels of VOCs with practical exposure times. Thus, passive sampling of the static headspace of fire debris or other non-liquid samples may be achieved with reasonable equilibrium times. Moreover, because the RVC-INCAT is able to obtain levels of VOCs in

the static headspace at short exposures, the device may be useful as a passive monitor for individual human exposure to VOCs in the air. Sampling of VOCs in air involves a dynamic environment, in which equilibrium is never achieved. However, since the VOCs are readily adsorbed by passive diffusion, a RVC-INCAT monitor could be worn by an individual working in an environment where exposure to VOCs is a risk. Since the exposure of this RVC-INCAT to the static headspace of the weathered gasoline at room temperature resulted in a large amount of analyte being adsorbed in a short time, it may be possible to obtain sufficient analyte in a dynamic environment (open circulating air) in a reasonable amount of time to quantify human exposure to VOCs.

References

[1]*Ultramet Foams*, at http://www-ferp.ucsd.edu/~flynn/EMEET/TILLACK/ultramet.html, Ultramet, Pacoima (1999).

[2]*Reticulated Vitreous Carbon*, at http://www.ergaerospace.com/rvc.htm, ERG Materials and Aerospace Corporation (1997).

[3]J. Chatten, Columbian Carbon Co., Personal Communication (2000).

CHAPTER 6 *Conclusions and Future Work with the INCAT Device*

Pattern recognition or fingerprint analysis is employed in the identification of complex mixtures. In this type of qualitative analysis, the identification of the individual components is not necessary. Rather, the relative proportions of the components in the mixture, serve to positively identify the sample. Headspace GC sampling methods are used in the analysis of complex mixtures of volatile compounds in situations where the liquid sample matrix might obscure or interfere with the detection of the components, or when a liquid sample is not available (i.e., foods, soils, fire debris, etc.).

Direct gas sampling of the static headspace is not in general a very sensitive sampling technique. To increase the sensitivity of headspace sampling, dynamic methods (CLS and P&T) and SPE devices have been employed. However, most of the SPE methods that are

currently employed require solvent desorption steps in order to obtain a liquid extract that can be introduced to the GC for separation, or pyrolysis devices to desorb the analytes from the solid phase.

The INCAT device can be used to actively sample the headspace (static or dynamic) of a sample, and concentrate the volatile analytes inside on the carbon adsorbent. However, the advantage that this device has over other SPE devices, is that it is a solventless extraction device, and the thermal desorption of the analytes from the solid phase can occur in the injection port of the GC instrument for direct introduction to the GC column. The fact that this device requires no solvent to prepare a liquid extract of the analytes, reduces the amount of sample preparation, and sampling error.

The use of the INCAT device has been demonstrated in the qualitative analysis of complex mixtures of petroleum distillates, and compared to the direct liquid sampling of these mixtures. Although the sample profiles of the liquid sample and the static headspace sample obtained from the INCAT method did differ with some samples, a characteristic profile was nevertheless obtained. The fact that the INCAT sampling method was able to fingerprint profiles for these complex mixtures, implies the usefulness of the method when a liquid sample is not available.

The application of the INCAT device to the analysis of fire debris evolved from the

qualitative analysis of complex mixtures of petroleum distillates. As a means of further demonstrating the usefulness of this sampling method when liquid samples are not available, the sampling of fire debris for residual accelerant was attempted. The results of the arson study show great promise that this sampling device could become a novel alternative to the current sampling methods of fire debris. Further study of the sampling of weathered accelerants for the detection limits of the device for the residual accelerant above the interference produced by different sample materials. The sampling of actual fire debris with the INCAT device is still pending, but this would allow an opportunity to compare the usefulness of the device to the granular carbon tube methods used in most forensic laboratories.

The use of the INCAT device as a sampler of indoor air was demonstrated from the sampling of air from an environmental chamber — a non-static environment. Unfortunately, the devices used to sample the chamber air were the colloidal graphite INCAT devices, which proved to reach adsorbing capacity at lower than desired levels. Activated carbon coated INCAT devices were developed in an effort to increase the adsorbing capacity of the device, and for increased stability of the adsorbed analytes on the device. Activated carbon provides a stable solid support for adsorbates, for sample storage or disposal. As such, the activated carbon coatings used for these devices should allow samples to be collected and stored for

long periods before sampling. This concept of sample storage is particularly important with regard to the samples obtained from fire debris. Since the sample material containing the residual accelerant will not likely be a stable substrate for long term storage of samples — a drawback in terms of evidence that may be required some time later. Like the carbon tubes currently used for the analysis of fire debris, the activated carbon INCAT could be used to obtain samples for evidence storage, without worry of sample degradation over time.

An important area of future work with the INCAT sampling method would be to examine the efficiency of sampling with activated carbon coated device for quantitative analysis of indoor air. Several attempts were made using the activated carbon devices for indoor sampling (e.g., a hospital ward, a tavern, and a production facility), which showed the device was able to detect VOCs at low levels, but the sources and concentration levels of the detected VOCs were not determined. Ideally, the INCAT device should be tested in areas where there is an occupational concern for exposure to VOCs. In this environment, the INCAT device could be connected to a personal air sampler that is set to actively draw air through at rates equivalent to human respiration. The average 70 kg human has a normal respiration rate of 4.8-8.8 L/min [1]. Sampling with the INCAT at this rate would be useful in monitoring human exposure to HAPs.

