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MUNICIPAL FIREFIGHTER EXPOSURES TO TOXIC GASES AND VAPOURS

by

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Dedicated to:

Alan Austin, my late father,
Edith Austin, my mother,
Elena Austin, my daughter,

who, each in his or her own special way,
have generously supported my efforts.

"It is not up to you to complete the work,
neither are you free to desist from the task."
- R. Tarphon

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ABBREVIATIONS, SYMBOLS, UNITS AND PREFIXES

Where, due to historical reasons or currently accepted laboratory practice, other measurement systems are used, the Système international (SI) equivalent is given in bold type. Prefixes are listed separately at the end of this section.

•	free radical
±	plus or minus
<	less than ...
>	greater than ...
α	alpha, chance of a Type I error of reporting a false positive
β	beta, chance of a Type II error of reporting a false negative
Σ	sum of ...
$\mu g/m^3$	microgram per cubic metre
μg	microgram
μm	micrometre
%	percent
%COHb	percent carboxyhaemoglobin saturation
a	the y-axis intercept in linear regression
ACGIH	American Conference of Government Industrial Hygienists
AIHA	American Industrial Hygiene Association
amu	atomic mass unit
ANOVA	analysis of variance
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
atm	atmospheres
	1 atm = 101.325 kPa
AQI	Air Quality Index
A&WMA	Air and Waste Management Association
b	the slope of the curve in linear regression (regression coefficient)

BCM	bromochloromethane
BEI	Biological Exposure Index (ACGIH, 1996)
BFB	1-bromo-4-fluorobenzene
BNQ	*Bureau de normalisation du Québec* Québec Standards Bureau
bp	boiling point
CANMET	Canada Centre for Mineral and Energy Technology
canmix	instrument calibration VOC standard mixture in a Summa™ canister
CBD	chlorobenzene-d5
cc/min	cubic centimetre per minute
cc	cubic centimetre
CDC	Centres for Disease Control (United States)
CFK	Coburn-Forster-Kane equation
CGA	Compressed Gas Association
CIMM	Canadian Institute of Mining and Metallurgy
CI	confidence interval
cm	centimetre
$cm^3/kg \cdot min$	cubic centimetre per kilogram per minute
CNS	central nervous system
CO	carbon monoxide
CO_2	carbon dioxide
COHb	carboxyhaemoglobin
CSA	Canadian Standards Association
CSST	*Commission de santé et sécurité du travail* Workmen's Compensation Board (Québec)
CV	coefficient of variation
c_x	the number of carbon atoms in a molecule
d	deuterium
d_5	hydrogens replaced by deuterium on the benzene ring of the i.s.
DFB	1,4-difluorobenzene

DL	detection limit (this terminology is not recommended)
dm	decimetre
DNA	deoxyribonucleic acid
DQO	data quality objectives
ECD	electron capture detector
EDB	dibromoethane
eg	example
EPA	Environmental Protection Agency (United States)
EPS	Environmental Protection Service (Canada)
Eqn	equation
et al.	and co-authors
eV	electron volt
exp	exponential
f	degree of freedom
F12	Freon12™ (dichlorodifluoromethane)
F13	Freon13™ (chlorotrifluoromethane)
F22	Freon22™ (monochlorodifluoromethane)
F113	Freon113™ (1,1,2-trichloro-1,2,2-trifluoroethane)
FEMA	Federal Emergency Management Agency, United States
$FEV_{1.0}$	forced expiratory volume (1.0 second)
FID	flame ionization detector
ft	foot
	1 ft = 0.3048 m
ft^3	cubic foot
	1 ft^3 = 28.31685 dm^3 = 28.31685 L
FTIR	Fourier transform infra-red spectrophotometer
FVC	forced vital capacity
GC	gas chromatograph
GC/MSD	gas chromatograph coupled with a mass selective detector
Hg	mercury

Hp	horse power (electric) **1 Hp = 746 W**
HP	Hewlett-Packard™
hr	hour
HR_f	heart rate
IARC	International Agency for Research in Cancer
ID	identification
i.d.	internal diameter
IDL	instrument detection limit
IDSP	Industrial Disease Standards Panel (now the ODP)
IFA	International Firefighters Association
IFSTA	International Fire Service Training Association
IISRP	International Institute of Synthetic Rubber Producers, Inc.
in	inch **1 in = 0.0254 m**
in Hg	inch of mercury **1 in Hg = 3.38639 kPa**
IRSST	*Institut de recherche en santé et sécurité du travail, Québec* Health and Safety Research Institute, Québec
i.s.	internal standard
ITD	ion-trap detector (mass spectrometry)
km	kilometre
km^2	square kilometre
kPa	kilo Pascal
L	litre
L/min	litre per minute
LC_{50}	lethal concentration (50% mortality)
LFG	landfill gas
LFL	lower flammable limit
LOD	limit of detection

log	logarithm
LOQ	limit of quantitation
M	affinity of CO for haemoglobin in a blood sample at equilibrium
m	metre
m^3	cubic metre
Mbyte	megabyte
MDL	method detection limit
MEK	methylethylketone
MHz	mega Hertz
mg	milligram
mg/m^3	milligram per cubic metre
min	minute
min^{-1}	per minute
mL	millilitre
MLOQ	method limit of quantification
mm	millimetre
mm Hg	millimetre of mercury
mp	melting point
MS	mass spectrometry
MSD	mass selective detector (mass spectrometry)
MSHA	Mining Safety and Health Administration
mtDNA	mitochondrial deoxyribonucleic acid
MW	molar mass
m/z	mass to charge ratio
N	mean baseline noise signal
n	number
n.d.	not detected
NAUI	National Association of Underwater Instructors (United States)
NBS	National Bureau of Standards (United States) - now, NIST
NFPA	National Fire Prevention Association (United States)

NIOSH	National Institute of Occupational Safety and Health (United States)
NIST	National Institute of Standards and Technology (United States)
NMOC	nonmethane organic compounds
No.	number
NO_x	Oxides of nitrogen (N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5)
NPD	nitrogen-phosphorous detector
NRC	National Research Council (United States)
n.s.	not significant
NTIS	National Technical Information Service (United States)
°C	degree Celsius
o.d.	outside diameter
ODP	Occupational Disease Panel (formerly, the IDSP)
°F	degree Fahrenheit
	°F = (°C x 9/5) + 32 °C = °F - 32 x 5/9
O_2Hb	oxyhaemoglobin
OPPBTP	*Organisme professionel de prévention du bâtiment et des travaux publics* (France) Building and public works professional safety organization (France)
OR	Odds ratio
OSHA	Occupational Safety and Health Administration
p	probability
Pa	Pascal
PAMS	photochemical assessment monitoring station
P_B	barometric pressure (in mm Hg)
PFTBA	perfluorotributylamine
PIC	products of incomplete combustion
PID	photoionization detector
PMD	Pollution Measurement Division, Environment Canada, currently the Ambient Air and Analysis Division, Air Toxics Section
PMR	proportionate mortality ratio
Po_2	partial pressure of oxygen in pulmonary capillaries

ppb	parts per billion
ppm	parts per million
	$\mathbf{mg/m^3 = \dfrac{ppm\ \ x\ \ Molar\ mass}{24.45}}$ $\mathbf{ppm = \dfrac{mg/m^3\ \ x\ \ 24.45}{Molar\ mass}}$
ppmC	parts per million carbon
	ppmC = ppm x the number of carbons per molecule
ppm	parts per million by volume
psi	pound force per square inch
	1 psi = 6.894757 kPa
psig	pounds per square inch, gauge pressure
PVOC	polar organic compound
QA/QC	quality analysis and quality control
r	correlation coefficient
RAM	random access memory
RDL	reliable detection limit
rev	revolutions
RMV	volume of air breathed (in L/min)
rpm	revolutions per minute
RR	relative risk
RRF	relative response factor
rsd	relative standard deviation
RSSQ	*Régie de services sociaux du Québec*
	Québec Health and Services Administration
RT	retention time
SCAN	total ion monitoring by the mass selective detector
SCBA	self-contained-breathing-apparatus
SCUBA	self-contained-underwater-breathing-apparatus
SD	standard deviation
sec	second
SFPE	Society of Fire Prevention Engineers (United States)

SI	*Système international* (metric units); International System
SIM	selective ion monitoring
SMOR	standardized mortality odds ratio
SMR	standardized mortality ratio
SPIM	*Service de la prévention des incendies de Montréal* City of Montréal Fire Department
STEL	short term exposure limit (Weighted average over 15 minutes)
STP	standard temperature and pressure (25°C and 760 mm Hg)
SVOC	semi-volatile organic compound
t	Student's t statistic
t	exposure time (in minutes)
$\mathrm{t}_{1/2}$	biological half-life
TAMS	Toxic Air Monitoring Stations
TEAM	Total Exposure Assessment Methodology
T_f	rectal temperature
THC	total hydrocarbon
TLV	Threshold Limit Value
TPM	total particulate matter
TWA	time weighted average
U.S.	United States
UATMP	Urban Air Toxics Monitoring Program
v	version
V_E	minute ventilation
Vo_2	oxygen consumption
Vo_{2max}	maximum aerobic capacity
VOC	volatile organic compound
vs	versus
W	Watt
yr	year

PREFIXES

Δ	Delta, change in ...
μ	micro (10^{-6})
c	centi (10^{-2})
c-	cis
d	deci (10^{-1})
k	kilo (10^{3})
M	mega (10^{6})
m	milli (10^{-3})
m-	meta (position 3 on a benzene ring)
n	nano (10^{-9})
n-	normal
o-	ortho (position 2 on a benzene ring)
p-	para (position 4 on a benzene ring)
sec-	secondary
t-	trans
tert-	tertiary

PREFACE

A. PUBLICATIONS

An article from this thesis has been accepted for publication in the Journal of Toxicology and Environmental Health under the title "*Carbon monoxide and water vapour contamination of compressed breathing air for firefighters and SCUBA divers*," the co-authors being C. Austin, D. Ecobichon, G. Dussault and C. Tirado.

Two communications from this thesis have been accepted for presentation at the 19th Annual Congress of the Association québecoise de santé et sécurité au travail and will be published in the Conference Proceedings under the titles, "*Indices de mesure de la contamination causée par le fonctionnement de moteurs diesel dans des casernes de pompiers*" and, "*Contrôle de la qualité de l'air comprimé respirable*," the co-authors being C. Austin, D. Ecobichon, G. Dussault and C. Tirado, and C. Austin, D. Ecobichon and G. Dussault, respectively.

B. ACKNOWLEDGMENTS

I gratefully acknowledge receipt of a three-year scholarship from the *Institut de recherche en santé et sécurité au travail* (IRSST) and a research grant from *Health Canada*. This project is not the result of an isolated experiment in the laboratory. It was carried to completion with the collaboration of many people to whom I am deeply indebted for their participation in the study and for their guidance, patience and support. This includes the City of Montréal firefighters and their superiors: Richard Ménard and collegues who were always available to collect samples at experimental fires; Guy Dussault, who has devoted countless, valuable hours to all aspects of this project related to firefighting and to the Fire Department; Romeo Noel, André Bourdeau and Alain Michaud who had the vision and the strength of leadership to see the project through to the end. Special thanks to

Carlos Tirado of the City of Montréal Environmental Laboratory, Chemistry Section, who was responsible for the method development and FTIR analysis of the QA/QC samples of compressed breathing air collected by the Fire Department.

It includes also: Don Williams, P. Eng., Tom Dann, P. Eng. and Daniel Wang, PhD, who very generously allowed me access to the Environment Canada laboratories (Ambient Air and Analysis Division, Air Toxics Section - formerly, the Pollution Measurement Division) for the purposes of method validation and sample analysis; Dr. Daniel Wang who built the VOC pre-concentrator used in the GC/MSD analysis of samples, who prepared the instrument calibration standards and who was invaluable in helping to overcome the many instrumental and analytical challenges inherent in the analysis of fire samples; Adrian Steenkamer who stood patiently by me while I learned the GC/MSD analytical techniques used in this study; Ron Halman with whom I enjoyed many discussions on quality analysis, quality control and methodology; Mike Lister who kindly ran my fire canisters through the automated cleaning process, and Jonathan Williams who collected Summa™ canister samples from landfill sites. Without the kind assistance of all of these people, this project would not have borne fruit.

Finally, but not at all least, it includes Dr. Don Ecobichon, PhD, to whom I am truly grateful for his advice, encouragement and patience. He has been an extraordinarily wonderful teacher and mentor. When I began this project, I felt privileged to have the opportunity to work with him. It is indeed a fortunate graduate student who can still say, as I can, that I think more highly of my supervisor, both as a scientist and as a human being, at the end of the project than I did at the beginning.

During the course of this study I have witnessed firefighters' courage in the face of danger and their selfless willingness to put others ahead of themselves, all the while maintaining a good sense of humour in the face of tremendous stress and adversity. As scientists, we sometimes lose sight of the people who turn to us for knowledge and assistance while we mull over our data, devise new theories and try to publish more articles. We can all learn from these men who constantly face new situations without predetermined answers where they must, nonetheless, rapidly assess new and complex problems, confront the unknown, arrive at decisions, take responsibility and, most importantly, act. I hope that this study will find a modest place in the body of knowledge we call science. Above all, I hope that the firefighters themselves will find in this work answers to at least some of their questions and concerns.

ABSTRACT

The hypothesis was that there is an association between cardiovascular, reproductive and oncogenic effects and chemicals (gases, volatile organic compounds (VOC's)) to which firefighters are exposed. The objectives of the study were to assess firefighter exposures to: (1) diesel emissions in firehalls; (2) contaminated self-contained-breathing-apparatus (SCBA's); and, (3) VOC's at fires. Carbon monoxide (CO) was used as a marker for diesel emissions. Air in SCBA cylinders was analyzed for chemical contaminants. The U.S. EPA TO-14 method for ambient air analysis was verified for the analysis of 144 VOC's in air samples collected in Summa™ canisters at experimental and municipal fires. Exposure groups were determined from firehall assignment and vehicle responses to alarms. Estimation of the percentage of time that firefighters used respiratory protection at fires was obtained from records kept for SCBA refills.

The mean maximum concentration of CO measured during the operation of two fire trucks in unventilated garages was 4.1±2.6 ppm (mean±SD, n=16). A linear relationship existed between levels of CO, CO_2 and NO_2 in diesel emissions. By implication, using CO as a marker, firefighter exposure to diesel emissions was low. Some SCBA's were found to contain levels of CO (up to 250 ppm) consistent with possible COHb poisoning. Distinctive firefighter exposure groups were identified. A Montréal firefighter attended some 19 to 62 fires per year (depending on firehall assignment), 46% being structural fires. Respiratory protection was used for 6% of the time spent at the firescene. No new or novel toxic VOC's were found in fire samples and a characteristic "fingerprint" of VOC's was identified. Three potential carcinogens (benzene, 1,3-butadiene, styrene) accounted for 25% of the 123 VOC's found in fires, maximum levels of these being 11, 5 and 2 ppm, respectively. Since the results suggest that firefighters are not exposed to high levels of carcinogenic VOC's, why then do epidemiological studies reflect adverse health outcomes?

SOMMAIRE

L'hypothèse de départ était une association entre les effets cardiovasculaires, reproductives et effets oncogènes et les substances chimiques (gaz et composés organiques volatiles (COV)) auxquels sont exposés les pompiers. Les objectifs de l'étude étaient d'évaluer l'exposition des pompiers: (1) aux émissions de diesel dans les casernes; (2) aux contaminants chimiques dans les cylindres d'air (APRIA); et, (3) aux COV lors d'incendies. Le monoxyde de carbone (CO) a été utilisé comme marqueur des émissions de diesel. L'air dans les APRIA a été analysé pour vérifier la présence de contaminants chimiques. Des cylindres Summa^{MD} ont été utilisés pour échantillonner l'air lors d'incendies expérimentaux et municipaux. Un total de 144 COV ont été analysés selon la méthode TO-14 du *EPA*. Des groupes d'exposition ont été identifiés à partir de l'affectation des pompiers en caserne et de la réponse des véhicules aux alarmes. L'utilisation de la protection respiratoire a été calculée à partir des registres tenus pour le rechargement des cylindres d'air.

La concentration moyenne maximale de CO mesurée alors que deux camions étaient en marche dans des casernes non-ventilées était de 4.1±2.6 ppm (moyenne±l'écart-type, n=16). Une relation linéaire entre le CO, le CO_2 et le NO_2 dans les émissions de diesel a été démontrée. Par implication, le CO servant de marqueur, l'exposition des pompiers aux émissions de diesel était faible. Jusqu'à 250 ppm de CO, compatible avec l'intoxication due au COHb, a été trouvé dans des APRIA's. Des groupes distincts d'exposition professionnelle ont été identifiés. Un pompier montréalais répondait à un nombre de feux variant de 19 à 62 par année (selon l'affectation en caserne) dont 46% étaient des incendies de bâtiment. La protection respiratoire fut utilisée pour une période équivalent à 6% du temps passé aux feux. Aucun COV nouveau ou inusité n'a été trouvé. Un "*fingerprint*" caractéristique, commun à la plupart des incendies a été identifié. Trois cancérogènes potentiels (benzène, 1,3-butadiène et styrène) comprenaient 25% des COV mesurés, les niveaux maximums étant 11, 5 et 2 ppm, respectivement. Puisque les résultats semblent suggérer que les pompiers ne sont pas exposés à des niveaux élevés de COV cancérogènes, pourquoi alors, les études épidémiologiques démontrent-elles des conséquences néfastes à la santé du métier de pompier?

CLAIM TO ORIGINALITY

(1) The source of toxic gases and vapours, including carbon monoxide (CO), found in compressed breathing air used in self-contained-breathing-apparatus (SCBA's), was traced to a malfunctioning compressor. Standard operating, maintenance and sampling procedures were developed along with a QA/QC program, and these were effective in controlling the levels of contaminants. Realistic and effective action levels were proposed.

(2) Development of an easy-to-use, rapid and accurate method (using Excel™ v5.0 spreadsheet software) to solve the Coburn-Forster-Kane (CFK) equation relating predicted levels of carboxyhaemoglobin (COHb) to ambient concentrations of carbon monoxide (CO) for various work levels.

(3) The U.S. EPA TO-14 method has never been applied to collecting and analyzing samples from structural fires. The utility of the method was demonstrated for volatile organic compounds (VOC's) in fire samples along with the verification of VOC fire sample stability in Summa™ canisters. Analytical sensitivity, reproducibility and accuracy of the method was also demonstrated.

(4) Results have suggested possibilities for the development of Summa™ canister VOC analysis as a new tool, useful to arson investigators, for the identification of accelerants used in criminal fires.

(5) VOC quantification in fire samples from experimental and actual municipal structural fires demonstrated no new toxic VOC's from new materials and, within reason, a common spectrum of VOC's formed at most fires.

(6) Estimation of firefighters' cumulative exposure to VOC's using ambient air concentration of VOC vapours, time spent at fires and work level.

(7) Development of rigorous criteria (including accurate estimations of actual time spent at fires and the use of SCBA's) identifying a minimum of eight occupational exposure groups among firefighters for the estimation of firefighter exposure/response relationships.

CHAPTER 1

INTRODUCTION

A. FIRE

1. Fire chemistry

The phenomenon known as "fire" is the product of a series of complex chemical processes known as "combustion" or "burning" and which include rapid, self-sustaining oxidation and reduction reactions accompanied by the evolution of heat and light. The following paragraphs are a brief summary of fire chemistry as described by Meyer (1989), Tuve (1985), Côté (1986) and DiNenno (1988). During any chemical reaction, bonds between atoms are broken and made. In the case of combustion, the excess energy (heat of combustion) is released to the environment in the form of the light and heat which we observe as "fire". The basic form of the overall combustion reaction of organic (carbon-containing) compounds is illustrated by the burning of methane:

$$CH_4 + 2O_2 + \text{Energy of activation} \Rightarrow CO_2 + 2H_2O + \text{Heat of combustion} + \text{Light}$$

The heat of combustion of fuel such as methane (natural gas), gasoline and fuel oils is approximately 2.5 times that of wood or paper. That is to say that these fuels provide about 2.5 times as much heat as the same amount of wood or paper. Given the appropriate ratio of fuel (wood, solvent, plastic, rubber, PCB, etc.), oxygen and combustion temperature, the products of combustion should be only water and carbon dioxide (CO_2). This is the overall result obtained from a series of consecutive, or chain, reactions involving molecular fragments (free radicals). The combustion of methane (CH_4) illustrates the formation of free radicals in an 11-step chain reaction the first two of which are:

$$CH_4 \Rightarrow CH_3^{\bullet} + H^{\bullet}$$

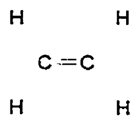
$$H^{\bullet} + O_2 \Rightarrow OH^{\bullet} + O^{\bullet}$$

In general, the burning substance behaves chemically as the reducer and the substance which is "supporting" the combustion as the oxidizer. Oxygen is the most common oxidizer but other commonly found electron-donating chemicals will also support combustion as well as, or better than, oxygen (peroxides, nitrates, nitrites, chlorates, bromates, persulphates, fluorine, chlorine, bromine). Ordinary burning occurs only in the gas phase. If the temperature of a substance is higher than its flashpoint, as is the case with flammable and combustible liquids and gases, then the vapour fuel/oxygen mixture requires only an ignition source in order to begin the combustion reaction. Other substances must first undergo chemical decomposition (brought about by the action of heat) in order to generate flammable vapours which will, in turn, ignite. This is known as pyrolysis. The heat produced, once the substance begins to burn, will feed back to break down the substance into more flammable vapours thus continuing the combustion process. Substances which undergo direct combustion include methane, acetylene, sulphur, gasoline, varsol, alcohol, and charcoal. Substances, where the products of pyrolysis undergo combustion, include wood, paper, textiles, plastics, rubber, paints (oil), cooking oils, leather, bread, and tar. The vapour evolving from the surface as a result of pyrolysis may include partially oxidized products, monomers, or polymer chains. Pyrolysis differs from smouldering in that pyrolysis requires an external heat source while smouldering is a self-sustaining combustion process. The temperature of a pyrolysing sample is in the range of 900-1,200°C, much less than the flaming gas phase temperature of 1,500-2,000°C. The temperature of a smouldering sample is typically 900-1,400°C. Most materials can be pyrolysed but only a few, including cellulosic materials (wood, paper, cotton, etc.) and flexible polyurethane, are able to smoulder.

Unfortunately, complete combustion is approached only under carefully controlled conditions, such as may be found in high-tech incineration, where air or oxygen is abundantly available during the burning process. Uncontrolled or unintentional combustion tends to be "fuel rich" and therefore less than ideal from a chemical and a toxicological standpoint. Since the free radicals normally involved in combustion are very reactive, other side reactions are propagated to yield hundreds, if not thousands, of chemical products and smoke. Neither the amount nor the colour of the smoke correlate well with the amount of toxic products of incomplete combustion such as carbon monoxide (CO). It is the products of "incomplete" combustion which are of greatest concern from the point of view of environmental and industrial health.

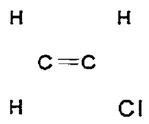
The burning of organic compounds which contain elements other than carbon and hydrogen, will yield combustion products in addition to CO_2 and water. These products of both complete and incomplete combustion include hydrogen cyanide, hydrogen sulphide, sulphur dioxide, nitrogen oxides, and ammonia. Heavy metals such as arsenic, lead, and mercury are also likely to be released, depending on the nature of the fire.

Wood, textiles and polymers (plastic and rubber) are involved in almost all common fires. Polyethylene, polyvinyl chloride, polyacrylonitrile, polytetrafluorethylene, polystyrene, and polymethacrylate are examples of addition polymers of similar monomers:



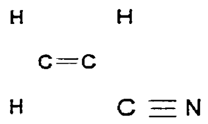
$H_2C=CH_2$

Ethylene



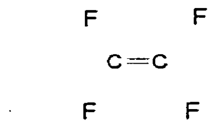
$H_2C=CHCl$

Vinyl chloride



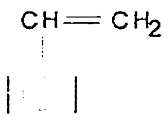
$H_2C=CH-C\equiv N$

Acrylonitrile

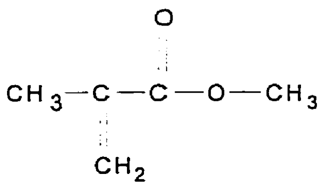


$F_2C=CF_2$

Tetrafluoroethylene



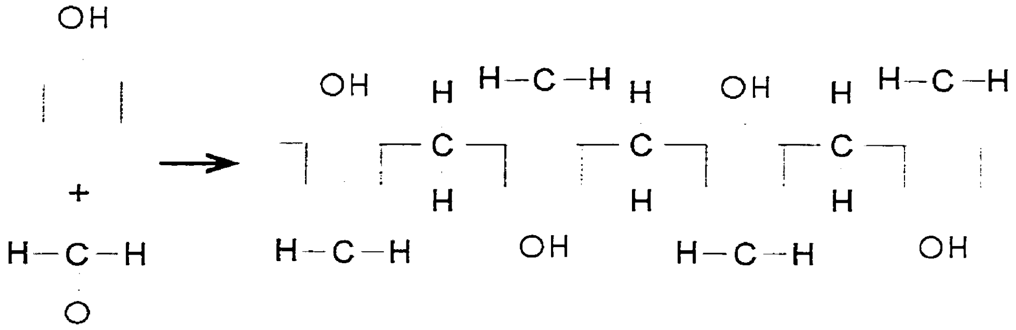
Styrene



$CH_3-C(=CH_2)-C(=O)-O-CH_3$

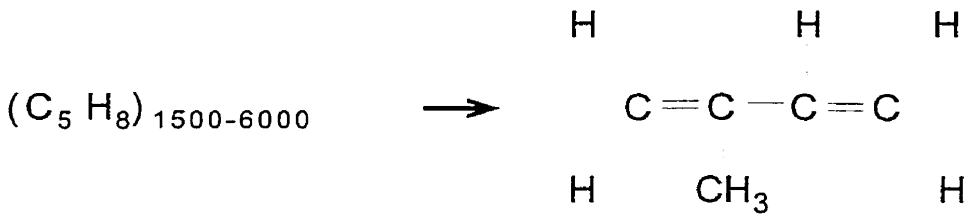
Methylmethacrylate

Phenol-formaldehyde resin is an example of a condensation polymer formed from two dissimilar monomers:



Most polymers found in buildings will burn. Unlike wood and solvents, these substances often melt prior to and during burning. Thermal degradation to the simpler monomers frequently occurs prior to any burning of the substance and may lead to inhalation of these substances far from the scene of the original fire. For example, heat that is conducted or radiated through a wall may cause the decomposition of the polymeric wall covering on the opposite side of the wall. Thermal degradation products include methane, ethane, ethylene, benzene, toluene, and ethylbenzene in addition to the monomers (ethylene, vinyl chloride, acrylonitrile, tetrafluoroethylene, styrene, methyl methacrylate, ethylene glycol, terephthalic acid, phenol, formaldehyde, hexamethylenediamine, adipic acid, propene, vinyl chloride, vinyl acetate, vinylidene chloride, chloroprene, 1,3-butadiene, ethyl acrylate, ethylene oxide, methylacrylate, urea, phenol, and isoprene). In general, the Threshold Limit Value (TLV) of these substances is orders of magnitude below the lower flammable limit. Flashover occurs when the concentration of vapour reaches the *lower flammable limit* (LFL) where an ignition source will cause the mixture of flammable vapour and oxygen to ignite. The burning of plastics typically produces voluminous amounts of soot together with higher levels of hydrogen cyanide (HCN), hydrochloric acid (HCl) and acrolein (CH_2=CHCHO) than the burning of materials such as wood and fossil fuels. More smoke tends to evolve from fires involving aromatic polymers such as polystyrene, as opposed to aliphatic polymers such as polyethylene.

Rubber is a natural or synthetic polymer having elastic properties. Natural rubber, found in the sap (latex) of several tropical rubber trees, is cis-1,4-polyisoprene. Thermal degradation of natural rubber yields the monomer, isoprene:

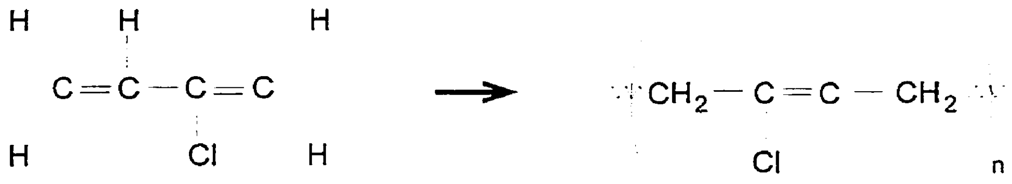


$$(C_5H_8)_{1500\text{-}6000} \longrightarrow \mathrm{H_2C{=}C(CH_3){-}CH{=}CH_2}$$

Natural rubber

Isoprene
(2-methyl-1,3-butadiene)

Vulcanized rubber is natural rubber which has been heated with sulphur. The sulphur atoms bond between the chains of polyisoprene. Sulphur is added in varying amounts depending on the desired properties of the final product. Foam rubber is made by whipping air into the latex or by adding ammonium carbonate. Neoprene is a synthetic rubber produced by the polymerization of chloroprene:

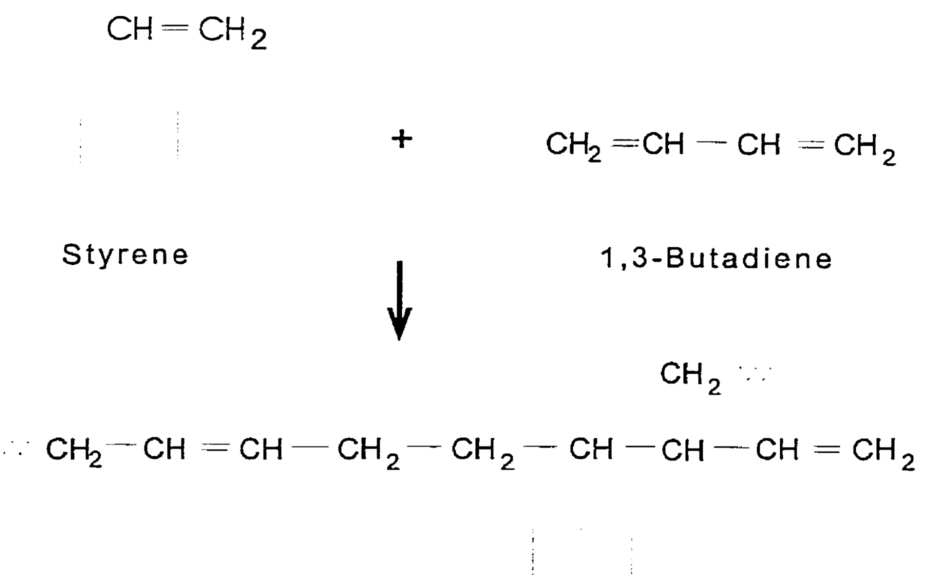


$$\mathrm{H_2C{=}CH{-}C(Cl){=}CH_2} \longrightarrow \left[\mathrm{CH_2{-}C(Cl){=}C{-}CH_2}\right]_n$$

Chloroprene

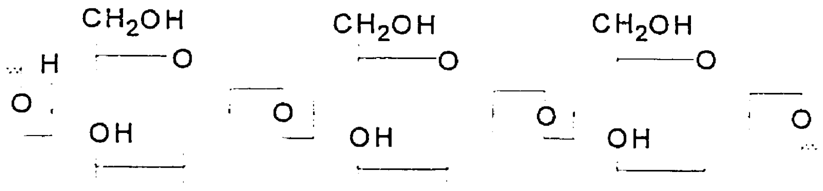
Neoprene

Styrene-butadiene rubber is used when the product must resist wear, such as in automobile tires:



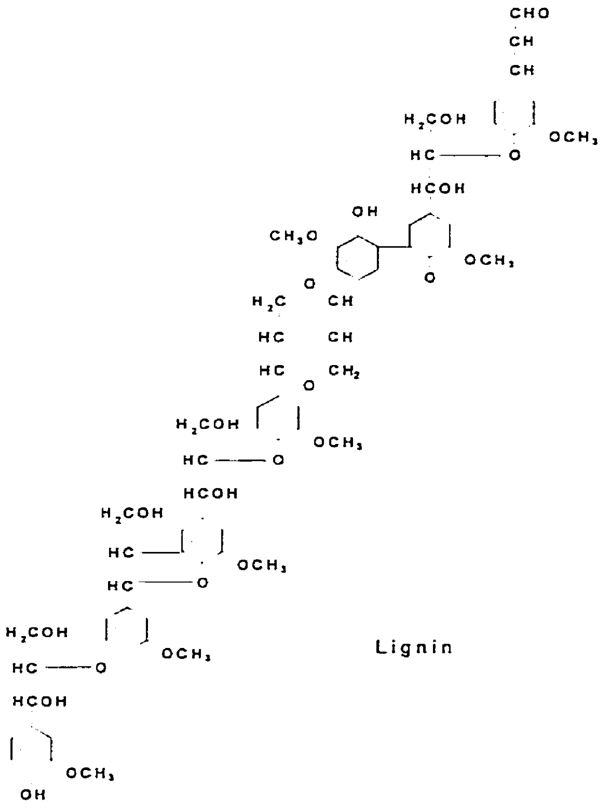
Styrene-butadiene rubber (SBR)

Paper made from wood or textiles made from naturally occurring vegetable fibres, such as cotton and linen (flax), are almost entirely cellulose. Cellulose is a macromolecule the repeating unit of which is β-glucose:



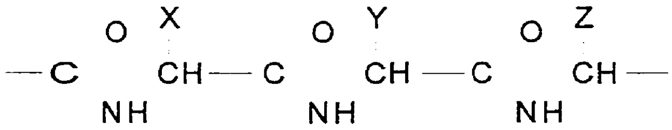
Cellulose

Cellulose is also the substance which remains after the lignin, which serves as a binding agent, is removed from wood. Wood is approximately 50% cellulose. All cellulosic materials burn, but they do not melt. Lignin, which constitutes up to 30% of all woods is a large network of branch-chain polymer molecules:



Lignin

Textiles made from animal fibres include wool and silk. Wool ($C_{42}H_{157}N_5SO_{15}$) is a protein containing sulphur, recurring amide groups ($-NH_2$) and amino acids (represented by X, Y and Z):



$$-\overset{\mathrm{O}}{\mathrm{C}}-\mathrm{NH}-\overset{\mathrm{X}}{\mathrm{CH}}-\overset{\mathrm{O}}{\mathrm{C}}-\mathrm{NH}-\overset{\mathrm{Y}}{\mathrm{CH}}-\overset{\mathrm{O}}{\mathrm{C}}-\mathrm{NH}-\overset{\mathrm{Z}}{\mathrm{CH}}-$$

Wool

Wool is difficult to ignite, burns slowly and is easy to extinguish. When wool does burn both sulphur dioxide (SO_2) and nitrogen oxides (NO_x) are produced. Silk ($C_{15}H_{23}N_5O_6$) consists of a mixture of two proteins, fibroin and sericin, but contains no sulphur. Burning silk will produce NO_x but not SO_2. Both wool and silk produce HCN but neither will melt.

In addition to the fire gases described above, smoke is produced under conditions of incomplete combustion. Smoke is an aerosol consisting of condensed phase components of the products of combustion and finely divided carbon particulates which have not undergone combustion but which remain suspended in the air. Although the particles themselves are microscopic in size (0.3-1.6 μm), they rapidly coalesce and thereby become visible. Not only does smoke consist of respirable particles, but these particles are also adsorbents (similar to activated charcoal) and are therefore, an additional vehicle for toxic combustion products. The heat release rate and generation rates of chemical compounds per unit surface area of the burning material increase to a maximum as the fire size increases. This increase in rates with fire size is due to radiative heat flux back to the burning material as well as airflow rate and mixing of air and fire products. Tewarson (1988) maintained that the generation of smoke in fires is generally associated not only with the reduction in visibility but also exposure to toxic environments. On the other hand, smouldering yields a substantially higher conversion of fuel to toxic compounds than does flaming, although this occurs more slowly (Ohlemiller 1988). In other words, the amount of toxic compounds is likely to be greater in flaming fires but the proportion and number of toxic compounds may be greater in smouldering fires because of the greater degree of incomplete combustion. This may be material dependent, however, some materials being more toxic in flaming mode and others in the non-flaming mode.

2. Fire toxicity

In Great Britain, from 1955 until 1971, there was a fourfold increase in casualties reported in the category "overcome by smoke and toxic gases" over the category "heat and burns" (Bowes, 1974). By the mid-1980's, half of all fatal casualties and a third of all nonfatal casualties of dwelling fires were reported in the category "overcome by smoke and toxic gases" (Home Office, 1983). This increasing trend occurred in spite of the fact that the total numbers of fires remained approximately constant over the same period of time (Purser, 1988). Accurate data for the cause of fire casualties in the U.S. was available from 1979 onward. From 1979 to 1990, the total number of fires and total fire deaths fell by 30%. Data from the U.S. National Centre for Health Statistics showed that the number of fire deaths attributed to burns, smoke inhalation and other causes fell by 50%, 15%, and 74% respectively (Hall and Harwood, 1995). However, the proportion attributed to smoke inhalation increased from 59% to 71% for the same period. Closer analysis from 1970 onwards for structural fires only, revealed that the number of fire deaths due to smoke inhalation increased by 11% from 1970 to 1979, and decreased by 27% from 1979 to 1990. The overall decrease in the number of fire deaths from 1970 to 1990 was 19%. However, the proportion of deaths attributed to smoke inhalation increased steadily from 72% to 89% for the same period. At the same time, most of the deaths due to smoke inhalation appeared to have occurred in incidents involving flashover where the victims were found in rooms other than the room of fire origin.

There are a number of possible explanations for the apparent increase in fire toxicity in recent years:

a. Greater awareness of smoke toxicity, leading to increased reporting;
b. Larger, modern, decompartmentalized structures where fire gases pass rapidly through ventilation systems, leading to more deaths due to smoke inhalation far from the fire itself;
c. Relatively few large, catastrophic fires involving the deaths of large numbers of people which would dominate the overall picture;
d. Advances in the treatment of burn victims, resulting in a higher survival rate than in previous decades;
e. Improvements in product design, safety and public behaviour, reducing the kinds of fires that lead to burn deaths;
f. Modern firefighting methods and equipment, resulting in the recovery of bodies before they became burned.

The realization that smoke toxicity appeared to be an increasing problem prompted a series of investigations to evaluate the toxicity of fire effluent. Two approaches were adopted. The first hypothesized that smoke from modern fires was more toxic due to the presence of new synthetic materials which released combustion products not present previously. Research focused on materials-based toxicity tests where the toxicity of the material was ranked in terms of animal LC_{50} (Purser, 1988). The second hypothesis was that the basic toxic products of combustion were essentially the same as they had always been, but that the rate of fire growth and the rate of evolution of fire effluent was greater. Research focused on following the time/concentration profiles of a few basic toxic products in large-scale fire tests. Both models were based on simplistic and erroneous assumptions concerning the effects and interaction of toxic products (Purser, 1988). The intent, in both cases, was to provide information to design engineers which would be useful in the prediction of the likely toxic hazard to occupants of various scenarios according to the materials used, the building design and factors such as ignition, flame spread and rate of smoke evolution. In both approaches, attention focused on the acute effects leading to death or incapacitation. Overall, in spite of a variety of materials and scenarios, toxicity seemed to be dominated by asphyxiants such as CO and hydrogen cyanide or by irritants. Although there were a few highly toxic products that were found (the bicyclic phosphate esters and the combustion products from PTFE), it appeared that the theory that smoke casualties have increased because new, highly toxic products were formed from modern materials was unlikely to be correct (Purser, 1988).

B. FIREFIGHTING

There are approximately 265,700 career and 807,900 active volunteer firefighters in the United States, and 4000 career and 17,000 part-time firefighters in Québec (Legault-Faucher and Levesque, 1991; Karter and Leblanc, 1993, 1994, 1995; Karter, 1995, 1996). The City of Montréal fire department is the largest in

Canada with a total of 1,883 full-time personnel (SPIM, 1994). The City of Montréal is located on a large island in the St. Lawrence River. It experiences rigorous climatic conditions with temperatures ranging from -30°C (-22 °F) in the winter to +32°C (+90°F) in the summer. The territory covers 175 km^2 and the city has a population of 1,018,000. There are also 29 other municipalities on the island, each with their own fire department, which include an additional population of 732,000. Between 1985 and 1994, the Montréal fire department underwent major restructuring to rejuvenate the force, to acquire new equipment and technologies, and to modernise firefighting strategies. During this period, 1000 new recruits were hired (60% of the force). In 1994, the fire department had specialized high angle (*spider*) rescue crews (41 firefighters), confined space rescue crews (144 firefighters), hazardous products response crews (61 firefighters) and marine rescue crews (249 firefighters). Firefighters also played a vital role in fire prevention and education, arson investigation, training and equipment repair and maintenance. In 1994, City of Montréal firefighters repaired or serviced 25,471 pieces of equipment, including 5,315 self-contained-breathing-apparatus (SCBA's), participated in 844 fire drills, concluded 618 arson investigations (of which 311 were criminal fires), testified at 1,206 court cases, conducted 59,416 inspections and home visits, responded to 8,462 complaints and issued 18,876 notices of infractions. Through fire safety classes, conferences, courses, school visits, information kiosks and other means, they also provided education to 48,486 members of the public. These prevention and education activities have contributed to a 17% decrease over eight years in the total number of structural fires. From 1987 to 1994, the number of structural fires declined from a total of 2041 to 1684.

1. Firehalls

Firehalls generally comprise office space, living quarters for firefighters and garages for emergency vehicles. There was considerable variation in the size and design of firehalls in Montréal, construction dating from 1891 to 1994, and in the number of alarms responded to by different firehalls. Firehall garages house diesel-fuelled trucks and, in some cases, gasoline-fuelled automobiles. In 1994, the Montréal fire department had 34 pump trucks, 10 multi-functional pump trucks, 21 ladder trucks, 10 aerial or platform trucks, two compressed air supply trucks, one mobile command post and 101 other assorted vehicles in service in 36 firehalls. Firefighters use an assortment of pneumatic and gas-powered tools in firefighting and rescue operations. Proper functioning of the power tools is checked inside the firehalls on a weekly basis. In 1994, most firehalls were not equipped with mechanical ventilation and the living quarters were usually separated from the garage by doors or by being located a story above the garage. Firefighters reported a subjective impression that diesel emissions were higher in some firehalls than in others. In the case of two firehalls, there was no mechanical ventilation system to remove diesel exhaust from the garage and the living quarters were not adequately isolated from the garage. The question arises as to whether or not diesel emissions in firehalls are sufficiently high to mandate the installation of mechanical ventilation systems to remove contaminants from firehall garages. Since there is no standard sampling method for the evaluation of diesel emissions, it was necessary to develop a monitoring protocol applicable to the situation of firehalls.

2. Activities

Firefighting consists of two phases: 1) *knockdown*, during which the fire is brought under control; and 2) *overhaul*, when the fire is extinguished and clean-up begins. It has been observed that approximately 90% of structural fires are either extinguished or abandoned and fought from the outside within 5-10 minutes, the average duration of heavy physical activity being 10 min. (Gempel and Burgess, 1977; Gilman and Davis, 1992). Temperatures at structural fires range from 38°C to 66°C and, on occasion, reach 200°C or higher (Abeles et al., 1973). Firefighters would not normally be exposed to temperatures exceeding 80°C. City of Montréal firefighters are required to don their masks when they enter a fire or "see smoke" but there is currently no standard operating procedure to determine when the masks may be removed. Burgess and Crutchfield (1995) were unable to find documentation which would permit estimation of firefighter on-scene time at structural fires. Through discussions with administrative and combat firefighters they estimated that Tucson firefighters spent no more than approximately 750 minutes per year inside municipal structural fires.

For a 70 kg man at rest or engaged in light, heavy or maximum work, it can be expected that the volume of air breathed will be 8.5, 25, 60 and 110 L/min., respectively. Louhevaara et al. (1985a, b) found that firefighters typically ventilated at a rate of 45 to 60 litres of air per minute (minute ventilation or V_E). The amount of contaminant inhaled is thus greater for the firefighter than for the typical industrial worker (Sothmann et al., 1992a, b). Given that a firefighter can be expected to engage in heavy to maximum work levels, an air cylinder containing 43 ft^3 (1,218 L) of air could not reliably be expected to supply air for more than 15 minutes. Metabolic rate, or work rate, can be measured by oxygen consumption (Vo_2). The maximal aerobic capacity (Vo_{2max}) of firefighters, at the 95th percentile, has been calculated to be 4.0 L/min (Horvath et al., 1975, Myhre et al., 1986). In simulated rescue situations, firefighters were found to have a mean Vo_{2max} of 3.0 L/min (75% of the maximum), a heart rate of 142-160 beats/min (78% of the maximum), and ratings of perceived exertion varying from "fairly hard" to "hard" (Luss et al., 1991). In 23% of cases, the heart rate exceeded the maximum heart rate attained in laboratory tests. Lemon and Hermiston (1977) found a mean Vo_{2max} of 3.5 L/min for firefighters. Table 1 summarizes the average Vo_2 and V_E for moderate, high and very high work rates (Kamon et al., 1975; Turner et al., 1995). Duncan et al. (1979) found that firefighters' plasma volume (determined from haemoglobin and haematocrit measurements) decreased by 5.2% when they were working in full turnout gear and in heat. The SCBA was carried but not used during these trials. Oxygen uptake could not be estimated from heart rate data since the increased heart rate might be due to high temperatures and psychological stress in addition to the increased energy demand resulting from the work load. Duncan et al. (1979) found that, although there were increases in heart rate (HR_f=172.7 min^{-1}) and rectal temperature (T_f=41.8°C) with increased work, there was no increase in oxygen uptake (10.80 cm^3/kg·min) for the same work load at higher temperatures.

Table 1. Work Levels and Metabolic Rates[a]

Work Level	Oxygen Consumption Vo_2 (L/min)	Ventilation Rate V_E (L/min)
Moderate	1.35	30.0
High	2.00	44.0
Very high	3.00	65.0

[a]Data of Kamon et al. (1975) and Turner et al. (1995).

Firefighters do not wear their SCBA's from the time they arrive until the time they leave the fire scene. They must have some way of determining when they can safely remove their respiratory protective apparatus. Currently, they have no way to judge the toxicity of the atmospheres in which they work other than the subjective "appearance" of the smoke, hardly a valid indicator of toxicity. A study, which included the fire departments of Pittsburgh, New York City, Phoenix, Boston, and Cincinnati, found that 70% of firefighters wore their masks less than 100% of the time during knockdown (Jankovic et al., 1992). This is to be expected since firefighters must be able to communicate with each other while working but often the only way that they can do so is to pull away the face-piece before calling to one another (Kramer, 1991). SCBA's are rarely worn during the smouldering phase of the fire or during mop-up operations. Brandt-Rauf et al. (1988 and 1989) noted that, in several fires, SCBA's were used only partially or not at all (presumably owing to the impression of low smoke intensity); yet it was at these same fires that firefighters were found to be exposed to appreciable concentrations of toxic contaminants (particulary CO and benzene). In 1977, Burgess et al. found that there was no significant difference in ambient concentrations of CO between firefighters who chose to wear their SCBA's for part of the time and those who did not wear it. These observations by both Brandt-Rauf and Burgess suggest that firefighters do not have the ability to judge when the SCBA's should or should not be worn.

3. Standards and Regulations

Exposure limits to chemical contaminants in ambient workplace air are the same for firefighters as for other industrial workers, and are expressed as an 8-hour time-weighted average. The limits may vary slightly from province to province in Canada but they are similar to the ACGIH (1996) *Threshold Limit Values* (TLV's). Emergency response guidelines (with higher exposure limits than the TLVs) can be used in life-and-death rescue situations to estimate the level of contamination to which rescuers can be exposed without experiencing or developing life-threatening health effects (AIHA, 1988). None of these limits take into account the increased absorbed doses in the case of firefighters who function at near maximum work levels.

There are also limits for allowable concentrations of chemical contaminants in compressed breathing air. These are found in the Canadian Standard Association standard *CAN3-Z180.1-M85* on *Compressed Breathing Air and Systems* (CSA, 1985). Specific, maximum allowable concentrations are included in the Standard, for CO, CO_2, methane, NO_2, nitrous oxide, non-methane hydrocarbons, trichlorotrifluoroethane, dichlorodifluoromethane, water vapour, oil, particulates and condensate (Table 2). These are ceiling levels not to be exceeded at any time. For other contaminants, the standard specifies a maximum allowable concentration of 1/10 of the current TLV documented by the American Conference of Government Industrial Hygienists (ACGIH). The Standard for medical air, Z305.1-92, is less stringent and must not be applied to compressed breathing air (CSA, 1992*)*. For example, twice as much nitrous oxide is allowed in Medical Air as in compressed breathing air, and the maximum concentration of unspecified

Table 2. Maximum Allowable Levels of Contaminants in Compressed Breathing Air[a]

Contaminant	Level	Units
Carbon monoxide (CO)	5	ppm[d]
Carbon dioxide (CO_2)	500	ppm
Methane (CH_4)	25	ppm
Non-methane hydrocarbons (NMOC)	1/10 of the TLV[c]	
Nitrogen dioxide (NO_2)	0.3	ppm
Nitrous oxide (N_2O)	2.5	ppm
Freon12, Freon22, Freon113[b]	5	ppm
Oil, particulates and condensates	1	mg/m^3
Odour	none	
Water vapour	The pressure dew-point shall be 5°C below the ambient temperature[e]	

[a] Adapted from the Canadian CAN3-Z180.1-M85 Standard on Compressed Breathing Air and Systems.

[b] Dichlorodifluoromethane (Freon12), Monochlorodifluoromethane (Freon22), 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon113).

[c] Threshold Limit Value as currently documented by the American Conference of Government Industrial Hygienists (ACGIH).

[d] 1mL/m^3 = 1 part-per-million (ppm) by volume.

[e] Water vapour levels shall never exceed 27 ppm measured at atmospheric pressure for systems at or above 1800 psi.

contaminants in Medical Air is five times higher than that which is allowed in compressed breathing air. Also, the atmospheric dew-point of compressed breathing air must not exceed -53°C (27 ppm) under any circumstances, while the atmospheric dew-point of medical air may be as high as -15°C (1,557 ppm). This corresponds to 2,216 psig pressure dew-points of -5°C and +10°C respectively. That is to say that, the water vapour in the air will condense and freeze the regulator if the ambient temperature is lower than the pressure dew-point. If compressed breathing air is used in an ambient temperature of -26°C, as frequently occurs outdoors in Canada, then the atmospheric dew-point must not exceed -70.5°C which corresponds to 2.3 ppm of water (Tables 3 and 4). Unlike ambient workplace air, there are no emergency response guidelines for toxic contaminants in compressed breathing air which can be used in life-and-death rescue situations to estimate the level of contamination to which rescuers can be exposed without experiencing or developing life-threatening health effects.

4. Compressed Breathing Air

a. Production of Compressed Breathing Air

Montréal firefighters changed over from pressure-demand to positive pressure SCBA's in 1985. It was not until 1987, however, that all firefighters in the department were issued individual SCBA's. Prior to 1993, breathing air was manufactured by the fire department using a Bauer™ model K21 (50 Hp 60 Hz), oil-lubricated 5000 psig compressor. This compressor is a 4-stage, 3-cylinder, air-blaster fan cooled, single-acting and reciprocating unit operating with an optimum oil pressure range of 850-950 psig (Bauer™, 1984). The air intake was located outside the building. Ambient air was drawn into the compressor through a micronic intake filter. The compressor was placed approximately three metres from the adjacent wall which allowed unrestricted flow of cooling air through the fan screen. The exhaust opening was on the opposite wall and close to the ceiling. A large

Table 3.

Approximate moisture content in compressed breathing air at 15.3 MPa (2,216 psig) typical of high pressure self-contained-breathing-apparatus[a]

MINIMUM STANDARD	Atmospheric dew-point measured at 21 °C and 101.3 kPa (14.7 psig)		Water vapour content at atmospheric pressure	Pressure dew-point at 15.3 MPa (2,216 psig)		Water vapour content at 15.3 MPa (2,216 psig)
	°C	°F	mL/m^3 (ppm)	°C	°F	mL/m^3(ppm)
	- 46	- 50	68	7	45	10 268
	- 49	- 55	48	2	36	7 248
	- 51	- 60	34	- 2	28	5 134
Underwater diving:	**- 53**	**- 63**	**27**	**- 5**	**23**	**4 077**
	- 54	- 65	24	- 6	21	3 624
	- 56.5	- 70	17	- 10	14	2 567
	- 59.5	- 75	11.5	- 14	7	1 737
	- 62	- 80	8	- 18	0	1 208
	- 65	- 85	5.5	- 22	- 8	831
	- 68	- 90	3.5	- 27	- 17	529
Firefighting:	**- 70.5**	**- 95**	**2.3**	**- 31**	**- 21**	**347**
	- 73	- 100	1.5	- 34	- 29	227

[a] Canadian Standard Association CAN3-Z180.1-M85 (CSA, 1985).

Table 4.

Approximate moisture content in compressed breathing air at 689.1 kPa (100 psig) typical of low pressure breathing gas distribution systems[a]

MINIMUM STANDARD	Atmospheric dew-point measured at 21 °C and 101.3 kPa (14.7 psig)		Water vapour content at atmospheric pressure	Pressure dew-point at 689.1 kPa (100 psig)		Water vapour content at 689.1 kPa (100 psig)
	°C	°F	mL/m³ (ppm)	°C	°F	mL/m³ (ppm)
	- 7	19	3 394	22	72	23 080
	- 8	18	2 996	20	68	20 370
	- 10	14	2 636	18	64	17 930
	- 13	9	2 035	14	57	13 840
Medical air:	**-15.5**	**4**	**1 557**	**10**	**50**	**10 590**
	- 18	0	1 181	6	43	9 030
	- 22	- 8	885	1	34	6 020
	- 25	- 13	635	- 3	27	4 320
	- 28	- 18	450	- 6	21	3 060
	- 32	- 26	316	- 11	12	2 150
	- 35	- 31	219	- 14	7	1 490
	- 38	- 36	150	- 18	0.4	1 020
	- 40	- 40	124	- 20	- 4	842
	- 42	- 44	102	- 23	- 9	692
	- 44	- 47	83	- 25	- 13	566
	- 46	- 51	68	- 27	- 17	462
	- 47	- 53	55	- 28	- 18	376
	- 49	- 56	45	- 31	- 24	305
Firefighting:	**- 50**	**- 58**	**36**	**- 32**	**- 26**	**246**
	- 52	- 62	29	- 35	- 31	198

[a] Canadian Standards Association CAN3-Z180.1-M85 (CSA, 1985).

amount of heat is generated when air is compressed and it is necessary to cool the air to nearly ambient temperature to prevent combustion of the lubricating oil and the production of CO.

The compressed air passes through a wall-mounted JMAR™ air purification system at 5,000 psig to remove contaminants before being stored in 300 ft^3 cylinders at 2,400 psig. The first stage of the purification system is a separator which eliminates oil, water vapour and solid particles greater than 0.5 μm by causing the aerosol droplets to coalesce. These larger droplets are collected in the sump for subsequent draining. The coalescer element should be inspected at least once a week and it should be replaced when dirt is found on the inside of the element. If this is not done, oil and water will enter the second stage of the purification system and reduce or degrade completely its ability to remove toxic and dangerous contaminants from the air. The second stage of the system consists of a series of chemical cartridges including silica gel, molecular sieve 13X, hopkelite 4A catalyst and activated charcoal which remove gases, odours and any remaining traces of oil and water vapour (JMAR™, 1990). Carbon monoxide is removed by catalytic oxidation to CO_2 which remains in the final product. Catalyst life is reduced in the presence of water vapour and/or heat. Purification cartridge life is calculated based on a process air temperature of 20°C. An increase to 35°C reduces the life of the cartridge by 50% of its original capacity (Jordair™, 1990). Cartridges must be replaced at least once every six months regardless of the amount of air processed. If it is necessary to replace one cartridge, all cartridges in the system must also be replaced at the same time. Alarms are installed to signal the presence of CO in the purified air at levels greater than 5 ppm and to signal the presence of water vapour at levels greater than 2.5 ppm.

b. Self-Contained Breathing Apparatus

In 1994 in the City of Montréal Fire Department, there were 862 SCBA cylinders at 2,216 psig each containing 43 ft^3 of air and there were 46 SCBA cylinders at 4,500 psig each containing 90 ft^3 of air in regular use. An audible alarm sounds when the air pressure in the cylinder is reduced to 500 psig. At this time, the firefighter exits the work area. All compressed air cylinders, as well as their locations, were identified by an inventory number. There were 676 cylinders permanently assigned to firefighting crews, 232 reserve cylinders permanently located in the two compressed air supply trucks, and 115 cylinders in reserve at the technical services department. The compressed air supply trucks also had a bank of 3,600 psig cylinders each containing 450 ft^3 of air. This stored, compressed air was used to refill firefighters' SCBA cylinders, both at the scene of large fires and at the firehalls. Firefighters needing extra air at very large fires, also borrowed reserve cylinders from the compressed air supply vehicle. No record was kept of which crews borrowed these cylinders. Until 1993, most of the air used was obtained from a 5,000 psig Bauer™ compressor (Model K21). This compressor was removed from service in 1993 and the compressed air supply vehicles replenished their banks of air from two other 5,000 psig compressors. Two additional 7,000 psig compressors were acquired in 1995.

c. Air-supplied Respirators

Firefighters assigned to confined-space entry carry a Hip-Pac supplied-air respirator. There are nine such units at the Montréal Fire Department. A 100 m breathing-hose connected to the air bank located in the air supply truck (vehicle 1600), supplies air at a line pressure of 100 psig to the firefighter's air regulator, bypassing the Hip-Pac, 2,216 psig, 8 ft^3 compressed breathing air cylinder. The regulator then reduces the pressure from 100 psig to the required 1 psig in the positive-pressure face mask. The air in the Hip-Pac cylinder is used for emergency escape only. In the case of firefighters working on aerial ladders, a 50 m (NIOSH-approved), rubber breathing-hose (at 100 psig) is attached directly to the face mask regulator. The air is supplied from 2,400 psig, 300 ft^3 cylinders located on the truck.

d. Reports of Contamination

Compressed breathing air is used by: (1) firefighters using SCBA's; (2) recreational and commercial divers using SCUBA's; (3) confined-space and construction workers using supplied-air respirators; (4) oil-field workers, armed-forces personnel and many other categories of workers who are exposed to toxic or oxygen-deficient environments.