Further investigations on making of the activated carbon paint are necessary in order

to improve the efficiency of the coated INCAT device. The three carbon blacks used in making coatings for the INCAT device (Saran, Super Sorb, and Raven-15), described in Ch. 3, showed surprising results in terms of the adsorptive abilities of the coatings. The surface areas for the three carbon blacks are: 126 m^2/g (Raven-15) [3], 1000 m^2/g (Saran) [4], and 2900 m^2/g (Super Sorb) [5]. It was then surprising to find that the coating made from the Raven-15 carbon black proved to be the most effective in the adsorption of the BTEX compounds, used to evaluate the coatings. One reason for greater sampling efficiency of the Raven-15 devices can perhaps be accounted for by differences in the grain sizes used in the carbon blacks. The smaller grain sized activated carbons are more easily suspended in the paint used to coat the devices, and therefore, more carbon may be deposited on the inner wall of the capillary as the paint is drawn through. However, it is also possible that the Saran and Super Sorb carbons have less external surface area for immediate adsorption sites. This difference in the external active sites would then require additional time for the adsorbed species to migrate into the internal surface of the pore structure. To better evaluate these coating materials, passive sampling with INCAT devices, made from carbon blacks with uniform grain size, should be applied to static headspace volumes with VOCs levels ranging from very low to high concentrations — for single and multi-component systems. However, as an active sampler, it may be more desirable to sacrifice high internal surface area, for more

external surface active sites. Greater external surface sites would increase the active sampling rate of the INCAT, but the overall capacity of the sampler would be reduced.

In addition to the study of the carbon blacks for coating the INCAT device, experiments should be designed to evaluate the use of reducing the capillary diameter. The 26 gauge capillaries used for most of the INCAT devices were chosen since they were easily coated without too much risk of clogging. However, alternative coating methods may allow for smaller capillaries to be used, and thereby reducing the void volume of the device. One such method for this was attempted and showed promise, and that was by depositing the carbon from a smoky flame onto the interior of the capillary. A capillary with low vacuum suction drew the smoke from a methane flame, through the length of the device for several minutes. This device showed very good adsorption when sampling a BTEX standard in both active and passive modes. However, the stainless-steel lost temper due to the high temperatures of the flame, and was therefore not as durable as the carbon paint coated devices. However, longer capillaries could be coated by this method, with only one end being exposed to the high temperature of the flame. The remainder of the capillary could be cooled to reduce the amount of steel that is affected by the heat of the flame. Following the depositing of the carbon soot, the capillary could be cut to remove the untempered portion and the remaining length could be sectioned for individual INCAT devices. The carbon deposited from the sooty

flame would be of very small particle size, and therefore could be used to coat capillaries with smaller inner diameters. However, although the inner diameter may be reduced, the outer diameter should not be reduced much from the 26 gauge capillary (0.46 mm o.d.). The thicker wall of the capillary tubing would lend strength to the device and make it more durable for sample handling and repeated use.

The use of RVC foam as the adsorbent inside the device opens a new area of research for the INCAT sampler. The RVC-INCAT device achieved unusually high performance considering that it is has such a low surface area (0.19 m^2/g) compared to the activated carbons used for coatings. However, the fact that the RVC is essentially all external surface, allows greater interaction between the adsorbent and analytes in active vapour flow. Moreover, the structural support of the RVC ligands would allow liquid fluid flow without risk of loss of material. The sampling of organic compounds in water may then be achieved without headspace sampling, since water is not adsorbed by the carbon. The sampling of organic species in aqueous environments could also be done in both active or passive sampling modes.

The fact that the RVC material has such a low surface area, would imply that it would reach capacity too readily — as with the colloidal graphite INCAT devices — and therefore be subject to competitive adsorption effects. Activating the RVC material would increase the

overall capacity of the adsorbent, but at the expense of loss of external surface sites. Therefore, RVC foams with greater numbers of pores per unit of length (i.e., smaller pores within the ligand framework), would increase the amount of adsorbing mass inside the INCAT device and some of the external surface could be sacrificed for greater internal surface area, during activation of the material.

The INCAT project although still in its infancy, has shown that this sampling method can be applied to the extraction of VOCs in both air and headspace samples. As an air sampler, in either passive or active modes, the device can be used to sample analytes reproducibly and easily. The subsequent analysis is simplified with respect to other SPE sampling methods, in that no solvent is used to desorb the analytes concentrated inside the device. The INCAT device is robust and simple to use. This sampling method would be easy for the layperson to use to obtain a sample, which could then be sent to a laboratory for analysis. Samples concentrated inside the device would then be supported on a stable solid phase for long periods. The simplicity of this sampling method opens many areas of application where the analyses of volatile compounds are required. Although the application to passive monitoring of HAPs is perhaps the most important application of the INCAT sampling device, there are many areas of routine laboratory analysis that would benefit from this simple, economic, and reusable sampling device.

References

[1]American Thoracic Society, *Am. Rev. Resp. Dis.*, 144(5), pp1202-1218 (1991).

[2]S. A. Shea, and D. P. White, *Disorders of Ventilatory Control*, In *Ceceil Textbook of Medicine*, 21st Edition, L. Goldman and J. C. Bennet eds., W. B. Saunders Co., Philidelphia (2000).

[3]J. Chatten, Columbian Carbon Co., Personal Communication (2000).

[4]J. W. Hassler, *Activated Carbon*, ch. 1, Leanoard Hill, London (1967).

[5]K. Robinson, Mega-Carbon Co., Personal Communication (2000).