Compressed breathing air may be potentially contaminated by water vapour, other gases (CO_2, CO, NO_2, N_2O) and various hydrocarbons. Periodically, there are reports of unexplained deaths of SCUBA divers. Daenens (1973) reported one case of a diver who was overcome with nausea, vomiting, progressive paralysis of the lower limbs and unconsciousness at a depth of 25 m. The case was presumed to be one of decompression sickness. Further investigation determined that the compressed breathing air contained 16,000 ppm of carbon monoxide (CO) and 22,500 ppm of carbon dioxide (CO_2), the origin of the contaminant gases being a malfunction in the compressor. This has been the only citation in the scientific literature of contaminated compressed breathing air. A coroner's investigation found the death of one diver to be due to the formation of ice in the regulator arising from water contamination of the compressed air (Paquin, 1990). A coroner's inquest into the deaths of nine SCUBA divers in Québec found that, in four out of seven cases where the SCUBA's were tested, the compressed breathing air was contaminated with water vapour (Boudrias, 1991). However, the breathing air was not tested for other contaminants. The coroner recommended that the *Canadian CAN3-Z180.1-M85 Standard on Compressed Breathing Air and Systems* be made obligatory and that air quality tests be performed twice a year by producers of compressed breathing air (CSA, 1985). Boudrias (1991) concluded that none of the accidents was due to improper functioning of the equipment and that, without exception, all of the deaths were due to "errors in judgment". Another coroner's investigation found that the death of one SCUBA diver was due to a heart attack (Viens, 1993). A more recent inquest into the deaths of ten SCUBA divers noted that the previous recommendation for compressed breathing air quality control had not been implemented (Boudrias, 1995). In none of these cases was the breathing air used by the victim tested for chemical contamination. In one case, the compressed breathing air used had a strong, foul odour and the victim died from asphyxiation due to aspiration of his own vomit. There are approximately 4,000 new divers certified yearly by various agencies in Québec and there are an estimated 25,000 Québecers who practise SCUBA diving at least once every year (Boudrias, 1991; RSSQ-MSSS, 1993). Between 1990 and 1996, SCUBA diving accidents have accounted for the deaths of 27 people in Québec (Boudrias, 1996). There were a total of 1,925 nonoccupational underwater diving fatalities in the United States between 1970 and 1989 inclusive (NUADC, 1991).

In response to a questionnaire to fifty-two fire chiefs in Finland, freezing of the SCBA was mentioned as being a problem because of contamination by water vapour (Mäkinen, 1991). In a survey of Alberta experiences regarding the use of respiratory protective equipment, the most prevalent complaint expressed was the difficulty in reliably producing low moisture content breathing air from compressor supply systems (Manecon, 1987). Lemire and Champagne (1980) reported that 80% of inspected SCUBA air cylinders were found to be excessively corroded, presumably due to the presence of excessive humidity. Radford and Levine (1976) reported that the mean carboxyhaemoglobin (COHb) concentration for nonsmoking firefighters who used their masks all of the time was 1.42%. In a study of the COHb levels in firefighters, one non-smoking firefighter who had been using his breathing apparatus showed increased COHb concentrations from 2.0% to 4.80% (Loke et al., 1976). Jankovic et al. (1992) sampled both inside and outside of the firefighter's mask at 22 structural fires. The concentration of carbon monoxide (CO) measured inside the mask varied from less than 1 to 105 ppm while the concentration of carbon dioxide (CO_2) was 460 to 21,300 ppm and that of benzene varied from 0 to 21 ppm. In none of these firefighter studies was the possibility considered that the findings might be the result of compressed breathing air contamination.

It has been observed that some young, apparently healthy firefighters in the Montréal Fire Department appeared to tire much more quickly than others, sometimes attaining exhaustion after only 15 or 30 minutes of work and occasionally complaining of headache and nausea (Dussault, 1993). The compressor air had been tested four months previously by a qualified laboratory and met all the purity requirements of the *Canadian CAN3 180.1-M85 Standard on Compressed Breathing Air and Systems*. A spot check of the compressor air did not reveal carbon monoxide contamination. However, a random check of an SCBA tank showed elevated levels of CO, thereby prompting an investigation of the possible sources of contamination.

5. Accidents, Injuries and Workmen's Compensation Claims

There were 130 firefighter accidents at fires in Montréal 1991, with 58 injuries, 10 burn and 4 smoke inhalation cases (SPIM, 1991). The Montréal accident rate was 29.2 fire scene injuries per 1,000 fires. There were 163 accidents during activities other than firefighting. The accident rate for American cities of comparable size to the City of Montréal was 26.7 fire scene injuries per 1,000 fires (Karter and Leblanc, 1994). In 1984, the CSST payed out $1,400,000 in workmen's compensation benefits to Québec firefighters (Devost, 1992). From 1983 to 1987, there were an average of 101,000 firefighter injuries and 121 firefighter deaths per year in 13,000 fire departments in the United States (Karter and Leblanc, 1993, 1994, 1995a, b). Buildings posing the highest risk to firefighters were vacant, under-construction, manufacturing or storage properties. Almost half of the injuries occurred at the fire scene, outside the building and above ground (Karter and Leblanc, 1994). By far, the largest category of non-fatal firefighter injuries associated with fires (39% of injuries) was reported to be contact with flames or smoke. The leading cause of non-fatal injury among younger firefighters was related to smoke inhalation (FEMA, 1990). Overall, 10% of non-fatal firefighter injuries were caused by smoke inhalation.

The number of deaths occurring in the line of duty was greater than that of any other occupation and half of these deaths were caused by heart attacks or cerebrovascular accidents at the fire scene (Green and Crouse, 1991). Some 97% of these heart attacks were attributed to "stress" (Washburn et al., 1990, 1993, 1995). The nature of fatal injury or illness accounting for the highest proportion of deaths in 1992 (51.4% or 38 deaths) was related to heart attacks (Washburn et al., 1993). All of the heart attack deaths were attributed to stress and overexertion (Karter, 1996). "Stress" was listed as the leading cause of death (54.1% or 40 deaths). The increased cardiovascular risk under the unusual conditions to which firefighters are routinely subjected is not well understood, but they are subjected to a number of stresses which place unusual demands upon the cardiorespiratory system (Barnard et al., 1976). Firefighters experience four sources of stress: 1) <u>psychological stress</u> during response to alarms; 2) extreme <u>physical stress</u> during the activities involved in firefighting; 3) <u>heat stress</u>; and 4) <u>chemical stress</u> following inhalation of toxic combustion products (Sothmann et al., 1992a). The physiological effects of firefighting include increased body temperature, near maximum heart rate and high ventilation rates (Barnard and Duncan, 1975; Duncan et al., 1979; Louhevaara et al., 1985a, b; White and Hodous, 1987; Sköldstrom, 1987; Gavhed and Holmer, 1989; White et al., 1989; Harber et al., 1991; Luss et al., 1991). It is conceivable that some accidents may be due to dizziness or impaired judgement resulting from the toxic effects of chemical contaminants. Some of the line-of-duty accidents and deaths which have been attributed to human error or cardiovascular disease induced by strain and exertion may have been due, in part, to acute or chronic effects of the chemicals and combustion products to which firefighters are exposed.

Several states in the U.S. apply rebuttable presumptions of causality to firefighters' claims for heart disease and cancer (IDSP, 1994). In Maryland, the presumption applies to claims for throat, prostate, rectal or pancreatic cancer and leukaemia (Larson, 1991). Massachusetts (1990) applies a rebuttable presumption of causality to firefighters' claims for any cancer affecting the skin or the central nervous, lymphatic, digestive, haematological, urinary, skeletal, oral or prostate systems. In Canada, firefighters claims for heart disease, heart attack and cancer are adjudicated by the Provincial Workmen's Compensation Boards on a case-by-case basis. British Columbia applies a rebuttable presumption of causality to claims for heart disease but not to claims for cancer. As of 1995, none of the Canadian jurisdictions recognized cancer as a professional disease for firefighters. In 1991, a British Columbia decision to reject claims filed by, or on behalf of, firefighters diagnosed with cancer was appealed with the support of the *International Firefighters Association* (IFA). Three applications were rejected by the appeal division, for non-Hodgkin's lymphoma, colorectal cancer and adenocarcinoma of the sigmoid colon. Two applications were allowed, for malignant melanoma and multiple myeloma. The transcript of these hearings revealed that the greatest weakness in all of the arguments presented before the court was the lack of actual sampling data in the scientific literature which could support or refute the apparent association between firefighting and cancer reported in various epidemiological studies. The Occupational Disease Panel (formerly the Industrial Disease Standards Panel) of Ontario completed an in depth analysis of the epidemiological evidence with respect to firefighting and cardiovascular disease and cancer (IDSP, 1994). The panel found that a probable connection exists between firefighting and the following: cardiovascular disease, atherosclerosis which results in aortic aneurysm, primary cancer of the brain, primary lymphatic and haematopoietic cancers, colon cancer, bladder cancer, kidney cancer, and rectal cancer. Guidotti (1995) has reviewed the epidemiological literature on disease risk among firefighters. Assessment of the likelihood of causation using legal criteria lead to the conclusion that firefighting is a likely cause of disease in the following cases: lung, colon, rectal, bladder, kidney, ureter, lymphatic and haematopoietic (aggregate) cancers, brain tumours (Guidotti, 1995).

C. EPIDEMIOLOGICAL STUDIES

1. Overall Mortality

Table 5 summarizes the results of the mortality studies of firefighters. This group did not show an increased risk of mortality overall with respect to the general population. However, there is no evidence that the *healthy worker effect* has reduced the overall mortality with respect to the general population either.

2. Heart Disease

Firefighting is a physically strenuous occupation (Gledhill and Jamnik, 1992; Guidotti, 1992a). In general, firefighters are selected according to stringent criteria for physical fitness and the distribution of cardiovascular risk factors has been found to be reduced relative to non-firefighters of the same age group (Barnard et al., 1976; Dibbs et al., 1982; Horowitz and Montgomery, 1993). One would expect that the "healthy worker effect" would result in a decreased risk of coronary disease relative to the general population. However, Horowitz (1990) found that Montréal firefighters had higher flexibility and muscular endurance, but had lower cardiovascular endurance and more elevated heart rate response to exercise than the general Canadian population. Friel and Stones (1992) found that firefighters consumed calories in excess of needs and that their high cholesterol levels and lifestyles made them vulnerable to heart attack on the job.

Howe and Burch (1990) calculated standardized mortality odds ratios (SMOR) based on four proportionate mortality studies (Milham 1976; Petersen and Milham 1980; Feuer and Rosenman 1986; Gallagher et al., 1989). The pooled results for heart disease were inconclusive. A number of epidemiological studies of firefighters have failed to show an association between heart disease and firefighting (Dibbs et al., 1982; Vena and Fiedler, 1987; Hansen, 1990; Howe and Burch, 1990; Rosenstock et al., 1990; Beaumont, 1991; Guidotti and Clough, 1992; Guidotti, 1992a). Other studies have found small, but statistically significant

Table 5. Epidemiological studies of firefighters

Author	Type	Mortality	95% C.I.	Firefighters	Cases	Years
Hansen (1990)	SMR[a]	0.99	0.75-1.29	886	57	
Guidotti (1993)	SMR	0.96	0.87-1.07	3328	370	1927-87
Vena (1987)	SMR	0.95	0.87-1.04	1867	470	150-79
Aronson et al. (1993)	SMR	0.94	0.88-1.01	5414	777	1950-89
Beaumont (1991)	SMR	0.90	0.85-0.95	3066	1186	1940-82
Tornling et al. (1994)	SMR	0.82	0.73-0.91	1116	316	1951-86
Demers & Rosenstock (1992)	SMR	0.81	0.77-0.86	4546	1169	1945-89
Eliopulos (1984)	SMR	0.80	0.67-0.96	990	116	1939-78
Heyer (1990)	SMR	0.76	0.69-0.85	2289	383	1945-83
Mastromatteo (1959)	SMR			1039		1921-53
Musk et al. (1978)	SMR			5655		1915-75
Lewis et al. (1982)	SMR			1559		1940-80
Bates (1987)	SMR			646		1949-59
Milham (1983)	PMR[b]					1950-79
Orris et al. (1992)	PMR				3084 deaths	1940-88
Grimes et al. (1991)	PMR			205		1969-88
Feuer & Roseman (1986)	PMR				263 deaths	1974-80
Decoufle et al. (1977)	PMR			1113		1967
Sama et al. (1990)	OR[c]				321 cancer	1982-86

[a]standardized mortality ratio, [b]proportionate mortality ratio, [c]relative risk

excesses of arteriosclerotic, ischemic, and overall circulatory disease (Feuer and Rosenman, 1986; Grimes et al., 1991; Orris et al., 1992). Sardinas et al.(1986) found a significant excess of ischemic heart disease (SMR=1.5). Bates (1987) found a significant excess of coronary heart disease (SMR=1.7). Aronson et al. (1993) found a significant excess of aortic aneurysm (SMR=2.3). An exploratory case-control study found that offspring of firefighters were associated with heart defects (Olshan et al., 1990). In general, the etiology of congenital anomalies in humans is poorly understood, with an estimated 60% of all human birth defects having no known cause (Kalter and Warkany, 1983). Occupations other than firefighters that may be associated with congenital heart defects included metal workers, fishermen, forestry workers and electronics workers (Olshan et al., 1991). These workers would be expected to be exposed to fuels, combustion products, metals or solvents (VOC's). See Table 6 for a summary of the epidemiological studies related to heart disease in firefighters.

3. Respiratory Disease (Excluding Cancer)

Musk (1979) found that firefighters experienced a one-second forced expiratory volume ($FEV_{1.0}$) decrease of 0.05 litres and that this decline was related to the severity of smoke exposure. Decreases in $FEV_{1.0}$ in excess of 0.10 litres were found in 30% of observations. Sheppard et al. (1986) found that decreases in forced vital capacity (FVC) and in $FEV_{1.0}$ lasted for as long as 18 hours after firefighting. Other studies have suggested an association between firefighting and reduced pulmonary function or increased pulmonary disease (Peters et al., 1974; Sidor and Peters, 1974a, b; Musk et al., 1977; Loke et al., 1980; Sparrow et al., 1982; Sherman et al., 1989). Sherman et al. (1989) have suggested several possible mechanisms underlying an observed increase in airway responsiveness lasting as long as 24 hours: 1) reflex bronchoconstriction caused by the stimulation of irritant receptors; 2) small airway obstruction resulting from mucosal injury and edema; or, 3) decreased airway calibre secondary to altered autonomic regulation

Table 6. Epidemiological studies of cardiovascular disease and firefighters

Disease	Author	Type	Mortality	95% C.I.	Firefighters	Cases
Aortic aneurysm	Aronson (1993)	SMR[a]	**2.26**	1.36-3.53	5414	19
Coronary heart	Bates (1987)	SMR	**1.73**	1.12-2.66	646	21
	Decoufle (1977)	PMR[b]	1.06	0.96-1.16	1113	450
Ischemic heart	Sardinas (1986)	SMR	**1.52**	1.23-1.81	306 deaths	115
	Hansen (1990)	SMR	1.15	0.74-1.71	886	24
	Orris (1992)	PMR	**1.11**	1.06-1.18	3084	
	Guidotti (1993)	SMR	1.06	0.87-1.28	3328	109
	Aronson (1993)	SMR	1.04	0.92-1.17	5414	289
	Tornling (1994)	SMR	0.98	0.81-1.17	1116	118
	Beaumont (1991)	RR[c]	0.95	0.87-1.04	3066	457
	Eliopulos (1984)	SMR	0.84	0.60-1.14	990	39
	Demers (1992)	SMR	0.82	0.74-0.90	4546	394
Arteriosclerotic heart	Feuer (1986)	PMR	**1.22**	1.01-1.46	263 deaths	115
	Grimes (1991)	RR	1.09	0.89-1.35	205	
Circulatory overall	Grimes (1991)	RR	**1.16**	1.10-1.32	205	
	Feuer (1986)	PMR	1.09	0.91-1.29	263 deaths	131
	Guidotti (1993)	SMR	1.03	0.88-1.21	3328	157
	Milhan (1983)	PMR	1.01	0.94-1.08		777
	Aronson (1993)	SMR	0.99	0.89-1.09	5414	384
	Vena (1987)	SMR	0.95	0.81-1.04	1867	250
	Musk (1978)	SMR	0.86	0.81-0.91	5655	1058
	Tornling (1994)	SMR	0.84	0.71-0.98	1116	161
	Eliopulos (1984)	SMR	0.78	0.60-1.01	990	55
	Heyer (1990)	SMR	0.78	0.68-0.92	2289	172
Arteriosclerosis	Guidotti (1993)	SMR	1.5	0.77-2.62	3328	12
	Aronson (1993)	SMR	1.41	0.91-2.10	5414	24
	Vena (1987)	SMR	0.92	0.79-1.07	1867	173
	Heyer (1990)	SMR	0.75	0.63-0.89	2289	133
Disease of veins	Milham (1983)	PMR	1.31	0.65-2.34		11
Heart	Guidotti (1993)	SMR	1.1	0.92-1.31	3328	130
	Beaumont (1991)	RR	0.89	0.81-0.97	3066	508
	Demers (1992)	SMR	0.79	0.72-0.87	4546	461
Heart overall	Decoufle (1977)	PMR	1.05	0.96-1.14	1113	527
Arteriosclerotic or coronary	Milham (1983)	PMR	10.5	0.97-1.14		622
Other circulatory	Demers (1992)	SMR	0.96	0.80-1.14	4546	131
	Orris (1992)	PMR	0.82	0.73-0.93	3084	

[a]standardized mortality ratio, [b]proportionate mortality ratio, [c]relative risk.

of bronchial smooth muscle. Increased airway responsiveness may be a risk factor for the subsequent development of chronic obstructive pulmonary disease. Howe and Burch's (1990) pooled results for respiratory disease were inconclusive.

4. Cancer

In considering the epidemiological literature related to cancer in firefighters, Howe and Burch (1990) calculated pooled standardized mortality ratios (SMR's) based on seven cohort studies to provide the maximum likelihood estimate of the relative risk of cancer (Mastromatteo 1959a, b; Musk, 1978; Howe and Lindsay, 1983; Eliopoulos, 1984; Rosenstock et al., 1988; Vena and Fiedler, 1987; Heyer, 1990). Years of service as a firefighter were used as a surrogate for "dose". Howe and Burch (1990) also calculated standardized mortality odds ratios (SMOR's) based on four proportionate mortality studies (Milham 1976; Petersen and Milham 1980; Feuer and Rosenman, 1986; Gallagher et al., 1989). With respect to deaths from all cancers, the pooled SMR is 0.92 (95% CI=0.85 to 0.98 and *p* for heterogeneity is 0.30). The pooled PMR (proportionate mortality ratio) is 1.09 (95% CI=1.01 to 1.17 and *p* for heterogeneity is 0.47). There did not appear to be an association between firefighting and risk of overall cancer mortality. Pooled estimates did not show an increased risk of lung cancer or of colon cancer (Howe and Burch , 1990). Pooled estimates appeared to suggest an association between firefighting and **brain** tumours (RR=1.44; 95% CI=1.07 to 1.89), malignant **melanoma** (RR=1.73; 95% CI=1.03 to 2.74) and multiple **myeloma** (RR=1.51; 95% CI=0.91 to 2.35). Decoufle et al. (1977) found a significant excess of **rectal** cancer (PMR=2.3). Vena and Fiedler (1987) found significant excesses of **colon** cancer (SMR=1.8) and of **bladder** cancer (SMR=2.9). Tornling et al. (1994) and Eliopulos (1984) found significant excesses of brain cancer with SMR's of 2.3 and 8.3, respectively. Milham (1983) also found a significant excess of brain and nervous system cancers (PMR=1.8).

Since Howe's survey of the epidemiological literature with respect to firefighters, there have been nine more studies published which have found significant excesses of cancer. Grimes et al. (1991), Aronson et al. (1993) and Demers et al. (1992) found excesses of **brain** and **nervous system** cancers with RR=3.8, SMR=2.0 and SMR=2.1 respectively. Beaumont (1991) found an excess of digestive system disease deaths (RR=1.3), primarily due to **oesophageal** cancer (RR=2.0) and **liver disease** (RR=2.3). Demers (1992) found an excess of **lymphatic/haematopoietic** cancer (SMR=2.1). Sama et al. (1990) found a significant excess of **non-Hodgkin's lymphoma** (OR=3.3), **melanoma** (OR=2.9) and **bladder** cancer (OR=1.6) in firefighters when policemen were used as a reference group. Vena (1987) and Aronson et al. (1993) also found an excess of bladder cancer with SMR=2.9 and OR=2.1 respectively. An excess of **kidney** and **ureter** cancer was found by Guidotti (1993) with an SMR=4.1. Grimes et al. (1991) found an excess of **genitourinary** cancer (RR=2.3). See Table 7 for a summary of the epidemiological studies related to cancer in firefighters.

Occupations, other than firefighting associated with melanoma, urinary bladder cancer, brain cancer or non-Hodgkin's lymphoma, included the rubber and plastics industries, printing, motor vehicle manufacturing, and the resin manufacturing industries (Hall and Rosenman, 1991). These industries were all heavy users of volatile organic compounds. There was a small, but significant association between diesel emissions and lung and bladder cancer in a number of studies. However, some of these studies suffered design deficiencies from confounding factors such as smoking, the use of in appropriate controls and from a lack of exposure data.

5. Surrogates of Exposure

The two major weaknesses in all of the cohort studies of firefighters has been the lack of estimates of contaminant levels and the use of years of employment as a surrogate for exposure. Misclassification in these studies, may have resulted in

Table 7. Epidemiological studies of cancer and firefighters

Disease	Author	Type	Mortality	95% C.I.	Firefighters	Cases
Brain and nervous system	Grimes (1991)	RR[a]	**3.78**	1.22-11.71	205	
	Vena (1987)	SMR[b]	2.36	0.86-5.13	1867	6
	Aronson (1993)	SMR	**2.00**	1.09-3.36	5414	14
	Demers (1992)	SMR	**2.10**	1.23-3.38	4546	18
	Milham (1983)	SMR	**1.77**	$p<0.05$		14
	Sama (1990)	OR[c]	1.52	0.39-5.92	321 cancer	5
Brain	Eliopulos (1984)	SMR	**8.33**	1.01-30.10	990	2
	Tornling (1994)	SMR	2.79	0.91-6.51	1116	5
	Lewis (1982)	SMR	**2.29**	1.22-3.92	1559	13
	Guidotti (1993)	SMR	1.45	0.30-4.29	3328	3
	Beaumont (1991)	RR	0.81	0.26-1.90	3066	5
Lymphatic/Haematopoetic	Demers (1992)	SMR	**2.05**	1.10-3.60	4546	12
	Eliopulos (1984)	PMR[d]	1.88	0.39-5.50	990	3
	Milham (1983)	PMR	1.35	0.96-1.85		39
	Guidotti (1993)	SMR	1.27	0.61-2.33	3328	10
	Heyer (1990)	SMR	1.26	0.65-2.22	2289	12
	Musk (1978)	SMR	0.63	0.39-0.95	5655	22
	Aronson (1993)	SMR	0.98	0.58-1.55	5414	18
	Beaumont (1991)	RR	0.65	0.35-1.09	3066	14
	Vena (1987)	SMR	0.55	0.18-1.29	1867	5
	Tornling (1994)	SMR	0.44	0.09-1.27	1116	3
Leukemia	Sama (1990)	OR	2.67	0.62-11.54	321 cancer	6
	Feuer (1986)	PMR	1.86	0.51-4.76	263 deaths	4
	Demers (1992)	SMR	1.27	0.71-2.09	4546	15
	Lewis (1982)	SMR	0.92	0.46-1.64	1559	11
	Decoufle (1977)	PMR	0.73	0.27-1.59	1113	6
	Heyer (1990)	SMR	1.73	0.70-3.58	2289	7
Lymphatic leukemia	Aronson (1993)	SMR	1.90	0.52-4.85	5414	4
Lymphomas	Sama (1990)	OR	**3.27**	1.19-8.98	321 cancer	14
	Aronson (1993)	PMR	1.21	0.64-2.07	1113	13
Lymphosarcoma	Aronson (1993)	SMR	2.03	0.42-5.92	5414	3

[a]RR (relative risk), [b]SMR (standardized mortality ratio), [c]OR (odds ratio),
[d]PMR (proportionate mortality ratio)

Table 7 (cont'd). Epidemiological studies of cancer and firefighters

Disease	Author	Type	Mortality	95% C.I.	Firefighters	Cases
Colon	Vena (1987)	SMR[a]	**1.83**	1.05-2.97	1867	16
	Sama (1990)	OR[b]	1.20	0.80-1.82	321 cancer	33
	Lewis (1982)	SMR	1.11	0.78-1.54	1559	37
	Grimes (1991)	RR[c]	0.91	0.37-2.20	250	
	Demers (1992)	SMR	0.85	0.54-1.26	4546	24
Colon and rectum	Aronson (1993)	SMR	0.60	0.30-1.08	5414	11
Colon and small intestine	Guidotti (1993)	SMR	1.61	0.88-2.71	3328	14
Intestine	Tornling (1994)	SMR	0.85	0.31-1.85	1116	6
Intestine except rectum	Heyer (1990)	SMR	0.79	0.32-1.64	2289	7
Large intestine except rectum	Beaumont (1991)	RR	0.99	0.63-1.47	3066	24
Rectal	Milham (1983)	PMR[d]	0.90	0.58-1.34		24
	Decoufle (1977)	PMR	**2.30**	1.34-3.68	1113	17
	Vena (1987)	SMR	2.08	0.83-4.28	1867	7
	Tornling (1994)	SMR	2.07	0.89-4.06	1116	8
	Beaumont (1991)	RR	1.45	0.77-2.49	3066	13
	Orris (1992)	PMR	1.64	1.14-2.30	3084	
	Milham (1983)	PMR	1.03	0.51-1.84		11
	Sama (1990)	OR	0.97	0.50-1.88	321 cancer	22
	Demers (1992)	SMR	0.95	0.41-1.87	4546	8
	Heyer (1990)	SMR	0.65	0.08-2.37	2289	2
	Lewis (1982)	SMR	0.30	0.06-0.86	1559	3
Rectal and rectosigmoid junction	Aronson (1993)	SMR	1.74	0.91-2.93	5415	13
Bladder	Guidotti (1993)	SMR	3.16	0.91-2.11	3328	4
	Vena (1987)	SMR	**2.86**	1.30-5.40	1867	9
	Sama (1990)	OR	**2.11**	1.07-4.14	321 cancer	26
	Aronson (1993)	SMR	1.28	0.51-2.63	5414	7
	Lewis (1982)	SMR	0.79	0.29-1.71	1559	6
Bladder and other urinary	Milham (1983)	PMR	**2.33**	$p<0.05$		6
	Beaumont (1991)	RR	0.57	0.19-1.35	3066	5
	Decoufle (1977)	PMR	0.55	0.15-1.41	1113	4
	Demers (1992)	SMR	0.23	0.03-0.83	4546	2
Kidney	Vena (1987)	SMR	1.30	0.26-3.80	1867	3
	Milham (1983)	PMR	1.15	0.50-2.27		8
	Tornling (1994)	SMR	1.10	0.30-2.81	1116	4
	Beaumont (1991)	RR	0.68	0.19-1.74	3066	4
	Demers (1992)	SMR	0.27	0.03-0.97	4546	2
Kidney and ureter	Guidotti (1993)	SMR	**4.14**	1.67-8.53	3328	7
	Aronson (1993)	SMR	0.43	0.05-1.56	5414	2
Genitourinary	Grimes (1991)	RR	**2.28**	1.28-4.06	205	
	Eliopulos (1984)	PMR	1.08	0.29-2.76	990	4
	Musk (1978)	PMR	0.09	0.71-1.17	5655	64

[a]SMR (standardized mortality ratio), [b]OR (odds ratio), [a]RR (relative risk),
[d]PMR (proportionate mortality ratio)

underestimates of the risk of disease. It has been found, in other studies for example, that years of employment were neither related to the number of fires fought, nor to the exposure to combustion products, nor to the decline in pulmonary function or airway responsiveness (Peters et al., 1974; Musk et al., 1977; Takehito and Maeda, 1981; Sparrow et al., 1982; Sherman et al., 1989). On the other hand, the number of fires fought has been correlated with the mean annual reduction in pulmonary function (Peters et al., 1974). Even amongst firefighters at the same fire, a statistically significant difference in exposure to combustion products has been found between front line firefighters and both squad leaders and ordinary firefighters (Takehito and Maeda, 1981). There was no significant difference found in the measured values between ordinary firefighters and the officers who accompanied them. There was no significant correlation between the level of CO exposure and the duration of CO exposure (Takehito and Maeda, 1981). Firefighting is a strenuous and hazardous occupation and many firefighters who, early on in their career develop symptoms, may be moved into other non-combat roles (Guidotti and Clough, 1992). This hypothesis is supported by Peters et al. (1974) who found that there was a higher prevalence of non-specific respiratory disease amongst firefighters in non-combat roles.

D. EXPOSURE STUDIES

1. Diesel Emissions

Diesel emissions are a complex mixture of organic and inorganic compounds which include respirable particles which are less than 0.05 μm diameter, CO, CO_2, NO_2, sulphur dioxide, aldehydes, aliphatic and aromatic hydrocarbons, polyaromatic hydrocarbons, organic acids and sulphates (Griest et al., 1988; Scheepers and Bos, 1992a). The characteristic diesel odour is apparent at very small concentrations but the substance responsible has yet to be identified (Spindt et al., 1971). It is known that this odour is not due to CO, NO_2, acrolein, aliphatic olefins, aliphatic aldehydes or to hydrocarbons having six or more carbon atoms (Scheepers and Bos, 1992b). The irritant effects of diesel emissions are attributable to the presence of high concentrations of NO_x, SO_2 and aldehydes. Threshold levels for irritant effects have been estimated to occur for NO_2 at approximately 10 ppm and for formaldehyde, acetaldehyde and acrolein at approximately 0.02 ppm. Compared to gasoline engines, diesel engines produce 50 to 100 times the amount of particulates, approximately the same amount of nitrogen and sulphur oxides and much less CO and hydrocarbons (Weisenberger, 1984). Higher PAH emissions are caused by advanced timing of the injection, extremely low and extremely high load conditions, cold start and decreasing fuel/air ratio (Scheepers and Bos, 1992a).

The rate of increase of diesel emissions is determined by fuel consumption, the ventilation rate and the volume of air space into which the pollutants are emitted (French, 1984). The amount of exhaust produced by a diesel engine varies almost directly with engine speed (Stewart et al., 1986a). High combustion temperatures lead to the formation of NO in the exhaust and some NO_2 is also produced in the exhaust during low-load operation (Stewart et al., 1986b). Platinum catalytic convertors convert CO to CO_2 and NO_2 to NO. The reaction mechanism is thought to be (Stewart et al., 1986b):

$$\mathbf{NO_2 + CO \rightarrow NO + CO_2}$$

The major advantages of catalytic convertors are the reduction of CO by up to 90% and the reduction of some hydrocarbons and odour (Dainty and Mogan, 1986). The disadvantages include: (1) conversion of SO_2 to H_2SO_4; (2) up to 40% conversion of NO to NO_2; (3) little effect on the soot content of the exhaust and no effect on the PAH content; and, (4) possible increase in mutagenicity of the exhaust particles (Mogan and Dainty, 1986; Mogan et al., 1986a, b). Other emission reduction devices include filters, water/oil emulsion, conventional water scrubbers and venturi water scrubbers which reduce emissions by 75%, 75%, 67%, and 43%, respectively (Dainty and Mogan, 1986).

Hurn (1975) proposed that CO_2 could be used as a surrogate for the measurement of the other diesel pollutants. Lavoie and Roberge (1991) have proposed an exponential model for the correlation of CO, NO, NO_2 and total particulate matter (TPM) with levels of CO_2 in ambient air measured in unventilated municipal bus garages. Schnakenberg (1986) has listed a number of reasons why a constant pollutant to CO_2 ratio might not be found: (1) Emission rates depend on the operating conditions of the engine (speed and load); (2) Emission characteristics of an engine can change due to engine malfunctions, age, clogged intake air cleaners and malfunctioning exhaust control devices. Waytulonis (1986) has shown that the following maintenance activities can measurably affect gaseous and particulate emission: (1) intake air filter change-out; (2) injection timing adjustment; (3) fuel rate adjustment; (4) injector nozzle cleaning and/or change-out; (5) exhaust restriction monitoring.

Waller et al. (1985) reported total particulate concentrations of 0.14-1.14 mg/m^3 for bus garages, Ulfvarson et al. (1987) reported levels of 0.1-0.3 mg/m^3 for car ferries, Wheeler et al. (1981) reported 0.91-2.15 mg/m^3 for mines while Reger et al. (1982) reported 0-23.0 mg/m^3 for mines. Sutter (1975) reported mean exposure levels of workers to diesel emissions during tunnel construction: NO (1.5-3.5 ppm), NO_2 (<0.5 ppm), CO (<10 ppm), CO_2 (<1000 ppm), SO_2 (approximately 0.02 ppm), methane equivalents of hydrocarbons (5-20 ppm) and soot (0.5-1.5 mg/m3). Little (1977) found similar levels in a study of mean breathing zone concentrations of diesel components in 22 metal and non-metal mines, and in 2 coal mines: NO (1-5 ppm), NO_2 (0.1-0.47 ppm), CO (1.5-14 ppm) and CO_2 (450-1150 ppm). Holland (1978) measured diesel emission levels in another 10 underground mines, obtaining the following results: NO (0.4-57 ppm), NO_2 (0-5.5 ppm), CO (0-23 ppm), CO_2 (145-5000 ppm), SO_2 (0-5 ppm) and soot (0.2-14 mg/m3). PAH's comprise a fraction of the total particulate matter produced by diesel engines. Mogan and Dainty (1986) found total PAH concentrations in underground mines (6.3 to 67 µg/m^3) to be just 0.4 to 4.4 times the average winter ambient levels in Hamilton, Ontario. Only one study has evaluated diesel emissions in firehalls

(Froines et al., 1987). A time weighted average (TWA) concentration for total particulates of 0.17-0.48 mg/m^3 was reported for ten firehalls in New York, Boston and Los Angeles. The experimental method did not control for particulates produced by cooking or by smoking. Froines et al. (1987) suggested that, although further research was necessary, it appeared that additional dilution ventilation in firehall garages to limit exposure to diesel particulates would be appropriate.

2. Carbon Monoxide

a. Health Effects

Carbon monoxide is known to decrease the threshold for angina and increase the risk of heart attack. Atherosclerotic disease of the heart increases the effect of CO since the overall delivery of oxygen to the tissues is reduced. Since there is a rather high prevalence of atherosclerotic disease there may be a large unidentified subgroup of firefighters (apart from smokers) who are more vulnerable to the toxic effects of CO. Tables correlating the physiological effects of CO with its ambient air concentration abound in the literature, are quoted by suppliers of breathing apparatus and compressors and are published in articles, documents and manuals destined for fire service personnel (JMAR™, 1990; IFSTA, 1982). These tables are based on humans at rest or engaged in light work and grossly underestimate the health risk to firefighters. In addition, these tables are not applicable to the case of CO found in compressed breathing air. There are no published tables which take into account the unusual working conditions of a firefighter. The lowest effective concentrations of COHb for human health effects associated with CO exposure of subjects at rest are shown in Table 8 (NRC, 1985). At the same carboxyhaemoglobin level, subjects engaged in even light to moderate exercise will be more seriously affected than sedentary individuals (Griggs, 1977; Purser and Berrill, 1985). Again, there are no published tables applicable to the case of firefighters.

Table 8. Health effects associated with carboxyhemoglobin.

%COHb[a]	Health effect[b]
< 3	None.
3-6	Slightly decreased exercise capacity (by 5-7%).
4-17	Slightly decreased exercise time in young healthy men during strenuous exercise.
	Confusion; Diminution of visual perception, manual dexterity, ability to learn, or performance in tasks such as driving.
16-20	Headache; Visual-evoked response abnormal.
30-40	Severe headache; nausea or vomiting; prostration; syncope.
50-60	Coma, convulsions, possible death.
67-70	Lethal if not treated.
80-90	Death in less than an hour.
90-100	Death within a few minutes.

[a] Percent carboxyhemoglobin for subjects at rest unless otherwise specified.

[b] Stewart (1973, 1975a,b), Horvath (1975), Shephard (1983), NRC (1985).

b. Estimation of Carboxyhaemoglobin from CO in Ambient Air

It is possible to calculate expected carboxyhaemoglobin (COHb) levels in blood for a given concentration of CO present as a contaminant in the breathing air. Purser (1988) gives two equations which may be used to predict %COHb levels. For short exposures to high concentrations of CO, COHb levels can be calculated approximately using the Stewart equation (Stewart et al., 1973):

$$\%\mathrm{COHb} = (3.317 \times 10^{-5})\,(\mathrm{ppm\ CO})^{1.036}\,(\mathrm{RMV})\,(t) \qquad \textbf{Eqn. 1}$$

where, CO = CO concentration in ppm

RMV = volume of air breathed (L/min)

t = exposure time in minutes

The Coburn-Forster-Kane (CFK) equation is based on all the main constants and variables that determine CO uptake and is believed to be a more accurate predictor of COHb levels, although it has been verified for humans only at low CO levels (Coburn et al., 1965):

$$\frac{A \bullet [\mathrm{HbCO}]_t - B \bullet V_{co} - p\mathrm{CO}_i}{A \bullet [\mathrm{HbCO}]_0 - B \bullet V_{co} - p\mathrm{CO}_i} = \exp\,(-t \bullet A / V_b \bullet B) \qquad \textbf{Eqn. 2}$$

Symbols, constants and other equations used to derive variables used in the solution of Equation 2 are indicated in Appendix 1 (Purser, 1988; Peterson and Stewart, 1975). Due to the complexity of the equation, a number of simplified versions have been in use, including a NIOSH modified equation and an incorrect U.S. *Textbook of Military Medicine* version, in addition to the Stewart equation (NIOSH, 1972; Zatjchuk et al., 1993).

c. Estimation of Carboxyhaemoglobin from CO in Alveolar Breath

The relationship between carboxyhaemoglobin (COHB) in blood and CO in alveolar breath has been investigated (Jones, 1958; Gydell, 1966; McIlvaine, 1969; Peterson, 1970; Stewart et al., 1976). Stewart et al. (1976) developed a rapid field method of estimating COHb accurately and rapidly from the electrochemically determined CO concentration in expired alveolar breath of firefighters.

The CO vs. COHb curve used by Stewart et al. (1976) to estimate firefighters' COHb from the alveolar breath concentration of CO was provided by the solution of the Haldane equation:

$$\mathbf{CO} = \frac{\mathbf{COHb\ (Po_2)}}{\mathbf{O_2Hb\ (P_B)\ (M)}} \times 10^6 \qquad \textbf{Eqn. 3}$$

where, CO = ppm CO in alveolar breath

M = CO affinity for haemoglobin in a blood sample at equilibrium

O_2Hb = % oxyhaemoglobin

COHb = % carboxyhaemoglobin saturation

P_B = barometric pressure in mm Hg

Po_2 = partial pressure of oxygen in pulmonary capillaries

d. Personal Measurements

Barnard (1979) reported ambient CO levels as high as 3,000 ppm at municipal, structural fires. Burgess et al. (1977) reported that during the 24% of the time that respirators were worn, the ambient concentration of CO was in excess of 500 ppm, but for 8.5% of the time when respirators were not worn, firefighters were still exposed to ambient CO concentrations in excess of 500 ppm. The highest exposure measured by a firefighter who was not wearing his mask was 17,000 ppm of CO (Burgess et al., 1977). Clearly, firefighters cannot judge safe and unsafe atmospheres.

Radford and Levine (1976) reported that, for nonsmokers, the mean COHb concentrations for firefighters who used their masks all of the time was 1.42% (SD=1.39 with a high of 7%) while the mean concentration for firefighters who did not use their masks was 2.47 % (SD=1.87 with a high of 12%). There was no significant difference between nonusers and intermittent SCBA users. On the other hand, Sammons and Coleman (1974) reported a COHb concentration of 5% for 27 randomly-selected non-smoking firefighters compared to 2.3% for controls. Controls were taken from a group of nonfirefighters and paired as to age, weight, height, race, smoking habits and family history of cardiovascular and pulmonary disease. Lawther (1971) found the COHb levels in nonsmoking firemen to range from 0.4% to 8.8%. Stewart et al. (1976) found a mean COHb level in nonsmoking firefighters of 5% with a high of 9.1%. Loke et al. (1976) reported that the COHb in nonsmoking firefighters increased from a baseline of 2.1% to 5.3%. One non-smoking firefighter who had been using his breathing apparatus showed an increase in carboxyhaemoglobin concentration from 2.0 % to 4.80%. Another nonsmoking firefighter who had not been using his breathing apparatus showed an increase in COHb from 2% to 13%. Although these levels may not be "toxic", they could be the cause of accidents due to the early effects of CO poisoning such as confusion or poor coordination (Table 8). Susceptible individuals may also experience a lower threshold for angina.

e. Synergistic Effects

Animal experiments suggest a synergism between CO and benzene (Ponsold et al., 1978). Benzene is a known contaminant in fire atmospheres (Burgess et al., 1979). Levin et al. (1987a,b, 1996) have found synergistic effects between CO and CO_2, additive effects between CO and other gases (eg. HCN, O_2, HCl, HBr and NO_2) and antagonistic effects between NO_2 and HCN. More research is needed on the possible additive, synergistic and inhibitory effects of fire gases and vapours, particularly those having chronic effects.

3. Other Chemicals

Volatile organic compounds (VOC's) are generally considered to be below the molecular weight of C_{10} hydrocarbons (Keith, 1991). VOC's may also contain oxygen, sulphur, nitrogen and halogens in their molecular structure and they are generally classified as those organics having saturated vapour pressures at 25°C greater than 10^{-1} mm Hg. Semi-volatile organic compounds (SVOC's) are organic compounds that are too volatile to be completely collected by filtration air sampling but not volatile enough for thermal desorption from solid sorbents. Most SVOC's are phase-distributed between the solid and vapour phases. They are generally classified as those organic compounds having saturated vapour pressures at 25°C between 10^{-1} and 10^{-7} mm Hg. As a group, VOC's have been linked to a number of toxic health effects including cancer, kidney & liver disease. Eight potential VOC carcinogens (acetaldehyde, benzene, chloroform, dichlorobenzene, dichloromethane, formaldehyde, perchloroethylene and styrene) have been found in previous studies of firefighting atmospheres (Table 9).

Most VOC's tested in a Total Exposure Assessment Methodology Study (TEAM), appeared in exhaled breath at 30%-40% of their average concentration in the air inhaled during the previous 12 hours (Wallace, 1986a, b). The main exception was perchloroethylene which appeared to be excreted almost exclusively through the breath and which also had a much longer half-life in the body (Wallace, 1986b). Although the toxicological significance of such doses remains to be determined (Raymer et al., 1989, 1991), the concentration of a number of VOC's in breath has been shown to correlate with an individual's exposure (Brugnone et al., 1976; Apostoli et al., 1982; Pellizzari et al., 1986a, b). In some cases, a body burden was shown to arise following exposure to levels two or three times lower than the TLV. There is rapid decay of 1,1,1-trichloroethane in the breath during the first 30 minutes followed by elimination from perhaps a second compartment (Raymer, 1990; Raymer et al., 1989, 1991). If VOC's generally follow this pattern, then a better description of the decay is obtained using alveolar breath rather than

Table 9. Potential VOC[a] carcinogens found at fires[b]

Compound	Target organs[c]
Acetaldehyde	Cancer (IARC 2B)[c]
Benzene	Cancer (IARC 1)[d]
	Bone marrow
	Respiratory disease
Chloroform (trichloromethane)	Cancer (IARC 2B)[e]
	Liver, kidney, heart
Dichlorobenzene	Cancer (IARC 2B)[d]
	Liver, kidney
	Respiratory disease
Dichloromethane (methylene chloride)	Cancer (IARC 2B)
	Liver, pancreas
Formaldehyde	Cancer (IARC 2A)[f]
	Respiratory tract
Perchloroethylene	Cancer (IARC 2A)[e]
	Liver, kidney, CNS
	Upper respiratory system
Styrene	Cancer (IARC 2B)[g]
	CNS
	Respiratory disease

[a] Volatile organic compound.

[b] Burgess et al., 1979; Treitman et al., 1980; Brandt-Rauf et al., 1989; Jankovic et al., 1992.

[c] ACGIH, 1991a; Lauwerys, 1982; Amdur et al., 1991.

[c] IARC (1985), [d] IARC (1987), [e] IARC (1979), [f] IARC (1982), [g] IARC (1994).

whole breath samples.

Results from a recent study of forest fires and of controlled fires on agricultural land indicate that fire emissions include smoke (with most particles in the less than 2 µm size range), NO_x and VOC's (Roberts and Anderson, 1991). Concentrations of plume NO_x and O_3 were in the order of 50 ppb. The concentration of benzene reported in a number of studies ranged from 0.200 ppm to 200 ppm. The concentration of the other VOC's covered narrower ranges (1-2 ppm for chloroform and styrene; 100-200 ppb for perchloroethylene and trichloroethylene) or were simply reported has having been detected. In a limited study, Abeles et al. (1973) and Lowry (1985b) reported that total hydrocarbons found at actual working fires were in the range of 300-700 ppm and 500-1,200 ppm, respectively. Lowry (1985a,c) has studied the production of free radicals during fires. He has found that their concentrations can be higher than CO during the first five minutes of a low-temperature fire and that they can remain high for 10 or more minutes after a fire is extinguished. Jankovic et al. (1993) found both short- and long-lived radicals during the overhaul phase of firefighting. Atlas (1985) sampled the smoke plume and ground concentrations of contaminants produced at a firefighter training facility where the combustion fuel was diesel oil. The most abundant compounds were aliphatic hydrocarbons and a suite of PAH's and alkyllated PAH's ranging from naphthalene to benzoperylene. In addition, the mutagenic potential of various samples was evaluated using the Salmonella-microsome assay which showed an average mutagenic response of 0.4 rev/µg.

Burgess et al. (1979) found that HCN levels were highest above the fire floor, that HCl and particulates were higher during knockdown than during overhaul, and that there was no significant difference between the concentrations of NO_2, HCN, or benzene during knockdown and overhaul. Benzene levels were highest at 4-alarm fires, in wood structures and before flashover. Nitrogen dioxide and HCl concentrations, by contrast, peaked at 2-alarm fires and were higher after flashover. Carbon monoxide concentrations simply increased with the number of alarms.

The focus of most previous studies of chemical exposures of municipal firefighters has been the monitoring of a short list of gases which have been of immediate concern due to their acute, toxic effects. A number of these studies have monitored structural fire gases and acids such as CO_2, CO, HCN, SO_2, NO_2 and HCl in real firefighting atmospheres (Burgess et al., 1977; Abeles et al., 1973; Gold et al., 1978; Burgess et al., 1979; Treitman et al., 1980; Turkington, 1984; Brandt-Rauf et al., 1988, 1989). Little or no attention has been paid to contaminants such as VOC's, known to have chronic effects, or to exposures to chemical contaminants from sources other than the immediate fire atmosphere. A few of the studies have included limited sampling of benzene, formaldehyde and acrolein. Burgess et al. (1979) found benzene in 181 of 197 samples, 33 of the samples containing more than 5 ppm benzene. Brandt-Rauf et al. (1988, 1989) studied 77 firemen in Boston with the objective of correlating personal exposures to health outcomes. The chemical contaminants found in smoke included CO, benzene, chloroform, dichlorofluoromethane, hydrochloric acid (HCl), hydrogen cyanide (HCN), methylene chloride, perchloroethylene, sulphur dioxide (SO_2), toluene, trichloroethylene and trichlorophenol. These results were obtained on the basis of 26 samples collected at 14 fires.

Firefighters can reasonably be expected to be exposed intermittently to extremely high concentrations of toxic compounds (Olshan et al., 1991). One might expect the number of toxic substances to be greater at the lower combustion temperatures characteristic of the latter stages of a fire. Although no studies have sampled specific firefighting tasks, it has been suggested that exposure to products of incomplete combustion may actually be greater during overhaul than during knockdown. Three studies provided limited data in this regard (Burgess et al., 1979; Takehito and Maeda, 1981; Jankovic et al., 1992). Although many of the same contaminants found during knockdown were also detected during overhaul, concentrations during overhaul were lower than during knockdown (Burgess et al., 1979; Jankovic et al., 1992).

The results of studies reporting chemical analysis of fire atmospheres are summarized in Table 10. Jankovic et al. (1992) obtained personal samples at 22 structural fires, with an attempt to differentiate between knockdown and overhaul concentrations. In addition, samples were taken both inside and outside of the firefighter's mask. One or more previous studies had evaluated the concentrations of CO_2, NO_2, acrolein, formaldehyde, and particulates. The knockdown concentrations of these substances were consistent with those reported in the earlier studies of Burgess et al. (1977), Gold et al. (1978), Treitman et al. (1980), Lowry (1985a) and Brandt-Rauf et al. (1988). However, the ranges varied enormously. Carbon monoxide was anywhere from 5 to 15,000 ppm while benzene ranged from 0.3 to 1,200 ppm, acrolein from 0.2 to 15 ppm, HCN from 0 to 75 ppm and particulates from 4 to 20,000 mg/m^3. Forty-eight additional organic compounds were identified, including PAH's (Jankovic et al., 1992). Chemical contaminants were generally found to be much lower during overhaul than during knockdown but aerosolized building materials, many of which were fibrous, were much higher.

Data obtained from experimental fires, training fires and other controlled burns have provided considerable information concerning combustion products but these results cannot be simply extrapolated to the working conditions of firefighters. All of the studies conducted at actual working fires have been limited by difficulties encountered at the scene of the fire, by the lack of a coherent sampling strategy and by the absence of verified sampling methods. These studies of firescene atmospheres have used *Draeger™* tubes, Tenax™ or activated charcoal to sample for VOC's. None of the sampling methods used in these studies have been verified for use under the severe conditions (temperature, humidity, reactive atmospheres, multiple contaminants) in which firefighters routinely work. The choice of monitored chemicals was essentially based on the availability of methods to collect and analyze samples. In view of the limitations of these techniques, the results of these studies should be considered semi-quantitative. These studies suffer also from a limited number of samples.

Table 10. Chemical contaminants found at fires

Compound	ppm[a] (mg/m^3)	Samples	Type of fire	Number of fires	Sampling method	Author
Acrolein	0.2-15	118	Municipal[c]	45	13X sieve	Burgess et al. (1979)
	0.2-15	29	Municipal	200	13 X sieve	Treitman et al. (1980)
	0.1-4	12	Knockdown[d]	22	polymer tube	Jankovic et al. (1992)
	0.2	1	Overhaul[e]			Jankovic et al. (1992)
	1	1	Inside mask			Jankovic et al. (1992)
Benzene	0.3-180	181/197	Municipal	45	charcoal	Burgess et al. (1979)
	0.2-180	55/181	Municipal	200	charcoal	Treitman et al. (1980)
	8-250	18	Municipal	14	detector tube	Brandt-Rauf et al. (1989)
	1-20	15	Knockdown	22	charcoal	Jankovic et al. (1992)
	n.d.[b]-0.3	2	Overhaul			Jankovic et al. (1992)
	3-20	4	Inside mask			Jankovic et al. (1992)
Carbon dioxide	1000-75000	89	Municipal	45	bag - detector tube	Burgess et al. (1979)
	1000-75000	16	Municipal	200	bag - detector tube	Treitman et al. (1980)
	300-5000	20	Knockdown	22	bag - FTIR	Jankovic et al. (1992)
	100-1000	7	Overhaul			Jankovic et al. (1992)
	500-20000	28	Inside mask			Jankovic et al. (1992)
Carbon monoxide	3-1000	60	Municipal		bag - Ecolyzer	Gold et al. (1978)
	15-5000		Municipal	45	bag - Ecolyzer	Burgess et al. (1979)
	15-5000	49	Municipal	200	bag - Ecolyzer	Treitman et al. (1980)
	n.d.-15000		Municipal			Lowry et al. (1988)
	11-1087	26	Municipal	14	detector tube	Brandt-Rauf et al. (1989)
	5-1900	33	Knockdown	22	bag - FTIR	Jankovic et al. (1992)
	5-100	7	Overhaul			Jankovic et al. (1992)
	20-100	6	Inside mask			Jankovic et al. (1992)
	n.d.-17	60	Forest fire		Dector tube	Kelly et al. (1992)

[a]parts per million, [b]not detected, [c]structural fires, [d]structural fires during knockdown, [e]structural fires during overhaul

Table 10 (cont'd). Chemical contaminants found at fires

Compound	ppm (mg/m^3)	Samples	Type of fire	Number of fires	Sampling method	Author
Carboxyhemoglobin	0-4-8.8%		Municipal		nonsmoking	Lawther (1971)
	5%		Municipal		nonsmoking	Sammons & Colemena (1974)
	5.3%		Municipal		nonsmoking	Loke et al. (1976)
	1.42-7%		Municipal		nonsmoking + mask	Radford & Levine (1976)
	5%		Municipal		nonsmoking	Stewart et al. (1976)
Formaldehyde	0.4-8.3	6	Municipal fire	14	detector tube	Brandt-Rauf et al. (1988)
	0.07-10	16	Knockdown	22	polymer tube	Jankovic et al. (1992)
	0.04-0.4	5	Overhaul			Jankovic et al. (1992)
	0.06-0.4	5	Inside mask			Jankovic et al. (1992)
Hydrogen chloride	18-150	5/90	Municipal		13X sieve	Gold et al. (1978)
	0.2-200	88/242	Municipal	45	13X sieve	Burgess et al. (1979)
	1-200	69	Municipal	200	13X sieve	Treitman et al. (1980)
	0-40		Municipal			Lowry et al. (1985)
	2.17-13.3	2	Municipal	14	detector tube	Brandt-Rauf et al. (1988)
	1.5-7	2	Knockdown	22	silica gel tube	Jankovic et al. (1992)
Hydrogen cyanide	0.02-0.89	33	Municipal		ascarite	Gold et al. (1978)
	0.2-4	27/253	Municipal	45	ascarite	Burgess et al. (1979)
	0.1-4	13	Municipal	200	ascarite	Treitman et al. (1980)
	0-40		Municipal			Lowry et al. (1985)
	0.8-75	9	Municipal	14	detector tube	Brandt-Rauf et al. (1988)
	0.5-20	12	Knockdown	22	soda lime tube	Jankovic et al. (1992)
	0.2-0.5	3	Overhall			

Table 10 (cont'd). Chemical contaminants found at fires

Compound	ppm (mg/m^3)	Samples	Type of fire	Number of fires	Sampling method	Author
Methylene chloride	0.28	1	Municipal	22	charcoal	Brandt-Rauf et al. (1988)
Nitrogen dioxide	0.02-0.89	8/90	Municipal		13X sieve	Gold et al. (1978)
	0.2-9		Municipal	45	13X sieve	Burgess et al. (1979)
	0.2-10	33	Municipal	200	13X sieve	Treitman et al. (1980)
PAH's[f]	0.284		Knockdown	3	polymer tubes + filters	Jankovic et al. (1992)
	0.022		Overhall	3	polymer tubes + filters	Jankovic et al. (1992)
Particulates	4-750	20	Municipal		25 mm glass	Gold et al. (1978)
	20-18000		Municipal	45	fibreglass	Burgess et al. (1979)
	20-20000	64	Municipal	200	fibreglass	Treitman et al. (1980)
	0-560		Knockdown	22	cascade impactor	Jankovic et al. (1992)
	0-45		Overhall			Jankovic et al. (1992)
Particulates (respirable)	370	26	Forest fire			Kelly et al. (1991)
Perchloroethylene	0.064-0.138	3	Municipal	14	charcoal	Brandt-Rauf et al. (1988)
Sulphur dioxide	0.4-41.7	12	Municipal	14	detector tube	Brandt-Rauf et al. (1988)
	0.6-3.0	29	Forest fire		detector tube	Kelly et al. (1991)
Toluene	0.16-0.28	3	Municipal	14	charcoal	Brandt-Rauf et al. (1988)
Trichloroethylene	0-250	2	Municipal	14	charcoal	Brandt-Rauf et al. (1988)
Trichlorophenol	0.1	1	Municipal	14	charcoal	Brandt-Rauf et al. (1988)
Xylene	0.06		Knockdown	22	charcoal	Jankovic et al. (1992)

[f] PAH's (polyaromatic hydrocarbons) calculated as the sum of 14 different compounds.

E. GENERAL CONSIDERATIONS OF SAMPLING AND ANALYSIS

1. Fire Atmospheres

The sampling of firefighting atmospheres poses many challenges, not the least of which is the chemical complexity and the rapidly changing system evolving from the emission of hundreds, perhaps thousands, of combustion products. As for any industrial hygiene protocol, there are a number of interrelated factors which must be considered in the choice of the sampling method:

a. the purpose of the data collected;
b. the compounds of interest;
c. the volatility, reactivity and stability of the components of the mixture;
d. the level of detection required;
e. the degree of selectivity needed; and,
f. interference from other target and non-target compounds.

Other constraints which may be just as important as the above include the cost, the accuracy, the precision required, and the number of samples needed. The sampling of firefighters under actual working conditions imposes additional sampling restrictions. The sampling system must be compatible with the 70 lb of equipment the men must carry. It must be rugged and able to withstand severe mechanical and thermal stress. It must not restrict the firefighter's movement and it must be easily and quickly turned on and off. It must be capable of collecting a representative sample over a short time period in sufficient quantity to overcome the sensitivity limitations of the analytical method. Working conditions will require that the sampler operate efficiently in dirty atmospheres, under conditions of high humidity and at high temperatures. Finally, sample integrity in a complex sample matrix which includes free radicals, reactive gases, corrosive gases and adsorptive particulates must be demonstrated. The existing database of actual fire atmosphere sampling is so small that evaluation and comparison of results is tenuous at best. There is, in fact, no sampling method which has been validated for use under such severe conditions.

Atmospheric chemists view the industrial hygienists' modelling of air as having remained rather primitive, treating pollutants as chemically independent and assuming the air to be some well-mixed volume (Nazaroff and Cass, 1986). This criticism is not without foundation. The industrial hygienist's solution to extracting useful information from an exceedingly complex system is to base exposure assessments on breathing zone samples, thus circumventing the need for a spatially and dynamically resolved understanding of the workplace atmosphere. In the case of firefighting, this solution imposes itself even more rigorously than in the usual industrial workplace. Generally speaking, continuous time-weighted-average sampling is preferred, physiologically, for evaluating cumulative systemic toxicants. Such long-term integrative sampling is suitable for relatively constant persistent emissions. However, this approach would provide meaningless data in the case of firefighters. The exposure patterns of firefighters are unpredictable, consisting of long periods of zero exposure to fire effluent interspersed with relatively brief exposures to potentially high levels of a myriad of undetermined combustion products which may or may not be reduced by the use of SCBA's. Short sampling periods are necessary for both the identification and the quantification of firefighter exposures. In view of the potentially high concentrations of combustion products, the usual requirement that the analytical method be capable of detecting and measuring very low concentrations of the target compound(s) may not apply. Instantaneous sampling by direct reading instruments would be an attractive solution for firefighters provided an instrument meeting the performance specifications mentioned above could be found. The sampling methods most frequently used in previous studies of firefighting atmospheres included detector tubes and sorbents.

2. Sampling Short-Lived Species

Conclusions about the air sampled or about worker exposures are based on the assumption that the sample average concentration is a reasonable representation of the true average concentration. The primary purpose of a sampling protocol should be to provide a representative sample. The validity of this assumption would subsequently be tested using statistical analysis. In addition to the usual factors which must be taken into consideration when planning a sampling protocol, sampling short-lived species requires that particular attention be paid to the following:

a. Equilibrium between gas and particulate phases;
b. Wall effects (adsorption to surfaces of sampling and apparatus);
c. Adsorption of gases onto particles trapped by pre-filters;
d. Gas-particle or particle-particle localized reactions;
e. Water soluble analytes (eg. H_2O_2, HNO_3 and NH_3) will pose serious sampling problems at high relative humidities;
f. "Sticky" gases (i.e. easily adsorbed onto surfaces) will always be a problem when the air sample must flow through a cell;
g. Sample contamination;
h. Unrepresentative sampling;
i. Lack of stable standards; and,
j. Lack of inter-comparison studies using independent measurement techniques.

Possible solutions to the above problems include:

a. Increase the analyte lifetime by keeping the sample at low pressure (as in a photolytic cell);
b. Increase the analyte lifetime by trapping it in a solid matrix (as in cryogenic trapping in solid CO_2);
c. "Fix" the short-lived analyte by selective derivatization;

d. Separate the reactive gases from particles by having the air stream pass through a denuder placed ahead of the filter;

e. Use remote sensing techniques to avoid the necessity of sample manipulation; and,

f. Ensure that all surfaces coming into contact with the sampled air are made of "inert" materials. Whether or not a material is inert depends on the substances being sampled.

3. Detector Tubes

Colorimetric detector tubes, such as Draeger™ tubes, are popular because they are highly portable, easy to use, require only a small sample volume and give the results of measurements in approximately one minute. However, due to the many limitations and potential errors, it is very difficult to obtain even semi-quantitative results. The detector tubes are calibrated at 20°C. Ambient temperatures higher or lower than 20°C will affect the both the sample volume and the rate of reaction between the reagent and the sample gas or vapour. Water droplets entering the tube or water condensing inside the detector tube due to temperature changes, will also have a serious effect on the reading. Detector tubes are formulated to react uniquely with a particular gas or vapour but numerous interfering reactions can occur with other volatile agents having similar chemical properties to the target compound. For example, hexane may interfere with CO readings, hexane may also interfere with benzene readings, and CO may interfere with benzene readings (Matheson™, 1990).

4. Sorbents

Activated charcoal sampling and analytical methods are widely used by industrial hygienists and, indeed, form the basis of the majority of the official analytical methods for organic substances recommended by NIOSH and OSHA (NIOSH, 1991). Carbonaceous adsorbents have good capacities for C_2-C_6

hydrocarbons, vinyl chloride, esters, ethers, alcohols, ketones, glycol ethers and halogenated hydrocarbons. However, less volatile compounds and reactive compounds such as amines, phenols, nitro-compounds, aldehydes and anhydrides are not recovered efficiently due to their strong adsorption. Since charcoal is nonpolar, sample streams of high relative humidity are not usually a problem (Lodge,1989). The microporous structure of activated carbon leads to difficulty in recovering adsorbed compounds such as benzene, toluene and xylene. Inorganic compounds such as NO_2, Cl_2, H_2S, SO_2 and ozone (O_3) react chemically with activated charcoal. A major disadvantage of charcoal methods is dilution of the sample with the desorbing solvent.

Organic, porous, polymeric adsorbents include *Tenax™, XAD-2™, Porapak™ and Chromasorb*™. These materials exhibit a low retention of water vapour, low background contamination and low reactivity. On the other hand, they do not capture highly volatile compounds or certain polar compounds. Upon exposure to atmospheric oxidants, *Tenax™* and *XAD-2™* can partially decompose producing compounds that can interfere with GC analysis of collected organics. *Tenax™* (or poly-2,6-diphenyl phenylene oxide) has a number of advantages over activated carbon. It has a good collection efficiency, is thermally stable (high desorption temperature of 350°C), has low background bleeding and low breakthrough volume (low affinity) for water. It is inert and suitable for a wide variety of non-polar organic compounds including non-polar aromatic and chlorinated hydrocarbons of moderate to low reactivity. As a sampling medium, *Tenax™* works well for compounds with boiling points in the range of 80-200°C. On the other hand, Tenax™ is not suitable for the collection of low molecular weight (MW) compounds in the alkane and alkene categories or for the determination of low MW unsaturated alkyl halides. *Tenax™* is known to have poor adsorptive capacity for very volatile organic compounds, aldehydes, nitriles, amines, alcohols and chlorinated hydrocarbons (Pilar and Graydon, 1973; Cox and Earp, 1982; Wang, 1984a, b). High moisture levels in the air being sampled may affect sample retention. Artifact formation may occur due to chemical reactions during sampling and/or thermal desorption. Benzene and toluene are present in *Tenax™* as impurities which are difficult to remove (Walling et al., 1986). Accuracy is strongly impacted by the potential for contamination and the formation of artifacts. Replicate analysis is not possible since the entire sample is used in thermodesorption.

Inorganic adsorbents include silica gel, alumina, florisil and molecular sieves. These substances are considerably more polar than organic porous polymeric adsorbents such as *Tenax™*, and allow efficient collection of polar compounds. However, they are rapidly deactivated by water.

Carbon molecular sieves include *Spherocarb™*, *Carbosphere™*, *Carbosieve™* and *AmbersorbXE™*. These substances have a spherical, macroporous structure which leads to better recovery of adsorbed compounds. They are suited for the collection of highly volatile (bp in the range of -15°C to 120°C), relatively non-polar organics such as vinyl chloride, vinylidene chloride, methylene chloride, benzene and toluene. *Ambersorb™ 340* is a carbonaceous polymeric adsorbent similar to organic polymeric adsorbents. It has few contaminants in the boiling point range of 100-300°C. *Ambersorb™ 348* is most similar to activated carbon.

The advantages over charcoal of the newer sorbent materials such as *Tenax™* include higher sensitivity, the absence of a solvent peak and a reduced effect of humidity on retention volumes (Brown and Purnell, 1979). The disadvantages of sorbent methods for VOC collection are well known and documented (Sennum, 1981; Hunt and Pangaro, 1982; Wang, 1984a,b; Pellizzari et al., 1984; Bidleman, 1985; Walling et al., 1986; Gordon, 1989). Their major disadvantage is the fact that no one sorbent or extraction technique is applicable to the entire range of volatilities and polarities of ambient organic compounds. Thermal desorption is most useful for compounds having boiling points less than 150°C and solvent extraction is very useful for compounds boiling above 300°C. Replicate analysis is impossible in the case of both charcoal and *Tenax*™. Breakthrough volumes are complex functions of temperature and gas composition and a comprehensive database representing such compositional complexity over typical temperature and concentration ranges does not exist (Gordon, 1989). Modification of adsorbed VOC's, such as by oxidation or thermal decomposition, and compound migration into or out of the sorbent's internal structure are potential problems which might lead to reaction products being mistaken for air pollutants (McClenny et al., 1991).

5. Whole-Air Sampling

a. General Considerations

An attractive alternative to sorbent sampling is to collect a sample of air into an evacuated container. A sampler consisting of a pre-filter, pump, flow controller, and/or flow restrictor, may be added to the container if necessary. This sampling method is referred to as "whole-air" sampling (EPA, 1990). Several types of containers can be used: gas-tight syringe, glass bottle, bag (Saran™, Mylar™ or Tedlar™/Teflon™) or metal container. The advantages of container sampling over sorbent methods include (EPA, 1990):

a. It allows whole-air sampling;
b. No breakthrough of target compounds;
c. No thermal or solvent desorption necessary;
d. It allows the use of multiple aliquots for replicate analysis;
e. Time-integrated samples can obtained by using controlled-flow pumps with bags or metal containers; and,
f. Samples larger than the container size can be obtained by pressurizing metal containers.

The disadvantages of whole-air sampling include (EPA, 1990; Keith, 1991):

a. Sample instability by adsorption onto the walls of the container;
b. Surface reactions on the walls of metal containers;
c. Sample permeation in or out of the container in the case of bags;
d. The volume of the air sample is limited by the size of the container

(except for metal containers which can be pressurised);

e. No exclusion of non-target compounds which may lead to:
   i. Sampling matrix effects such as the possible reaction of VOC's with ozone or nitrogen oxides.
   ii. Analytical interference;

f. Condensation;

g. Adsorption of target compounds onto particles collected onto the pre-filter; and,

h. Bulkiness.

b. Summa™ Canisters

Many of the problems associated with sample stability in containers have been overcome recently, by a new, proprietary electropolishing technique of preparing the metal surface of metal containers. The product is marketed under the brand name Summa™ canister. The Summa™ electropolishing process coats the interior surface of #304 stainless steel containers with a pure chrome-nickel oxide layer (Hsu et al., 1991). This passivation procedure reduces the number of adsorption sites. Canisters are cleaned by evacuation to 30 µm Hg at a temperature of 100°C. They are then filled with purified, humid air and analyzed for contamination. Humidity has been found to enhance the passivation of the internal surface, apparently by occupying active adsorptive sites (McClenny et al., 1991). Canisters are certified clean when <0.2 ppb of each target compound and <0.020 ppm total carbon is found when analysing a total air volume of 350 mL. Hydrocarbon and substituted hydrocarbon VOC's, particularly the halogenated hydrocarbons, with vapour pressures above 0.5 mm Hg at 25°C store well in canisters (Purdue, 1991). McClenny et al. (1991) found that VOC's were stable in Summa™ canisters for periods of 7-30 days. The compounds which have been tested included non-polar VOC's and a few polar VOC's: light alkanes and alkenes, light aromatics, halocarbons, some terpenes, and some hydrocarbons with more than six carbons (EPA, 1988). Oliver et al. (1986) found that 3-8 ppb levels of ethyl acrylate, methyl methacrylate, acetone, acrylonitrile and isopropanol can be stored for 7 days with a relative standard deviation (rsd) of less than 10%. Air samples containing the reactive species H_2O, CO_2, O_3, NO and NO_2 were found to be stable for 7-30 days when simultaneously spiked with 15 VOC's, including vinyl chloride (Oliver et al., 1986). Gholson et al. (1989) sampled incinerator gases containing high concentrations of H_2O and HCl. No degradation of surface passivation occurred. Purdue (1991) found that, in general, organic compounds that were soluble in water, such as oxygenated hydrocarbons, aldehydes, ketones and alcohols, did not store well in canisters. The additional advantages of whole-air sampling of VOC's using Summa™ canisters include (Keith, 1991):

a. Rugged and safe to use;
b. No field calibration necessary;
c. No degradation of trapping materials;
d. Detection and measurement of a wide range of non-polar VOC's;
e. Sample stability;
f. Greatly reduced contamination problems;
g. Easy cleaning;
h. Consistent recoveries;
i. No electrical power is needed to fill canisters to atmospheric pressure;
j. Increased sample volume is possible by canister pressurization.

Additional disadvantages of using Summa™ canisters include:

a. Not generally applicable to polar VOC's;
b. High initial cost; and,
c. Complex analytical techniques.

6. Detectors for Gas Chromatographic Analysis

Sample conditioning for the adsorbent methods involves solvent or thermal desorption, cryogenic trapping and focusing (NIOSH, 1991). Sample conditioning for the canister method involves Nafion™ dryer and cryogenic trapping (Wang, 1987; EPA, 1988). Identification errors can be reduced by verification of key components to detect shifts in eluting order or retention time, or by employing simultaneous detection by different detectors. Detectors most commonly used are thermoconductivity detector (TCD), flame ionization detector (FID), photoionization detector (PID) and electron capture detector (ECD).

FID is a non-selective (or universal) detector. FID is most appropriate for simple saturated hydrocarbons. It provides good sensitivity and uniform response based on the number of carbon atoms in the compound (Purdue, 1991). The electron capture detector is appropriate for the analysis of electron deficient compounds, particulary the poly-halogenated and nitro-substituted compounds. The photoionization detector is sensitive and selective for aromatic compounds. The non-selective detector system can provide a "snapshot" or "fingerprint" of the constituents in the sample allowing determination of the extent of misidentification due to overlapping or co-eluting compounds, the position of compounds with respect to the desired concentration range, and retention time shift patterns (Hawkins et al., 1991). However, interferences on the non-specific detectors can still result in identification errors for complex samples. In that case, multiple detector methods are required or a specific detector such as a mass spectrometer or a mass-selective detector (MSD) must be used. Positive compound identification and quantitative information can be obtained by analyzing the sample twice using dissimilar gas chromatographic columns (not possible for thermal desorption analysis), by using dual (parallel or series) detectors or by using a GC-MS or GC-MSD system.

Non-specific detectors in series include:

ECD-PID: Volatile aromatics and chlorinated hydrocarbons
PID-FID: Aromatic hydrocarbons and normal (saturated) hydrocarbons
ECD-FID: Hydrocarbons and chlorinated hydrocarbons
PID-ECD: Aromatic and halogenated VOC's

PID-NPD: Amines

Non-specific detectors in parallel include:

NPD-FID: Nitrogen or phosphorous compounds

FPD-FID: Sulphur compounds

For the GC analysis of 18 VOC's in incinerator gases, ECD detection provided excellent results (Wang et al., 1983; Gholson et al., 1989). FID detection showed a positive interference for trichloroethylene, toluene and chlorobenzene. The samples contained high concentrations of H_2O and HCl. A mass selective detector (MSD) may be used as an alternative to more expensive GC-MS system. It has high sensitivity (ng and sub-ng detection limit) and excellent accuracy and precision. It can be used as both a specific and a universal detector. MSD's have a wide dynamic range, good response to all organic compound classes and provide positive compound identification.

7. U.S. EPA TO-14 Method

An air sample taken from an urban environment typically contains 100 to 150 detectable VOC's in the C_2 through C_{12} carbon range (Wang, 1986; Dann et al., 1991). The typical concentration range of these compounds is 0.1 ppbC to 50 ppbC (parts per billion of carbon). The U.S. EPA has developed a sampling and analytical method for the use of Summa™ canisters in ambient air monitoring programs targeting 40 VOC's. The method, known as *EPA Compendium Method TO-14*, is based on the collection of whole air samples in Summa™ canisters, with subsequent gas chromatographic analysis coupled to one or more detectors (EPA, 1988). In addition to the EPA method, descriptions of the analytical techniques used can be found in the literature (McClenny et al., 1984; Pliel et al., 1987, 1988).

The TO-14 method is applicable to a wide range of non-polar compounds and to a limited number of polar VOC's. The Summa™ canister is pressurized to 20 psig during sample collection. Pre-treatment of the sample by a Nafion™ dryer (a tubular, hygroscopic semi-permeable membrane) is necessary to remove moisture which could cause: a) formation of ice in the cryogenic trap causing blockage of the sample flow, b) pressurization of the mass sprectrometer's ion source, c) increased variability in GC retention time by overloading the stationary phase of the GC column d) ice blockage of the carrier gas flow through the column (although the use of 0.32 to 0.53 mm i.d. columns allows a higher loading of analytes including water vapour), e) detector baseline shifts, f) extinguishing of the hydrogen flame of an FID (Pleil et al., 1987).

The problem of small sample size is dealt with by the use of a selective, cryogenic, pre-concentration, NuTech™ Model 320-1 concentrator (-150°C at 30 mL/min) as part of the analytical procedure. The concentrator's cryogenic trap is fabricated of 0.32 cm o.d., high purity nickel tubing and packed with glass beads over a 5 cm length to increase trap surface-to-volume ratio (McClenny et al., 1991). The major constituents of the air are vented to the outside. The organic components are revolatalized by flash heating (to 120°C in 60 sec) and transferred to a high resolution GC equipped for sub-ambient temperature programming.

An internal standard (i.s.) spiking mixture, added to the sample during cryogenic pre-concentration, consists of bromochloromethane (BCM), chlorobenzene-d_5 (CBD), and 1,4-difluorobenzene (DFB) at 10 ppm each in purified humid air. The initial calibration must meet the acceptance criteria for the relative response factors (RRF's). The %rsd of the 5 RRF's for all target compounds must be less than 30% (McClenny et al., 1991). All samples are initially run undiluted. The sample is collected at 35 mL/min until a total fixed aliquot volume in the range of 250-500 mL has been processed. When atmospheric concentrations are greater than the low ppb range, smaller aliquots may be used. Samples are appropriately diluted and re-run when an analyte exceeds the linear calibration range of 1-100 ppb.

The sample is re-focused (-50°C with liquid nitrogen) at the head of a 50 m by 0.32 mm id fused silica micro-bore capillary column in the gas chromatograph. Under a flow of helium, the column is slowly ramped to higher temperatures (up to

180°C at 8°C/min) to allow the elution of all the organic compounds while the mass selective detector is scanning. This procedure allows not only for optimum separation but also for the quantification of highly volatile (>C_2) compounds which are not easily analyzed by other methods. Data is recorded by computer for subsequent processing. The Hewlett-Packard™ (HP) 5890 II gas chromatograph is considered to have the most stable and reliable heating and cooling controls which is vital for speciation and fingerprinting (Hawkins et al., 1991). Known analytical problems include (McClenny et al., 1991):

a. Vinyl chloride which exhibits an 8-12 sec wide peak because it is not effectively refocused on the column;

b. m-Dichlorobenzene/benzyl chloride, tetrachloroethane/0-xylene and m-/p-xylene are not baseline resolved by this technique.

Quantification is best performed by the method of relative response factors, where the proportionate system responses for analyte and standard are determined prior to the analysis of the sample and this relative system response is used to determine the quantity of compound present in the sample. Accuracy and replicate precision of GC-MSD analysis have been determined to be 25-30%, respectively (McCallister et al., 1991).

Recovery efficiencies in ambient air sampling have been found to be 85%-115% (Maier, 1990). For the 1989 EPA Urban Air Toxics Monitoring Program (UATMP), 397 ambient air samples were analyzed for 38 VOC's (Rice, 1990). The coefficient of variation (CV) for instrumental precision averaged ±0.44%. The CV for sampling and analysis precision averaged ±0.62%. The analytical accuracy of the GC/MSD and GC/MS systems averaged ±1.2% and ±0.31% bias, respectively. Positive confirmation by GC/MS of the GC/MSD identifications for all compounds was 94.1%.

The average method detection limit (defined as the product of the standard deviation (SD) of seven replicate analyses and the one-sided Student's *t* value for 99% confidence) for TO-14 compounds was 0.55 ppb (McClenny et al., 1991).

McClenny et al. (1991) found that the precision and accuracy were of the order of 15% and 10% respectively.

F. DEFICIENCIES IN THE PUBLISHED LITERATURE

Orris et al. (1995) point out that the health and safety of firefighters have frequently been neglected issues, the hazards of firefighting being assumed to be obvious and uncontrollable, and that little time has been spent analyzing both the acute and chronic pathologies related to firefighting and how to prevent them. One study has attempted to monitor firefighter exposure to diesel emissions and only total particulate matter (TPM) was measured (Froines et al., 1987). There have been no studies reported in the literature which evaluated the quality of the compressed breathing air used in the SCBA's. Due to the complexity of the CFK equation, its solution has been largely the exclusive domain of a few select researchers in academic institutions (Smith et al., 1996). As a result, users have employed inaccurate approximations of the CFK equation to estimate COHb levels from known ambient air concentrations of CO.

A review of the literature confirmed the apparent lack of quantitative data concerning the exposure of firefighters to potentially toxic VOC's at the scene of a fire. The fire literature is dominated by studies concerned with combustion toxicology (more than 70 papers) and epidemiology (more than 40 papers), the number of articles published increasing steadily since 1975. There has also been considerable interest in pulmonary function, cardiovascular disease, biological monitoring, post-incident studies and in the study of combustion products under laboratory controlled conditions. In contrast to this, there has been very little sampling of real fires or personal sampling of municipal firefighters. The work which has been done has focused on the sampling of gases having short-term, acute health effects. None of the studies has focused on the analysis of VOC's or other organic compounds with the objective of determining any long-term health risks to firefighters. The seven papers which have been published provided some preliminary data but a comprehensive study to identify and quantify air contaminants in structural fires has yet to be done. In all of these studies, the choice of chemicals monitored appears to be based on the availability of methods to collect and analyze samples rather than on a desire to assess firefighter exposures to toxic substances, especially those having long-term effects. There has been no validation of the suitability of sampling methods when used in fire atmospheres.

Little or no attention has been paid to the carcinogenic potential of fire atmospheres. None of the previous studies has limited sampling to one particular type of fire. None of the previous studies has attempted to correlate sampling with specific firefighting tasks or with the use (or non-use) of respiratory protection. Only one study has made a distinction in sampling between the knockdown and overhaul phases of the fire (Jankovic et al., 1992). Clearly, real fire data is needed by those researchers working in the fields of combustion toxicology and epidemiology. Finally, there are no published studies or existing databases which would permit realistic estimates of the time which firefighters actually spend at the scene of fires.

Consideration must be given to the possible long-term effects to firefighters of chemical contaminants which may be contributing factors in heart disease, liver disease and cancer. Due to the complex exposure patterns of firefighters to a wide variety of toxic chemicals, the choice of target compounds, the sampling strategy and the interpretation of the results are far from straight forward matters. Even in the event that individual toxic components were to be found in relatively low concentrations, the combined effect of a large number of substances and their possible synergistic effects are important unknowns.

Given the unpredictability of firefighting atmospheres, the assessment of risk to firefighters due to exposure to toxic chemical contaminants is tenuous at best. The nature of the burning structures and contents changes from fire to fire, conditions change rapidly during a single incident and contaminants are difficult to sample and characterize. Of the thousands of potential contaminants to be found in firefighting atmospheres, little is known concerning their toxicity as a complex mixture. Only a limited number of constituents have been either qualitatively or quantitatively identified.

The generation of toxic contaminants varies from fire to fire and is dependent on many variables including the nature of the burning material, the temperature at which pyrolysis or combustion occurs, the concentration of oxygen and the efficiency of combustion (Brandt-Rauf et al., 1988, 1989). Numerous attempts have been made to assess the complex problem of toxicity of fire effluent using mathematical models which take into account the chemical nature of the tested material and the analytically determined concentration data of major components such as CO, HCN and HCl. Sasse (1988), however, considers all efforts to date to be inadequate since none of the methods proposed permits an adequately reliable estimate of either acute toxicity of fire effluent or the risk of toxic hazards from real fires. There is, at present, no Standard respecting the evaluation of the toxicity of the atmosphere at the scene of a fire. Such a complex mixture is difficult to assess toxicologically. This has serious implications both for the firefighters themselves and for the surrounding community.

G. THE HYPOTHESIS

There is an association between cardiovascular, reproductive and oncogenic effects and chemicals (gases and VOC's) to which firefighters are exposed.

H. STATEMENT OF OBJECTIVES

There are, potentially, three major sources of occupational exposure of firefighters to toxic contaminants: A) diesel emissions in firehalls; B) contamination of compressed breathing air; and, C) combustion products at the scene of fires. It is the objective of this study to assess the contribution to firefighter exposures from each of these three sources.

(1) An attempt will be made to identify an easily monitored component of diesel emissions in firehalls which can be used to quantitatively estimate the levels of other toxic co-contaminants.

(2) Compressed breathing air will be analyzed for contaminants, particularly CO and water vapour, both of which are sensitive indicators of compressor and/or air filtration problems. Water vapour and CO will be assessed for use as possible markers for the presence of other toxic co-contaminants.

(3) An attempt will be made to develop user-friendly and easily accessible software to accurately solve the CFK equation, predicting COHb levels for known ambient air concentrations of CO and various work levels.

(4) A modified U.S. EPA TO-14 method will be verified for suitability as a sampling/analytical method for fire samples.

(5) Air samples will be collected at experimental fires burning various combustible materials. An attempt will be made to: (i) track the pattern and evolution of combustion products over time; (ii) identify a characteristic chromatographic "fingerprint" of combustion products generated at fires; and, (iii) identify useful marker compounds.

(6) Firescene air samples will be collected, emphasis being placed upon the analysis of VOC's and on the identification of potential carcinogens. The identification of VOC's are of interest not only in terms of their toxicity but also because of their potential to identify accelerants used in criminal fires.

(7) An attempt will be made to estimate the total time which firefighters spend at fires and to identify distinctive exposure groups.

CHAPTER 2

MATERIALS AND METHODS

I. DIESEL EMISSIONS IN FIREHALLS

Field data were collected in collaboration with the City of Montréal Fire Department. The presence of diesel emissions was monitored in nine firehalls (Nos. 5, 16, 19, 20, 30, 35, 40, 46 and 49) during the winter, when all doors and windows were normally closed, and with mechanical ventilation, if any, turned off. These included the busiest (Nos. 5 and 19) and the least busy (Nos. 30, 40 and 46) firehalls in the fire department, a firehall with mechanical ventilation (No. 35) and the firehalls where living quarters were not isolated from the garage (Nos. 40 and 49). The criteria to classify firehalls as "busy" or "not busy" was based on the time per year spent at fires.

Pump and ladder trucks used 6-cylinder, indirect fuel injection, 500-600 rpm, 250-400 Hp diesel engines. The various types of vehicles located at stations are represented by code numbers (Table 11). For example, a 200 vehicle is a pump truck, a 400 vehicle is a ladder truck, etc. The location of the vehicles is identified by replacing the last two digits in the code by the firehall number. For example, a pump truck (200) located at firehall number 05 is identified as vehicle number 205. All types of gas- and diesel-powered vehicles and tools were operated under normal conditions.

Carbon monoxide and total hydrocarbons were measured directly from the exhaust tailpipe of a small sample of vehicles using a direct-reading, exhaust analyzer (Model Infra-Two Exhaust Analyzer, Sun Electric Corp.). Baseline levels of carbon monoxide (CO), carbon dioxide CO_2, and nitrogen dioxide (NO_2) were determined in firehall garages. All measurements of components of diesel and gasoline emissions were reported as levels above baseline concentrations in order to isolate the contribution made by the operation of the machinery. Pollutant

Table 11. Fire department vehicles (City of Montréal)

Vehicle	Code	In Service (in reserve)	Firefighters per Vehicle	Engine Type
Pump truck	200 or 300	34 (7)	4	Diesel
Multi-purpose pump truck	600	10 (1)	4	Diesel
Ladder truck	400	21 (6)	3-6	Diesel
Aerial ladder truck	700 or 7000	10 (1)	2-3	Diesel
Rescue truck	500	9	4	Diesel
Command post bus	1000	1	2	Diesel
Compressed air supply truck	1600	2	2	Diesel
Hazardous chemicals truck	1700	1	4	Diesel
Boat	1800	3	1	Gasoline
Tow truck	1900	1	1	Diesel
Cars (chiefs)	100	23 (1)	1	Gasoline
Support vehicles	900	15	1	Gasoline
Van	1100	1	1	Gasoline
First-aid van	1200	1	1	Gasoline
Mobile canteen van	1300	2	1	Gasoline
Mechanical repair van	800	2	1	Gasoline
Diesel fuel supply struck	800	2	1	Diesel
Service truck	800	15	1	Gasoline
Bus	1400	3	1	Diesel

reactions (particulate agglomeration or NO to NO_2 conversion, for example) were assumed to be negligible over the time and distances involved. Ambient levels of carbon monoxide were monitored continuously for 24 hours during normal operations and response to alarms, both in the garage and in the adjoining office space and living quarters, using CO as a marker (Model 190 CO Datalogger™, National Draeger™ Inc.). There was no smoking during this time. Evaluation of the level of diesel emissions in the garages was based on peak levels of contaminants found in area samples measured at a height of 75 cm. from the floor, centred along the back wall of the garage, approximately five metres behind the trucks. Results were reported as arithmetic means ± 95% confidence intervals (CI) equal to $\pm t_{\alpha/2,n-1}$ times the standard deviation divided by the square root of the number of samples (Caulcutt, 1983; Taylor, 1990; Natrella, 1963). The difference in the levels of CO found in tailpipes and the peak levels of CO found at the location where area samples were measured was used to estimate the exhaust dilution. One-way analysis of variance (ANOVA) was used to determine differences in means of peak CO levels between firehall garages and between the number and types of vehicles operating within them. All vehicle movements were recorded. The average time taken to start up vehicles and to leave the firehall in response to an alarm was calculated. The total number of minutes that vehicles operated inside the firehall was calculated per 8-hour shift. All statistical tests were performed at the 95% confidence level (α=0.05) on transformed data which were normally distributed.

Following the 24-hour sampling period during normal operations, firehalls were temporarily removed from service and worst-case scenario experiments were conducted with different types and numbers of vehicles and tools operating in the firehall, with the doors closed, for two to four times the maximum time observed during alarms. Carbon monoxide, CO_2 and NO_2 were measured simultaneously in three of the nine firehalls using a direct-reading *CO_2 Analyzer* (ADC Instruments) and data-logging CO and NO_2 instruments (Model 190 Datalogger™, National Draeger™ Inc.). Ambient levels of CO, CO_2 and NO_2 were allowed to return to baseline levels between experiments. All instruments were calibrated according to the manufacturer's instructions before and after each sampling period. Area samples in garages were obtained in the same manner as was previously done for alarms. The rate of formation of CO_2 in firehall garages was calculated for the simultaneous operation of two diesel trucks with the doors closed. The rates of decay of CO_2 were calculated for the case when the doors were closed immediately upon exit of the trucks and when they were left open.

Additional samples were also obtained half a metre and 1.5 m from the exhaust tailpipe. The correlation between the components of diesel emissions (CO, CO_2 and NO_2) was determined by multiple regression of all the data obtained from samples located 0.5, 1.5 and 5 m from the exhaust tailpipe. Since the data reported were the concentrations above baseline levels, regression lines were forced to pass through the origin. The simplest model (linear, logarithmic, exponential or polynomial regression) yielding the best fit was chosen and compared to results obtained by other researchers.

II. COMPRESSED BREATHING AIR

1. Sampling strategy and sample collection

In spite of an apparently properly functionning compressor operated by the City of Montréal fire department, satisfactory results of air analysis performed by a qualified laboratory four months previously and a negative CO test during a spot check of compressor air, a random check of a firefighter's SCBA tank in March, 1993 showed elevated levels of CO. This prompted an investigation of the possible sources of contamination and of the possibility of a link with the observation that some young, apparently healthy firefighters appeared to tire much more quickly than others, sometimes attaining exhaustion after only 15 or 30 minutes of work and occasionally complaining of headache and nausea. Upon detection of the first samples of contaminated breathing air, all Montréal Fire Department SCBA's and cascade storage systems were emptied and refilled from a commercial supplier within 24 hours. The Department's Bauer™ (Model K21) compressor was withdrawn permanently from service and two alternate compressors (Jordair™ Model K180US3E) used by divers in the Montréal Parks and Recreation Department were used. Testing continued during this time in an attempt to evaluate the extent of the problem and to discover the source of the contamination. Given the urgency of the situation, it was impossible to formally randomize sampling procedures or to collect a large number of samples for statistical purposes.

Sixteen SCBA air bottles were selected from fire stations in the Montréal Fire Department. One SCBA air bottle was selected from each of eight other fire departments in communities adjacent to Montréal. One SCBA bottle was selected from a Montréal area diving equipment store. Two samples were taken from each of two air reserve tanks. Eleven samples were taken directly from the Montréal Fire Department compressor. A total of 40 samples were tested for the presence of CO. All measurements were taken at atmospheric pressure.

Eight of the samples were analyzed for CO, CO_2 and methane (CH_4) using a direct readout multi-gas analyzer (GasTech™ Model GX91). The remaining samples were analyzed for CO using a hand-held dataloging instrument (Model 190 Datalogger, National Draeger™ Inc.), a pocket-sized sensing and logging device which continuously monitors the presence of CO. It operates with a high performance electrochemical sensor and was calibrated with 50 ppm of CO. Initially, the compressed breathing air was allowed to flow into the SCBA facemask which was placed in a plastic bag together with the CO detector and the direct readout of the CO concentration was noted when the concentration inside the bag had stabilized. Two of the measurements were taken in quadruplicate, otherwise they were single readings. Subsequently, a regulator was attached directly to the air tank together with a flow controller and adaptor which fitted directly onto the CO detector. One sample was analyzed as described above, with confirmation of the result being obtained from an independent testing laboratory.

2. Quality analysis/quality control

An exhaustive six-month study of the breathing air production, storage and distribution systems was undertaken. Standard operating procedures and a quality analysis/quality control (QA/QC) program were developed for the production of compressed breathing air. These included detailed procedures for: (1) the installation, operation and maintenance of the compressors and air purifying units; (2) a sampling strategy and analysis of compressed breathing air; (3) the storage and distribution of compressed breathing air; and (4) the filling of cylinders. Log books were maintained to track the production, distribution and use of compressed breathing air by firefighters. Two new Ingersoll-Rand™ compressors (Eagle Model BAP25HV3), operational since 1995, were installed at the Fire Department while the two Jordair™ compressors owned by the Parks and Recreation Department continued to be used as backup.

The Environmental Laboratory of the City of Montréal developed a method for the analysis of compressed breathing air using a Nicolet™ Model 520 Fourier Transform Infrared Spectrophotometer (FTIR) equipped with a 11.2 metre gas cell. The patented logic of the Nicolet™ (1993) FASTFIT™ analysis program was used to define spectral regions for quantitation (allowing for interferences and overlapping of components) of the following gases: NO_2, N_2O, CH_4, non-methane organic compounds (NMOC as ethane equivalents) and the halogenated hydrocarbons Freon12™, Freon13™, Freon22™ and Freon113™. This was added to the information included with the software for H_2O, CO, CO_2 and NO (Table 12). Corrected calibration curves were calculated for all target compounds except ethane, Freon12™, Freon22™ and Freon113™ which do not obey Beer's Law in the expected range of concentrations. Accuracy of the method was verified using certified standards obtained from Matheson™ Gas Products Canada. Oxygen was determined using a Hewlett-Packard™ (Model 5890) gas chromatograph equipped with a thermal conductivity detector.

Compressed breathing air was tested for the presence of the above

Table 12. Fourier Transform Infrared Analysis of Compressed Breathing Air.

Infrared Wavenumber Assignments		Limits of Detection	Target Compounds	Interferences
From (cm^{-1})	To (cm^{-1})	ppm		
890	1200	0.3	F12, F13, F22, F113[a]	
1220	1400	0.1	N_2O	NO_2
1563.4	1659.9	0.1	NO_2	H_2O, CH_4, C_2H_6
1665	1750	0.2	H_2O	
1800	1950	0.3	NO	H_2O, CH_4
1992.6	2220	0.15	CO	CH_4
2300	2390	1	CO_2	N_2O
2800	3180	0.2	CH_4, C_2H_4	F22

[a] Dichlorodifluoromethane (F12); Monochlorodifluoromethane (F22); Chlorotrifluoromethane (F13); 1,1,2-Trichloro-1,2,2-trifluoroethane (F113)

contaminants before and after compressor or air purifier maintenance or at least once every three months. Testing was also performed every six months, by an independent analytical laboratory, the samples being analyzed for oxygen, nitrogen, argon, halogenated hydrocarbons, non-methane hydrocarbons (as methane equivalents), other compounds, odour, oil, particulates and condensates in addition to CO_2, CO, NO_2, N_2O, CH_4 and H_2O. A total of 75 compressed air samples from four compressors were tested by the City of Montréal Laboratory over a period of 42 months (1993-1996). Non-detected amounts were assigned a value equal to the method detection limit. A total of 16 compressor air samples were tested by an independent testing laboratory (Novamann Laboratories, Toronto). Seven of these were taken at the same time as other samples were sent to the City of Montréal laboratory for analysis.

Inter-laboratory comparisons were performed using the F-test for differences in variances and the two-tailed paired Student's *t*-test for differences in means between to the laboratories for the components analyzed. Analysis of variance was used to determine if there was a difference in means between the four compressors for each of the components analyzed. Where there was no statistically significant difference in means, the results were combined into one database for the calculation of arithmetic means, standard deviations and approximate 95% confidence intervals about the mean (Caulcutt, 1983; Taylor, 1990; Natrella, 1963). The same formula was used for both normal and non-normal distributions since, according to the Central Limit Theorem the sample mean of a random sample of measurements will have a distribution that is approximately normal if the number of samples is sufficiently large. The upper limit of the approximate 95% CI was compared with the maximum concentration of contaminants allowed by the *Canadian CAN3-Z180.1-M85 Standard on Compressed Breathing Air and Systems.* The air purity requirements of the Canadian Standard are approximately equivalent to ANSI/CGA Grade "G" air (CGA, 1990). The one-tail Student's *t*-test (assuming unequal variances) for differences in means between the levels of contaminants found before and following implementation of the new operating procedures was used to determine if there had been an improvement in the quality of the compressed breathing air. Expected values of potential contaminants were used to propose upper warning limits. The correlation between the levels of different components analyzed was investigated by calculating the covariance of data sets divided by the product of their standard deviations. All statistical tests were performed at the 95% confidence level (α=0.05) on transformed data which were normally distributed.

A detailed analysis of the levels of VOC's in compressed breathing air was also performed. Compressed breathing air was collected in Summa™ canisters from the end of 25-30 m of NIOSH approved breathing hose before and after 5-minute purges. VOC's found in 500 mL samples of this undiluted breathing air were analyzed by a modified U.S. EPA TO-14 method as described below in Part III.

3. Water vapour and carbon monoxide contamination

The ambient temperature at which a breathing apparatus might freeze was calculated for measured amounts of water vapour content in compressed breathing air. Theoretical blood COHb levels were calculated for subjects at rest and at maximum work levels for measured values of CO by solution of the Coburn-Forster-Kane (CFK) equation (see page 43 and Appendix 1). Values given by Peterson and Stewart (1975) were substituted into the equation as realistic estimates for maximum work levels (Table 13). Alternate values to those originally used by Coburn et al. (1965) and by Peterson and Stewart (1975) for subjects at rest have been suggested in more recent literature (Tikuisis et al., 1987; McCartney, 1990; Tikuisis et al., 1992; Smith et al., 1996). However, these have not been used in order to permit comparisons with the allowed exposure levels which were developed based on the original CFK equation (ACGIH, 1991a). The disadvantage to using the CFK equation (Eqn. 2) is its complexity (Appendix 1). The variable being determined (concentration of carboxyhaemoglobin) appears on both sides of the

Table 13. Values of Variables Substituted into the CFK Equation[a]

Variable	At Rest	At Maximum Work	Units
Atmospheric pressure	750	750	mmHg
Blood volume	5500	5000	mL
Breathing rate	110	8.5	min-1
Diffusivity of the lung	30	30	mL/min
Endogenous CO	0.01	0.01	mL/min
Haemoglobin concentration	15.94	15.94	g/mL
Haldane coefficient	218	218	
Oxygen content of the air	21	21	%
Partial pressure of water	47	47	mmHg
Pre-exposure COHb	0.8	0.8	%

[a] Values used by Coburn (1965) and Peterson (1975). See text for details.

equation and in an exponent of *e* on one side of the equation. A direct solution of the CFK equation is therefore impossible and an iterative procedure must be used. Given a set of assumed constants and the concentration of carbon monoxide in inspired air, a computerized algorithm can be used to solve the CFK equation for predicted %COHb concentrations. As part of this study, a computerized algorithm was developed to solve the CFK equation using Excel™ v5.0 spreadsheet software. A print-out of the algorithm is included in Appendix 2. The program is fast, flexible, accurate and easy to use. A menu-driven interface was created that enabled the substitution of different values for variables in rapid "what-if" analyses.

III. VOLATILE ORGANIC COMPOUNDS IN FIRE ATMOSPHERES

A. SAMPLING STRATEGY

1. Sampling Protocol

The initial objective of the sampling protocol was to collect data that would be useful in the assessment of structural firefighting exposures to VOC's known to have long-term health risks by inhalation. Fire fighting consists of two phases: 1) knockdown during which the fire is brought under control; and 2) overhaul, when the fire is extinguished and mop-up begins. Firefighter tasks were classified as either high or low expected exposures during both knockdown and overhaul. The intention had been to collect representative samples for one high exposure task during knockdown and again during overhaul, and to do the same for another low exposure task during these same two phases of the fire. This would have provided two samples during knockdown and two samples during overhaul for each fire. It was estimated that over the course of twenty fires a reasonable measure could be made of the ranges of firefighter exposures to toxic VOC's. It was felt that this information would be a valuable factor in the design and interpretation of epidemiological studies of the health risks of firefighting.

The sampling protocol was limited to municipal structural fires involving inner-city, multi-unit dwellings and small apartment buildings having shops on the ground floor. The objective was to restrict sampling to fires having similar combustible materials while including the types of fires occurring with the highest frequency. Even with good cooperation on the part of the fire department the sheer logistics of collecting samples as planned proved to be impossible to resolve. It frequently happened that the fire was extinguished within a few minutes or that the building was allowed to burn to the ground and there was no entry by the firefighters and no opportunity to collect samples. It was impossible to have sampling equipment on every fire truck on the territory and to train 1,200 firefighters in the sampling protocol. The alternative was to train a small team of men to do the sampling but, even then, they could not be at every suitable fire that occurred in the territory. Even when the sampling equipment was on location, it was not always possible for a firefighter, already working under conditions of maximum physical and psychological stress and carrying fifty to seventy pounds of gear, to depart from his standard operating procedures in order to carry out this additional task. Finally, during the risks associated with a fire, sampling equipment was sometimes lost or damaged. The fire department tried a number of different strategies to maximize the chances of being able to sample during knockdown and overhaul, but there were many situations of the sort described where it was impossible to obtain useful or representative samples. Burgess et al. (1977) noted that firefighters did not take their samplers to every fire to which they responded and that firefighters made individual judgements as to when to turn the samplers on and off. Mäkinen (1991) experienced difficulty in collecting data from fire departments, with information returned on only 6% of incidents: firemen were exhausted and therefore unwilling to perform extra tasks; firemen considered some types of alarms so common that they did not want to repeat the same thing many times; firemen "forgot" to collect data in spite of the training and orders received from their chiefs. The fire chiefs themselves were more enthusiastic participants, 79% of them having returned an information questionnaire. These various reasons echo some of the problems encountered in this study.

Part way through the study, the Fire Department was obliged to withdraw from the VOC protocol prior to its completion, "given the possible ramifications which might result as a consequence of the findings of the study." It was clear that this stemmed neither from Fire Department management nor from the firefighters union. In sharp contrast to this, the Montréal Fire Department demonstrated extraordinary cooperation and effort in the other three aspects of the study: diesel emissions in firehalls, contaminated breathing air and firefighter job matrix. Eventually, the project was reconsidered and the Fire Department did participate fully in the VOC study until its completion.

As a result of the delays and difficulties described above, the original plan (to sample high and low exposure tasks during knockdown and overhaul) was abandoned and replaced with sampling from a series of controlled experimental fires and a simplified sampling scheme from municipal structural fires. The modified protocol has, in fact, enhanced the quality of the final database. In particular, three new objectives were added to the original plan: (1) to track the pattern and evolution of various combustion products over time; (2) to identify a characteristic chromatographic "fingerprint" of combustion products produced at municipal structural fires; and (3) to identify useful marker compounds.

2. Controlled Experimental Fires

Seven air samples were collected from each of 15 experimental fires built in the basement of a two-story brick house using different combustible materials. Conditions were constructed to be realistic approximations of those found in actual structural fires encountered by municipal firefighters during the course of the year. One experimental fire was built using each of the following combustibles: a mattress, cardboard boxes, rigid foam roof insulation and a foam sofa. Two experimental fires were built using each of the following combustible materials:

plywood, varsol, alcohol and *Ultramar™* gasoline. Three experimental fires were built using spruce planks. "Grab" samples of air and photographs were taken at timed intervals (0, 2, 5, 10 and 15 min) to follow the evolution of smoke at these fires. Two simultaneous samples were collected at the 10 minute interval. An additional sample was collected after the fire was extinguished and following five minutes of natural ventilation when the firefighters entered the area without their SCBA's.

3. Municipal Structural Fires

Nine Summa™ canister air samples were collected by firefighters working under field conditions at a total of nine inner-city structural fires. Four of these samples were 15-minute, time-integrated samples. An integrated sampling time of 15 minutes was chosen, since this was the maximum length of time a firefighter could be in a burning building before his compressed breathing air supply would run out. Firefighters were instructed to collect samples inside structural fires under conditions where they judged that at least some firefighters would remove masks.

4. Sample Stability

Both fire samples and ambient air samples were analyzed repeatedly to determine if there was reactive interaction with the walls of the Summa™ canisters or between chemicals in the sample. One high level smoke sample from an inner-city structural fire was analyzed repeatedly over a period of five months. In the case of the ambient air experiment, two samples were collected on a weekday across the street from an inner-city bus terminal. One 24-hour sample was collected in a control canister which had never been used for anything other than the sampling of ambient air. The other 24-hour sample was collected during the same time period the following week in a clean canister which had previously been used for sampling fire atmospheres. These samples were analyzed repeatedly over a period of four months.

5. Replicate Sampling of Fire Atmospheres

Simultaneous 15 minute time-integrated samples (into four 3-litre and four 1.0-litre canisters placed in close proximity to each other) were obtained at two inner-city structural fires.

B. SAMPLE COLLECTION

Whole-air samples were collected into previously cleaned and evacuated (-30 in Hg) Summa™ electro-polished stainless steel canisters. Three-litre and one-litre canisters were used for sampling and these were obtained from SIS™ or BRC-Rasmussen™. The Summa™ canisters were equipped with a sampler consisting of a 2 µm, sintered, #316 stainless steel filter (Nupro™ Model SS-4F-K4-2) alone or in combination with a mechanical flow controller (Figures 1 and 2). The stainless steel filter was used alone for the collection of "grab" samples where the canister was opened and filled to atmospheric pressure within approximately 30 seconds (Figure 3A). The filter and flow controller assembly were used together for the collection of time-integrated samples (Figure 3B). A Matheson™ electronic flow meter, to be used for the calibration of the flow controllers, was itself calibrated using a Gilibrator™ bubble meter as a primary standard. The "constant down-stream" mechanical flow controller (Millaflow™ Model SC421), was calibrated at different initial flow rates to determine the range of linear flow. Time and vacuum were recorded beginning at -30 in Hg until atmospheric pressure was attained. Prior to sampling, the flow rate was adjusted in the laboratory so that the canister would fill to approximately 0.5 atm during the desired sampling time of 15 minutes. Under these conditions, the sampling rate remained constant over the collection period.

The mechanical flow controller was cleaned before and after use by purging with purified, humid air at 200 mL/min. for 48 hours. The 2 µm stainless steel filters were normally discarded after use. Those filters which had no visible particulates were cleaned in deionized water (no cleaning agent) in an ultrasonic

Figure 1. A schematic representation of the construction of the 2.0 µm Nupro™ stainless steel, sintered filter and holder used with Summa™ canisters to capture particulate matter.

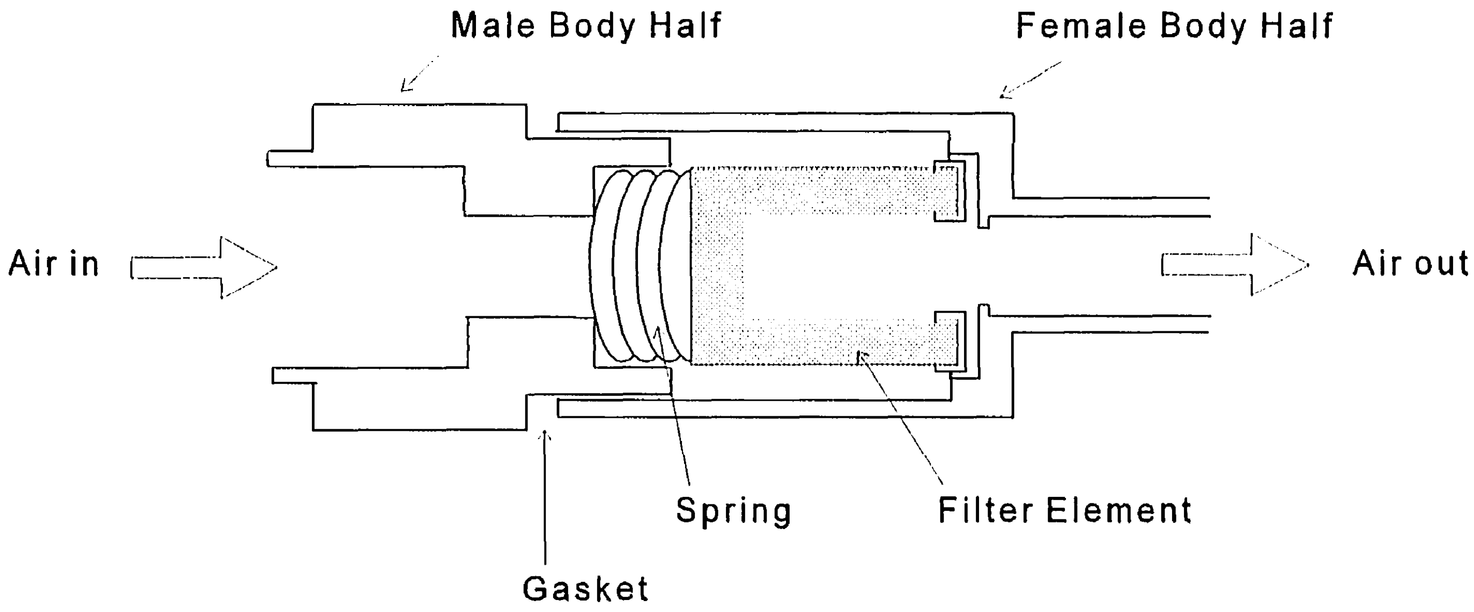
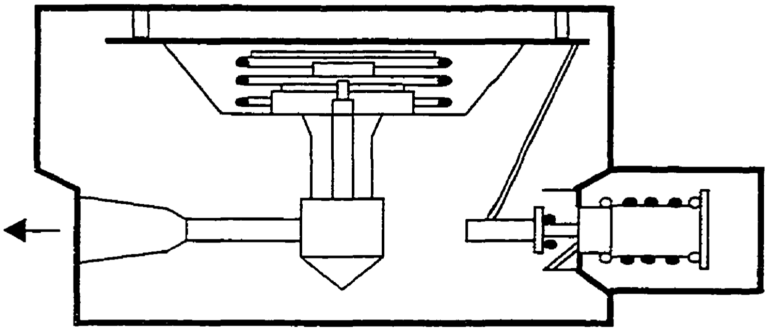
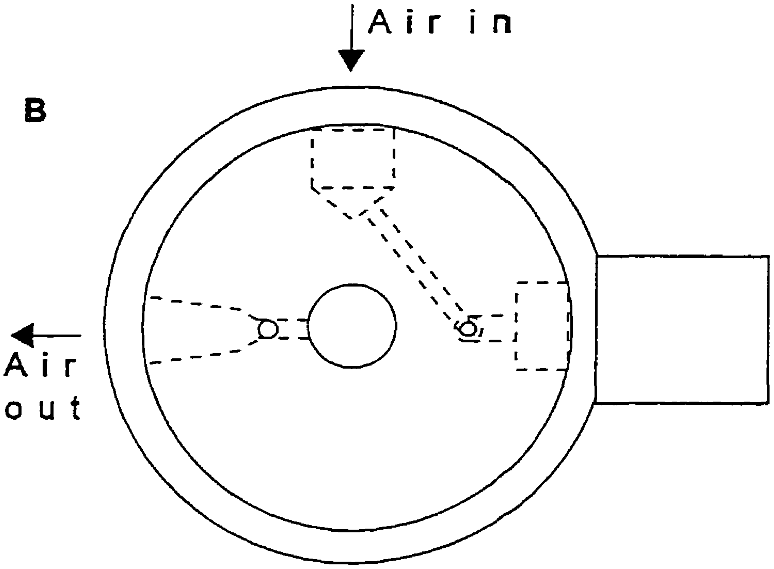
Male Body Half
Female Body Half
Air in
Air out
Spring
Filter Element
Gasket

Figure 2. A diagram, adapted from the Millaflow™ technical data sheet, showing side (A) and top (B) views of the Model SC421 mechanical flow controller (constant downstream reference) (C) used to regulate the rate of sample collection (5 to 500 mL/min) into Summa™ canisters. The flow controller, constructed with #316 stainless steel, Kel-F™ diaphragm Teflon™ seals and Viton™ seat material, weighs approximately 0.68 kg.

A



B



C

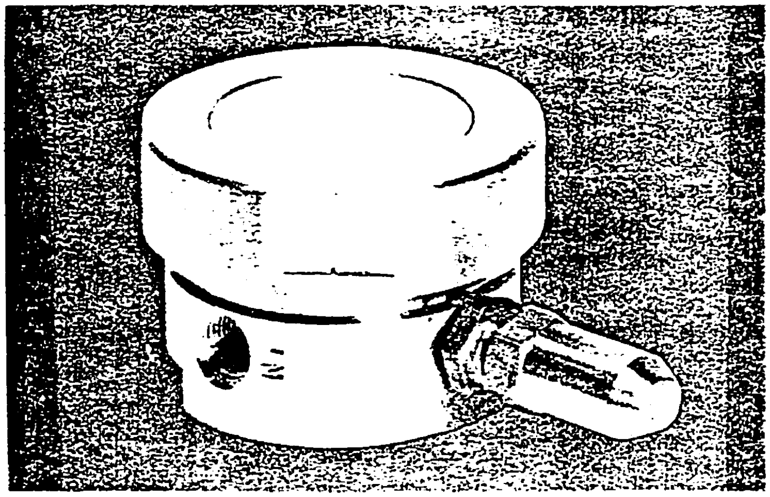
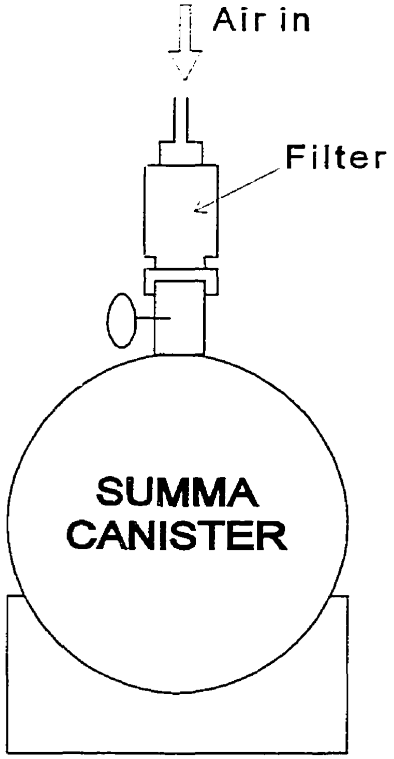
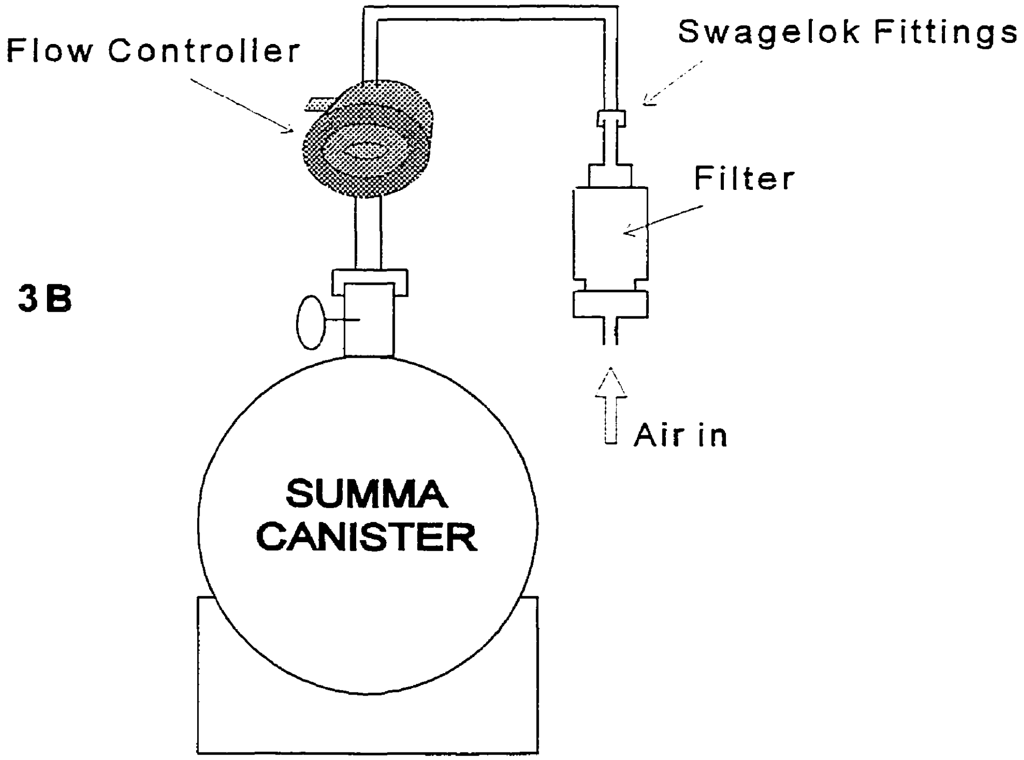


Figure 3. A schematic diagram of Summa™ canister sampling device showing: (3A) the attachment of the NUPRO™ filter, and/or, (3B) the Millaflow™ flow controller.

3A


Air in
Filter
SUMMA
CANISTER

3B


Flow Controller
Swagelok Fittings
Filter
Air in
SUMMA
CANISTER

bath for 3 hours at 65°C. Holders, connectors and adaptors were put through two 90-minute cycles of cleaning and rinsing in a 65°C ultrasonic bath and solution of Sparkleen™. The cleaned sampler (flow controller plus filter assembly) was fitted to a clean canister and this canister was filled with purified humid air to serve as an equipment blank. The sampler was certified clean when the analytical result for this blank met the acceptance criteria described below for canisters.

Canisters were cleaned by successive evacuation, heating and purified, humid air fill cycles. The canisters were evacuated to -30 in Hg and warmed with a heat gun to 80°C. After remaining under vacuum for 30 minutes, the canisters were filled to 30 psig with purified, humid air. This cycle was repeated three times. The canisters were then placed in a specially constructed, automated oven in which this cleaning process continued to operate through 16 additional one-hour cycles. Water molecules preferentially occupy reactive sites on the Summa™ polished canister surface. Therefore, use of humidified air increased the stability of VOC's stored in these canisters. The canisters were filled to 20 psig with purified, humid air and the contents were analyzed using a cryogenic pre-concentrator interfaced directly to a flame ionization detector (FID). The canisters were considered clean when the level of total non-methane organic compounds (NMOC) was less than 20 parts-per-billion of carbon (ppbC). Canisters were cleaned in batches of sixteen. The dirtiest canister in each batch was then analyzed by the same method used for sample analysis (pre-concentration and GC-MSD) and the chromatogram obtained was inspected for unusually high background levels of individual compounds. Canisters were certified clean when no compound was found to be present at levels higher than 2 ppb in the test canister. If high residual levels of high boiling point compounds were found, the cleaning procedure described above was repeated for all of the canisters in the set. If further cleaning was required, the valves were removed from the canisters and the canisters were rinsed with dilute nitric acid (5%), then filled with approximately 100 mL of deionized water, refitted with temporary valves and heated in an oven for 3 hours at 60°C. The manual and automated cleaning processes were repeated once again. The cleanliness of the canisters was verified and the cleaned canisters were evacuated to -30 in Hg and sent to the field for sample collection.

C. THE MODIFIED U.S. EPA TO-14 METHOD

The analysis of volatile organic compounds (VOC's) and a number of polar volatile organic compounds (PVOC's), having saturated vapour pressures at 25°C greater than 10^{-1} mm Hg, and the lighter semi-volatile organic compounds (SVOC's), having saturated vapour pressures at 25°C between 10^{-1} and 10^{-7} mm Hg, was based on a modified version of the United States Environmental Protection Agency's *Compendium Method TO-14* (EPA, 1988). This canister-based, whole-air method was applicable to the entire range of VOC's from C_2 to C_{10} and some selected SVOC's from C_{10} to C_{12}, with the exception of polar organic compounds. The TO-14 method is a complex, relatively new technique which has not been widely used in industrial hygiene applications. The analytical procedure involved the addition of an internal standard (i.s.) to the fire sample, removal of water vapour by a Nafion™ dryer, cryogenic trapping and pre-concentration of the volatile components of the sample, then separation and identification by gas chromatography. The accuracy of species identification was confirmed by mass spectral selected ion monitoring (SIM). While the TO-14 method has been used for monitoring "clean" indoor and outdoor ambient air, it has never been applied to the sampling and analysis of highly contaminated samples such as those found in fires. Validation of the technique included experiments to determine the stability of fire samples in the Summa™ canisters, repeatability and reproducibility. A Bruel&Kjaer™ Model 1302 multi-gas analyzer was used to monitor the presence of CO_2, CO, H_2O and SO_2 in a small proportion of the canister samples.

A 144-component instrument calibration standard mixture (canmix) was prepared in a Summa™ canister from seven C_2 to C_6 multi-component gas mixtures and three C_6 to C_{12} multi-component liquid mixtures. The gas mixtures were purchased from Scott™ Environmental Technology Inc. and the neat, liquid compounds were purchased from different sources. The liquid mixtures were prepared in the laboratory using gravimetric techniques and consisted of one 25-component alkane/alkene mixture, one 26-component aromatic mixture and one 31-component halogenated hydrocarbon mixture (Appendix 3). These stock liquid mixtures were stored separately in 0.5 mL amber ampoules. To prepare the instrument calibration mixture, an 82-component gas mixture was first made from the stock liquid mixtures in a 3-litre flask equipped with two Teflon™ stopcocks. Ten µL of each of the three liquid mixtures was weighed by difference and injected into the 3 L flask filled with purified, humid air. The flask was heated to 50°C for 1 hour to allow the components to vaporize and then left overnight at room temperature to allow for equilibration. This gravimetric standard which was prepared in the laboratory was compared with Scott Extra-Life multi-component toxic organic mixtures and was required to agree to within 15%. The final standard mixture was prepared by withdrawing aliquots from the prepared gas mixture (82 components) and from the seven Scott™ gas mixtures (62 components) with gas tight syringes (Pressure-Lok™, Precision Sampling Corp.). These aliquots were injected into an evacuated 15 L Summa™ polished canister together with purified humid air generated by the AADCO™ clean air generator. The resulting mixture was pressurized to 120 psig to produce an instrument calibration standard mixture (canmix) of approximately 10 ppb for each of the target compounds (Appendix 3). However, the newly filled, 15 L canisters containing the 144-component standard calibration mixture exceeded the pressure tolerance of the sample pre-concentrator. Therefore, another clean, evacuated canister was filled to 60 psig with the standard calibration mixture and then attached to the pre-concentrator. Since high molecular weight components were lost at lower pressures, this canister was replenished with standard mixture from the 15-L canister when the pressure decreased to 30 psig. The instrument calibration standard mixture was compared with an NIST (U.S. National Institute of Standards and Technology, formerly the National Bureau of

Standards) aromatic hydrocarbon primary standard and was required to agree to within 5%.

An internal standard mixture consisting of 1,4-difluorobenzene, bromochloromethane, chlorobenzene-d_5 and 1-bromo-4-fluorobenzene was prepared in a Summa™ canister using Scott™ Environmental Technology Inc. gases. The presence of the i.s. allowed monitoring of system performance during data acquisition. Data analysis was based on the internal standard method of quantitation which compensated for run-to-run system variations, thereby improving the precision. Clean air used for the cleaning of the canisters and for the dilution of samples was generated by an AADCO pure air generator (AADCO Instruments Inc.). Clean air used for the preparation of standards was obtained from LiquidCarbonic™ UltraPure compressed air cylinders. In both cases, the air was humidified by bubbling through deionized water. The bubbler was purged for 24 hours before use to remove any volatiles which may have been present in the fresh water. The air was certified clean when it contained less than 5 ppb of hydrocarbons.

D. SAMPLE CONDITIONING AND PRE-CONCENTRATION

1. Sample Dilution

Dilution calibration curves, corrected to standard temperature and pressure (STP=25°C and 760 mm Hg), were prepared for each size of canister in use. A mass flow controller delivered air to the evacuated canister at 200 mL/min. Time and vacuum readings were recorded beginning at -30 in Hg until +40 psig. Two calibration curves were prepared for each size of canister. One curve covered the range from -30 in Hg to atmospheric pressure. The other curve covered the range from atmospheric pressure to +40 psig. The slope and intercept were calculated for each curve and used to calculate the dilution factors for samples.

Following sampling, canisters were either at atmospheric or sub-atmospheric pressure. The exterior surfaces were cleaned to remove visible soot and dirt and the canister was attached to a source of purified, humid air. All transfer lines were evacuated and purged with clean, humidified air. The canister valve was opened, the initial sample pressure was recorded and the canister containing the sample was pressurized to 40 psig using a flow rate of approximately 200 mL/min. The flow rate was monitored by an electronic mass flow controller and verified with a Gilian™ soap-film bubble, electronic flowmeter. The fill time was determined with a stop-watch and the dilution factor was calculated from the previously obtained calibration curves. Initial and final canister pressures, flow rate, fill time and atmospheric temperature and pressure were recorded. Sample and dilution volumes were adjusted to standard temperature and pressure. If, upon analysis, the sample proved to be too concentrated, it was diluted a second time. An aliquot was transferred to another clean, evacuated canister and then pressurized as before. Care was taken to purge and evacuate all transfer lines prior to opening the canister valves. A certified clean canister was also filled with clean air (from the same fill lines) and served as a blank. A dilution factor adjustment for carbon dioxide (CO_2) was calculated from this blank sample.

2. Sample Aliquots

Aliquots of the fire sample were transferred to the VOC "Sample conditioning and pre-concentrating unit" which included two electronic mass flow controllers (FC260 with RO-32 control box, Tylan™ Corp.), a Nafion™, PermaPure™ dryer, and a cryogenic pre-concentration trap (Figures 4 and 5). Details of the operating procedures used for the pre-concentration and injection of sample aliquots are provided in Appendix 4. Prior to withdrawal of an aliquot of sample from the Summa™ canister, transfer lines were flushed with helium for 30 minutes and then evacuated to -30 in Hg.

A needle valve was fitted to the Summa™ canister containing the pressurized sample and adjusted to 50 mL/min with a rotameter prior to attachment to the

Figure 4. A schematic diagram of the analytical instrumentation in the **"collection mode"** showing the movement of air sample from the Summa™ canister through Nafion™ dryer, a cryogenic pre-concentrator to the gas-liquid chromatograph (GC) and mass selective detector (MSD). This equipment was designed and built by Dr. D. Wang, Environment Canada, Ambient Air and Analysis Division (Air Toxics Section), Ottawa, Canada.

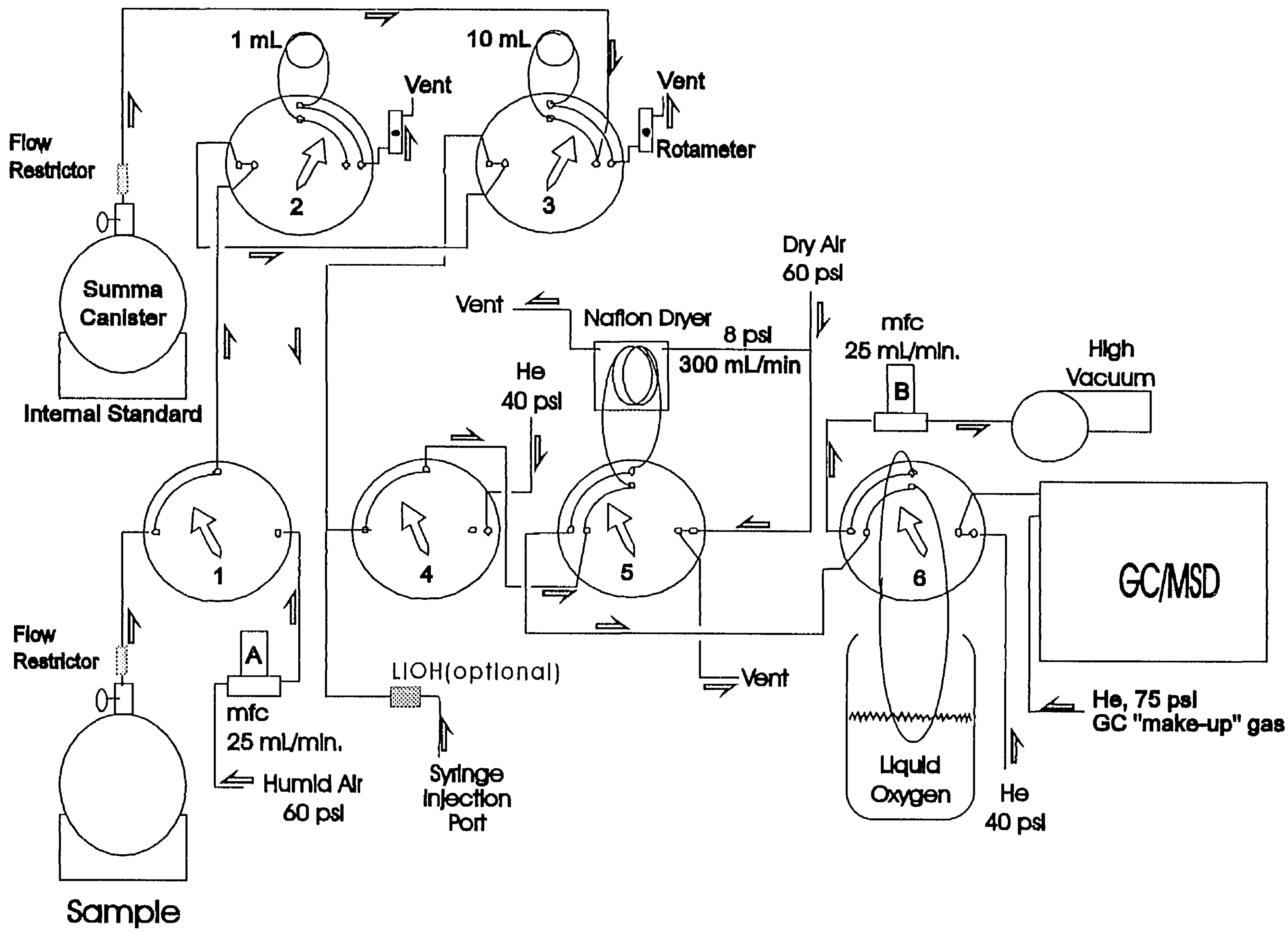
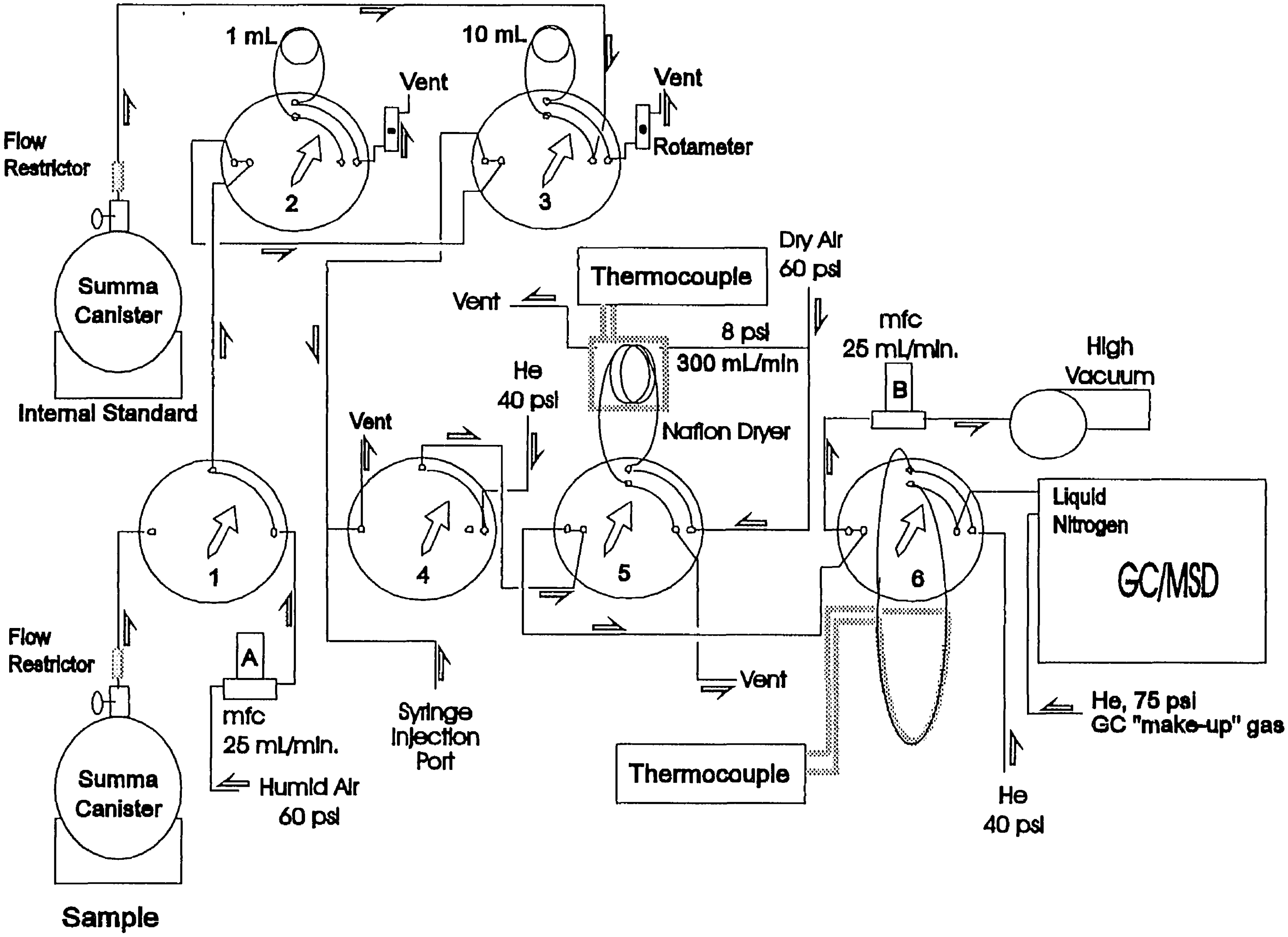

1 mL
10 mL
Vent
Vent
Rotameter
Flow
Restrictor
2
3
Summa
Canister
Internal Standard
Dry Air
60 psi
Vent
Nafion Dryer
8 psi
300 mL/min
mfc
25 mL/min.
B
High
Vacuum
He
40 psi
1
4
5
6
GC/MSD
Flow
Restrictor
A
mfc
25 mL/min.
Humid Air
60 psi
LIOH(optional)
Syringe
Injection
Port
Vent
Liquid
Oxygen
He
40 psi
He, 75 psi
GC "make-up" gas
Sample

Figure 5. A schematic diagram of the analytical instrumentation in the **"injection mode"** showing the movement of the trapped VOC's from the cryogenic pre-concentrator to the gas-liquid chromatograph (GC) and mass selective detector (MSD). The position of the thermocouple is indicated where the VOC sample must be flash heated. This equipment was designed and built by Dr. D. Wang, Environment Canada, Ambient Air and Analysis Division (Air Toxics Section), Ottawa, Canada.


1 mL
10 mL
Vent
Vent
Rotameter
Flow Restrictor
2
3
Summa Canister
Internal Standard
Thermocouple
Dry Air 60 psi
Vent
8 psi
300 mL/min
mfc 25 mL/min.
B
High Vacuum
He 40 psi
Nafion Dryer
Vent
1
4
5
6
Liquid Nitrogen
GC/MSD
Flow Restrictor
A
mfc 25 mL/min.
Humid Air 60 psi
Syringe Injection Port
Vent
Thermocouple
He, 75 psi GC "make-up" gas
He 40 psi
Summa Canister
Sample

sampling lines. This needle valve was found to be particularly susceptible to contamination. It was removed between runs, heated gently with a heat gun and flushed separately with clean air. Care was taken to avoid overheating since this could cause deterioration of the Viton™ O-ring gasket in the needle valve. When the needle valve showed evidence of contamination, it was dismantled and cleaned in an ultrasonic bath as described previously. The parts were then baked in a vacuum oven for three or four days. A blank was run on the GC-MSD to verify that all traces of contamination were removed.

For samples exhibiting a very broad range of concentrations amongst target components, it was necessary to do repeated analysis using different sample volumes in order to obtain results for all components within the calibration range. The ability to do repeated analysis on the same field sample was one of the major advantages of the whole-air canister sampling method. In general, it was sufficient to analyze each sample twice, beginning with a small 1 mL aliquot and, based on the initial results, using a larger, 10 mL or 250 mL, aliquot. The Summa™ canister was connected to the "Sample conditioning and pre-concentrating" unit of the analytical system. One mL or 10 mL aliquots were withdrawn by means of a sample loop from the pressurized canister (Figure 4). A correction factor was applied to the volume to account for differences from standard temperature and pressure. The sample loop volumes were calibrated using an NIST propane primary standard.

Larger aliquots (250 mL to 1000 mL) were withdrawn from the canister for 10, 15, 20 or 30 minutes at a constant flow of 25 mL/min. The flow rate, maintained by an electronic mass flow controller located upstream from a vacuum pump, was verified with a Gilian™ soap-film bubble flowmeter. Changes in temperature and pressure did not affect the analytical result when the sample was withdrawn from the canister using the timer/mass flow controller system, since the errors so introduced cancel out when the calibration mixture is analyzed under the same conditons. In the case of very highly concentrated samples, an aliquot of the sample was transferred to another clean, evacuated canister. This second canister was pressurized and then processed as described above.

Use of a gas-tight syringe for the injection of sample aliquots into the pre-concentrator introduced additional potential error because ambient laboratory air leaked into the system through the septum. It took two minutes to inject 50 mL at 25 mL/min., affording ample opportunity for air to leak in around the edges of the needle. Marker compounds for laboratory air included toluene and dichloromethane. This problem was minimized by making sure that the line was not under vacuum while the needle was inserted through the septum. Better results were obtained when the samples could be diluted such that it was possible to use either a sample loop or a timer and mass flow controller instead of a syringe.

A 10 mL aliquot of the 4-component i.s. mixture was introduced into the same lines which carried the sample to the pre-concentrator. This was done by opening the canister to flush a 10 mL sample loop, which was subsequently flushed with purified humid air into the sample line.

3. Removal of Carbon Dioxide

High levels of CO_2 in a sample might potentially cause two problems: 1) CO_2 produces a large, broad peak and, at high levels, it could saturate the MSD detector which would cause a suppression of the response to early-eluting target compounds; 2) high levels of CO_2 freeze and block the pre-concentrator cryogenic trap. For samples high in CO_2, the carbon dioxide may be selectively removed by passing the sample air stream through a lithium hydroxide (LiOH) trap located upstream from the Nafion™ dryer. However, it would not be necessary to do this if the concentration of target compounds was sufficiently high to allow the use of small sample aliquots of the order of 1 to 10 mL.

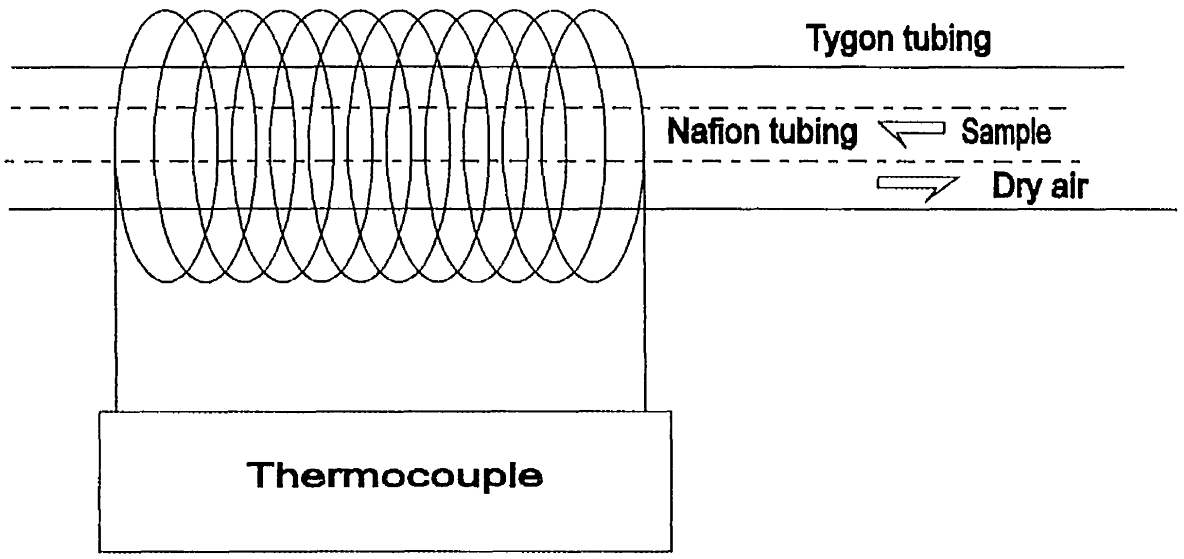
4. Removal of Water Vapour

One litre of air at 70% relative humidity at 25°C contains approximately 20 µL of water. The presence of moisture in the sample air stream can cause multiple problems, including: 1) suppression of signals in the region between benzene and toluene (which includes the i.s. 1,4-difluorobenzene); 2) severe retention-time shifting of the earlier-eluting compounds; 3) column deterioration; 4) excessive pressure in the MS ion source resulting in instrument shut-down; and 5) blockage of the trap and/or capillary column by ice formation at reduced temperature.

Water was removed from the sample air stream by a Nafion™, PermaPure™ dryer placed in-line, upstream from the cryogenic trap (Figure 4). Nafion™ is a semipermeable copolymer of tetrafluoroethylene and fluorosil monomer, developed by Dupont Corporation, which selectively allows water and other polar compounds to pass through the membrane. The "dryer" consisted of 2.0 m of 1.6 mm o.d. Nafion™ tubing inserted into 2.0 m of larger diameter (3.2 mm o.d.) Teflon™ tubing and coiled to fit into a 100 cm metal cylinder around which was placed heating tape connected to a thermocouple (Figure 6). Dry air passed through the Teflon™ tubing over the Nafion™ tubing, counter-current to the sample flow, thereby removing any moisture diffusing out of the sample air stream. New dryers usually exhibited a large peak (principle ions 81, 47, 96) eluting just after chloromethane at approximately 8.9 minutes. Another large peak (principal ions 155, 156, 157, 125) eluted at approximately 19.7 minutes, just before hexane. A small constellation of contaminants was also found in the vicinity of 25 minutes near the elution time of toluene. New dryers were purged with clean, dry air and baked out repeatedly at 100°C over a few days to eliminate these contaminants.

To prevent build-up of residual moisture and hydrocarbons in the dryer during normal operation, the dryer was heated to 80°C and purged with purified dry air at 300 mL/min. for 20 min. following each sample injection. The air pressure in the line was maintained at 8 psig. If the dryer permitted an excessive amount of moisture to pass through to the GC, this may have been caused by one of the

Figure 6. A schematic diagram showing the construction of the "dryer" which contains the Nafion™ tubing inserted through 2.0 metres of Teflon™ tubing coiled to fit inside a 10 cm. metal cylinder covered by heating tape connected to a thermocouple. This equipment was designed and built by Dr. D. Wang, Environment Canada, Ambient Air and Analysis Division (Air Toxics Section), Ottawa, Canada.

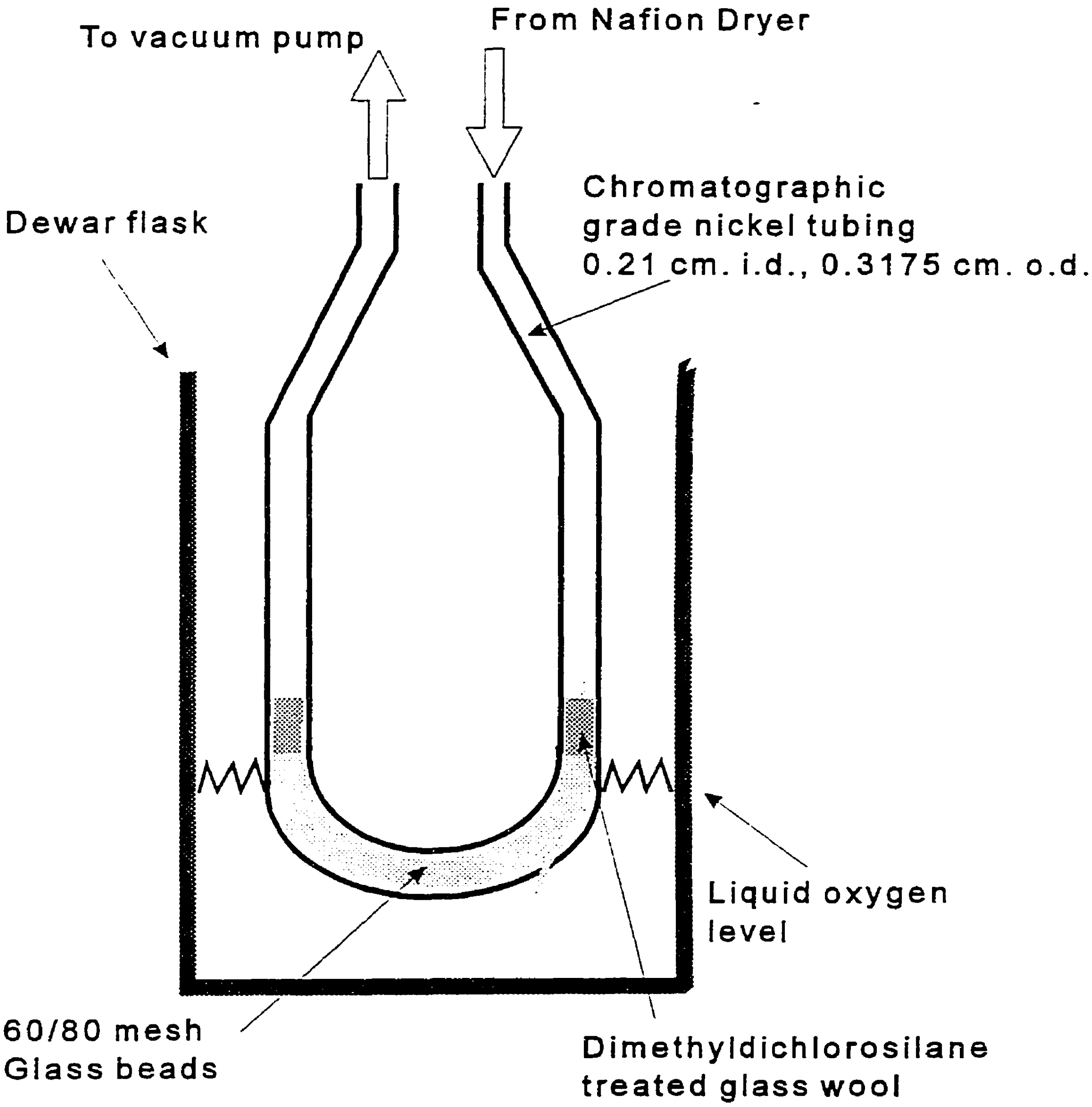

Tygon tubing
Nafion tubing
Sample
Dry air
Thermocouple

following: 1) the fittings were too tight on the tubing surrounding the dryer thereby restricting flow of counter-current purge air; 2) the dryer had collapsed because it had been placed under vacuum while hot; or 3) an excessive amount of water flowing through the dryer caused it to swell, thereby reducing purge-air flow in the surrounding tubing.

5. Cryogenic Trapping and Re-volatilization

The air stream containing the sample and the internal standards passed through a cryogenic trap consisting of a 30 cm., 0.32 mm O.D. nickel tube packed with 60/80 mesh untreated glass beads held in place by dimethyldichlorosilane treated glass wool plugs (Figure 7). The trap was immersed in a Dewar™ flask containing liquid oxygen (-183°C) which had been condensed from ambient air by liquid nitrogen. The trap condensed the non-methane organic components (NMOC) from the fire sample while allowing air and methane to pass through to the exhaust. Following the trapping phase, the cryogen level was raised approximately 3 cm., the six-port valve to the cryogenic trap was switched to the inject position (Figure 5) directing the helium carrier gas through the trap for a few seconds in the direction opposite to the previous air sample flow. The trapped VOC's were then re-volatilized by simultaneously removing the cryogen and flash-heating to 100°C. The pre-concentrator was interfaced directly to the gas chromatograph. Helium gas carried the VOC's through a heated transfer line to the GC whose injection mode was synchronized with the flash heating of the trap in the pre-concentrator via computer software. Between runs, the trap was purged with helium and baked out at 100°C. The dryer was heated to 80°C and purged with dry air. The transfer lines were left on slow helium purge (5 mL/min) overnight.

Figure 7. A schematic diagram showing the construction of the cryogenic trap with the immersion of the nickel tubing (30 cm, 0.32 cm o.d.), containing 60/80 mesh glass beads, in a Dewar™ flask containing liquid oxygen (-183°C).


To vacuum pump
From Nafion Dryer
Chromatographic grade nickel tubing 0.21 cm. i.d., 0.3175 cm. o.d.
Dewar flask
Liquid oxygen level
60/80 mesh Glass beads
Dimethyldichlorosilane treated glass wool

E. CHEMICAL ANALYSIS

1. GC/MSD Instrumentation

The gas chromatograph used for component species separation, identification and quantitation was a Hewlett-Packard™ (HP) model 5890 series II gas chromatograph capable of sub-atmospheric temperature programming and equipped with an HP model 5971 quadrupole mass selective detector (MSD). The volatiles were separated on a Hewlett-Packard™ 50 m, 0.32 mm I.D. fused silica capillary column with a 1.0 µm-thick film of HP-1 bonded liquid phase.

The mass spectrometer parameters were adjusted (tuned) to meet standard performance criteria (Table 14). To maintain optimum performance, the instrument was adjusted weekly for maximum sensitivity over the full scan range. The method used was based on the ions with mass to ion ratios (m/z) of 69, 219, and 502 present in the spectrum of perfluorotributylamine (PFTBA) which was used as the tuning calibration gas. Since the volume of PFTBA injected varied with ambient temperature, it was important that the instrument be adjusted at the same ambient temperature as that used to run samples.

2. Gas Chromatographic Separation of Sample Components

The re-volatilized sample from the pre-concentrator was cryo-focused on the GC column using liquid nitrogen (Figure 5). The initial temperature of the column, which was -60°C, was held for three minutes then raised to 250°C at a rate of 8°C/min. The rate was then increased to 20°C/min. and the temperature was held at 280°C for 8 min. after which it was lowered to 150°C. The total chromatographic separation time was 57.75 minutes, including a 5-minute solvent delay time. Overnight and between runs, the GC was left on standby at 150°C.

Table 14. Mass spectrometer adjustment (tuning) performance criteria[a]

PARAMETER	ACCEPTANCE CRITERIA
Electron multiplier voltage	No increase (approx. 1,920 volts)
Entrance lens offset	No decrease (approx. 14.00)
Peak widths	0.4 to 0.6 amu
Mass assignments:	
m/z 69.00	68.8 to 69.2 amu
m/z 219.0	218.8 to 219.2 amu
m/z 502.0	501.8 to 502.2 amu
Relative abundances:	
m/z 69.00	100%
m/z 219.0	>30%
m/z 502.0	> 1%
Ratios of isotope masses:	
m/z 70.0	0.54 to 1.6%
m/z 220.0	3.2 to 5.4%
m/z 503.0	7.9 to 12.4%
Air leaks	
Nitrogen m/z 28	Use air & water check menu item.
Water m/z 18	

[a] Hewlett-Packard (1990).

3. Mass Spectral Selected Ion Monitoring

The sample flowed from the chromatograph into an ion source where it was bombarded by 70 eV electrons causing the molecules to fragment and ionize. A lens system focused a beam of positive ions into the quadrupole mass filter where ions with specific mass to ion ratios were allowed to pass through to the detector and all others were rejected (Hewlett-Packard™, 1990). The solvent delay allowed the carrier gas (helium) to elute without being ionized. The selected ion monitoring method (SIM) method comprised 27 data acquisition windows. Each acquisition window monitored three to 17 ions (Appendix 5). The HP™ selected ion monitoring (SIM) acquisition method was modified to identify and quantitate the 144 target compounds and four internal standards. Each eluting compound was automatically monitored by the computer software for one characteristic target ion and one or more characteristic qualifier ions (Appendix 6). The instrument calibration mixture chromatogram was checked daily to ensure that all target ions fell within the expected acquisition windows despite drifts in retention times.

4. Mass Spectral Identification of Unknowns

A second aliquot of the fire sample was analyzed in SCAN mode which monitored all the molecular ion fragments, from 35 amu to 500 amu, present in the mass spectrum. Tentative identification of major non-target compounds was made by comparison of the mass spectrum obtained with appropriate reference spectra found by searching NBS75K computerized mass spectral and molecular structures libraries (NIST, 1992).

F. DATA PROCESSING

1. Computer software

Chromatographic and spectrographic data were automatically downloaded from the GC/MSD to an IBM™-compatible computer equipped with 8 Megabytes

(MBytes) of RAM and a 520 Mbyte hard drive. HPChemStation™ G1034C (vC.02.00 1989-93) software operating under Windows™ v3.1 in conjunction with Excel™ v4.0 controlled the operation of the GC/MSD and simultaneous downloading of data. Results of the automated data analysis were saved on the hard drive and printed out on a Hewlett-Packard™ LaserJet-3™ printer following each run. This raw data was also backed up onto tape using an internal Irwin™ tape drive and 3M™ DC2120 120 Mbyte Ximat™-formatted mini data cartridge tapes.

Final data processing was done using a Comax™ Model 486DX4, 100 MHz computer equipped with 16 MBytes of RAM, one 1.2 gigabyte (GByte) hard drive and one 3.2 GByte slave hard drive. In addition to the software used for data acquisition, data processing used Hewlett-Packard™ G1032C Enviroquant™ (vC.02.00) software. The calibration method was updated and the data was reprocessed using the automated data analysis. The data was reprocessed a third time to manually verify the identification and integration of each of the 144 target compounds. This processed data was backed up onto tape using an external Connor™ tape drive and 3M™ DC2120 120 Mbyte Rhomat™-formatted mini data cartridge tapes. Statistical analysis was accomplished with Excel™ v5.0 software. The hard drive was defragmented daily. A Hewlett-Packard™ LaserJet- 4™ was used for printing. Other software used included Connor™ Backup-Basics™ v2.0, Excel™ v5.0, CorelDraw™ v4.0, WordPerfect™ v8.0 and Windows95™. Details of data analysis and data management procedures are provided in Appendix 7.

2. Compound Identification

Compounds were identified by best retention time of the target ion and best qualifier ion ratio match with one or two qualifier ions present to within 20% of the theoretical relative responses. Response was measured by peak area. The selected ion monitoring (SIM) detection technique was highly specific and sensitive. Depending on the ions being monitored, the sensitivity in SIM mode was approximately 10 times that in SCAN mode.

3. Integration

The ChemStation™ software offered a choice of three integrators: a) *Auto Integration*, which automatically selects integration parameters based on the data to be integrated; b) *Integration*, which is a full-featured integrator designed to handle any chromatographic situation; and, c) *RTEint*, which is a fast, 2-pass integrator designed to handle simple chromatographic situations based on operator-set integration parameters. The *RTEint* integrator was used for integration of VOC peaks found in the fire samples. On the first pass, the *RTEint* integrator attempts to detect as many chromatographic peaks as possible to a maximum of 250. The second pass selects the target compound peaks. The peaks reported are the largest peaks that exceed the area threshold rejection value. Data smoothing was not used. Detection filtering was set at 5 points, start threshold at 0.200 and stop threshold at 0.050. Peak location was at the top of the peak. The minimum size peak which was automatically integrated was 500 area counts. The baseline preference was baseline drop or else baseline tangent. The baseline was reset after 5 points or more if the leading or trailing edge was less than 100%.

4. Calibration Curves

Data was quantified on 5-point calibration curves obtained by linear regression and forced through the origin. In order to insure that the observed linearity was not produced by chance alone, the correlation coefficient was required to be greater than 0.88 (3 degrees of freedom at the 95% confidence level). The appropriateness of the least squares method for linear regression and the use of the *t*-distribution for confidence intervals and tests of significance depended on the assumption that the residuals were normally distributed (Bland, 1989).

The regression method does not provide any information about how close the linear relationship is between two variables. The correlation coefficient, *r*, (or product moment correlation coefficient), which is based upon the sum of the products about the mean, does measure how close the points are to a straight line.

By dividing the sum of products by the root sum of squares of deviations of each variable, the correlation coefficient is made to lie between -1.0 and +1.0. When there is no relationship between the points $r=0$ because the sum of the products is zero. It does not matter which variable is taken to be y and which to be x since there is no choice of predictor and outcome variable as there is in regression. The correlation coefficient is related to the regression coefficient, b, in a simple way (Bland, 1989):

If $Y = a + bX$ is the regression of Y on X, and

$X = a' + b'Y$ is the regression of X on Y, then

$r^2 = b\,b'$

Correlation coefficients must be treated with caution, especially when derived from small samples. The null hypothesis that $r=0$ is numerically equivalent to testing the null hypothesis that b=0. The test is valid provided that at least one of the variables is normally distributed. If this condition is not met, then one of the rank correlation methods may be used. Because the correlation coefficient does not depend on the means or variances of the observations, the distribution of the sample correlation coefficient when the population coefficient is zero is easy to tabulate (Bland, 1989). As can be seen from Table 15, the values of r which can arise by chance with small samples are quite high.

A correlation coefficient of 0.95 would not be significant for a 3-point linear regression line (one degree of freedom) at the 95% confidence level. The critical value for an acceptable 3-point linear regression would be $r=1.00$ ($p < 0.05$). There would then be a 5% chance that the observed correlation (or slope of the line) had arisen by chance. The critical value for a 5-point linear regression (3 degrees of freedom) would be $r \geq 0.878$.

Five-point calibration curves were prepared weekly on the GC/MSD for each of the 144 target compounds. This was done by withdrawing known amounts from the standard VOC mixture at 25 mL/min for 10, 20, 30, 40 and 50 minutes giving 250, 500, 750, 1000 and 1250 mL aliquots respectively. Processing of the standard

Table 15. Significance of linear regression for small samples[a]

Number of samples	Degrees of freedom	Critical values for the correlation coefficient (r) ($p<0.05$)	Critical values for the correlation coefficient (r) ($p<0.01$)
3	1	1.000	1.000
4	2	0.950	0.990
5	3	0.878	0.959
6	4	0.811	0.917
7	5	0.754	0.874
8	6	0.707	0.834
9	7	0.666	0.798
10	8	0.632	0.765
11	9	0.602	0.735
12	10	0.576	0.708

[a] Adapted from Crow et al. (1960).

calibration mixture was identical to that of the sample canisters described above. A mid-range concentration of the instrument standard calibration mixture was run daily to monitor system performance and calibration. Continuous calibration curves were prepared daily by updating one of the 5 calibration levels. New 5-point curves were prepared when the continuing calibration curves no longer met the acceptance criteria, or following system modifications such as cleaning the MS detector, replacing the dryer, etc.

5. Quantitation

The internal standard method of quantitation was used. All target compounds in the quantitation database were corrected for the response of the associated internal standard. Errors in the response of the i.s. could, potentially, degrade the data. This may happen in two ways: 1) different volumes of i.s. are added from one sample to the next; or 2) the response of the i.s. is suppressed (by the presence of water, for example). In the first case, the precision of the volumes was insured by the use of a sample loop. In the second case, if the response of the i.s. was suppressed due to the presence of water, then the affected data was corrected by the same factor as the error in the i.s. or the data was quantified by using the external standard method.

G. ANALYTICAL QUALITY CONTROL

Analytical quality control was based on criteria defined by the U.S. EPA *Contract Laboratory Program: Statement of work for analysis of ambient air* (EPA, 1991). Calibration curves were required to have a correlation coefficient better than or equal to the critical value at the 95% confidence level (i.e. $r \geq 0.88$ for a 5-point curve), an average response factor > 0.1 and an average response factor %rsd ≤30%. Compounds for which the calibration curve correlation coefficient exceeded the critical value at the 99% confidence level (i.e. $r \geq$ 0.0.959 for a 5-point curve) were also identified. The other analytical criteria included: (a) limit of quantitation

(LOQ), defined as 10 x SD of the noise, lower than or equal to 5 ppb; (b) analytical accuracy better than or equal to ±30%; (c) inter-day precision of the area counts for internal standards better than or equal to ±40%; (d) analytical precision for replicate standard mixture samples better than or equal to ±7% at the 10 ppb level; (e) analytical replicate precision for field samples better than or equal to ±25%; and (f) no target compound present at or above the LOQ of 2 to 5 ppb, depending on the compound, in blank samples. Data quality was also compared to the more recent technical acceptance criteria found in the U.S. EPA TO-15 method (EPA, 1997).

IV. FIREFIGHTER EXPOSURE TIME AT FIRES

Each year, the Montréal Fire Department collects statistics concerning the types, location and severity of fires, the types of vehicles and the number of alarms to which they are called, the identification and assignment of breathing apparatus, the number of firefighters and their assignments, injuries and fatalities. In addition, in 1991, the Fire Department maintained statistics on the movement of each emergency vehicle, the number and type of alarm to which each vehicle was called and the number of minutes spent there. These databases were analyzed to yield information concerning the distribution of time and personnel for various firefighter tasks. In particular, estimates were made of the total time that firefighters spent at the fire-scene. As part of this study, standard operating procedures were developed for the maintenance of log books which tracked the storage and distribution of all compressed breathing air and the filling of SCBA cylinders. Beginning in 1995, detailed information was recorded for each storage tank and SCBA cylinder used, including its ID number, the time, date and place of its use, its initial and final pressures. Analysis of this database provided an estimate of the percentage of time that firefighters used respiratory protection while at fires.

CHAPTER 3

RESULTS

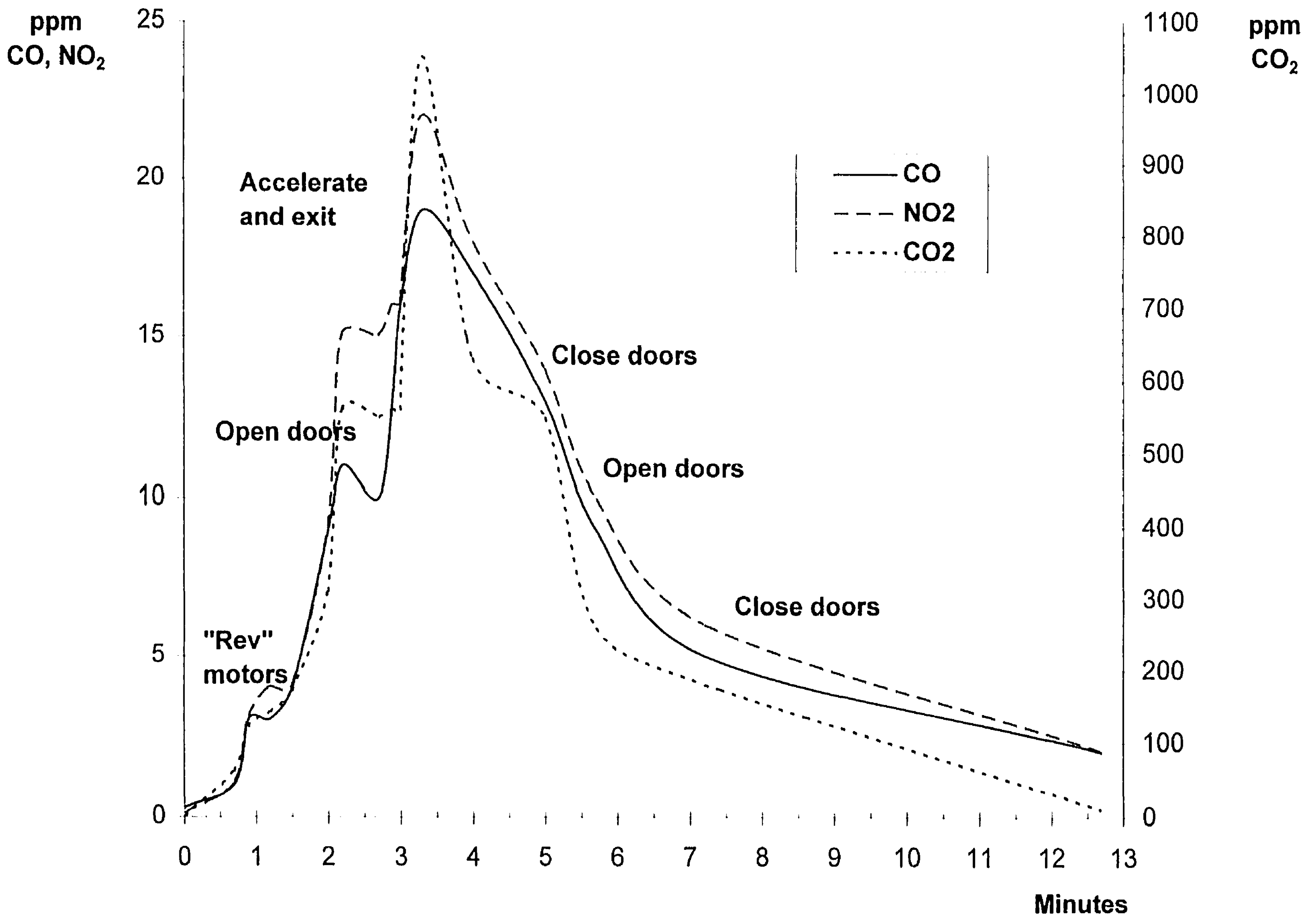
I. DIESEL EMISSIONS IN FIREHALLS

The results of the investigations conducted to determine firefighter exposures to diesel emissions suggest that firefighters are not exposed to excessive levels of contaminants in firehall garages. Baseline concentrations of CO and of NO_2 in firehall garages were below detectable levels (1 ppm and 0.1 ppm, respectively) while those for CO_2 were normally distributed with a mean concentration of 436 ppm (SD=4), some 36 ppm above outdoor ambient levels. Vehicle engines would be started within firehall garages an average of 13 times in a 24-hour period (range of 8 to 20 start-ups). No detectable levels of CO or of NO_2 were found in the living quarters of firefighters at firehalls due to vehicle activity in garages. It was assumed that CO_2 levels did not rise above baseline levels in firehall living quarters.

Upon receiving a fire alarm, vehicle engines would normally be operated inside the garage for 25-60 seconds before exiting. The doors remained closed while the engines idled and were opened only when the trucks were ready to exit. Figure 8 shows a typical example of a worst-case experimental scenario of vehicular start-ups (one pump truck and one ladder truck) in an unventilated garage with the doors closed. All three contaminant gases (CO_2, CO and NO_2) were sensitive indicators of the vehicular activity in the garage and of the opening and closing of garage doors. The detected levels of the gases reflected the starting of the engines, the "revving" of the motors, the acceleration and the exiting of the vehicles. The subsequent dispersal of the gases was related to the opening and closing of the doors.

The levels of emissions found in the undiluted tailpipe exhaust were 506±84 ppm of CO and 9±3 ppm hydrocarbons (95% CI). Using CO as a marker, the dilution factor for diesel emission gases at the point of measurement for area

Figure 8. A "worst-case" experimental scenario of diesel vehicular start-ups (one pump truck and one ladder truck) in an unventilated firehall garage with (doors closed), showing the patterns of toxic gas formation and dispersal upon opening the doors and allowing the vehicles to exit.


ppm
CO, NO$_2$
25
20
15
10
5
0
ppm
CO$_2$
1100
1000
900
800
700
600
500
400
300
200
100
0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
Minutes
CO
NO2
CO2
Accelerate and exit
Open doors
"Rev" motors
Close doors
Open doors
Close doors

samples in firehall garages was 0.0045. Peak levels of CO ranged from 2.3±0.7 ppm to 9.6±7.4 ppm (95% CI) in a dose related manner dependent upon the number of diesel-fuelled vehicles responding to the alarms (Table 16). The 95% CI for mean peak levels of CO measured during 2-truck response to alarms was 4.1±0.7 ppm (n=16). One-way analysis of variance (ANOVA) revealed a difference in mean concentrations between the levels of CO produced by one vehicle and two vehicles ($p \leq 0.01$). There was also a difference between the levels found for two vehicles and three to five vehicles responding to alarms ($p \leq 0.01$). During worst-case scenarios, there was no difference in mean CO concentrations between the operation of one to two vehicles and the operation of three to five vehicles ($p \geq 0.05$). Automobile emissions of CO in garages containing gasoline-fuelled vehicles were far higher than the levels produced by diesel-fuelled fire trucks, eg., 18 ppm versus 2.3 ppm for one car and one truck, respectively. The highest levels of CO, 65±26 ppm (95% CI), were produced by gasoline-fuelled generators and power tools undergoing weekly maintenance checks. Analysis of variance (ANOVA) confirmed the subjective impression of firefighters that some firehalls experienced higher levels of diesel emissions than others. There was no significant difference in mean levels of CO between the least busy firehalls (firehall No. 30 and firehall No. 40) for two-vehicle responses to alarms ($p \geq 0.05$). Similarly, there was no significant difference in mean levels of CO between the two busiest firehalls, firehall No. 5 and firehall No. 19, for two-vehicle response to alarms ($p \geq 0.05$). The pooled mean for firehalls No. 30 and No. 40 was 1.5±0.5 ppm (95% CI) and for firehalls No. 5 and No. 19 was 4.4±1.9 ppm (95% CI). Comparison of the busiest with the least busy firehalls revealed a statistically significant difference between the respective levels of CO ($p \leq 0.001$), but, given the low ppm levels of CO actually produced, this is of no practical consequence.

The level of diesel emissions could be predicted as a linear function of the time during which vehicles operated inside firehall garages with the doors closed. The 95% CI for the rates of formation of CO_2, CO and NO_2 for 2-vehicle response

TABLE 16. Peak carbon monoxide levels in firehall garages

	Arithmetic Mean (ppm)	95% C.I.	SD	n
DIESEL VEHICLES: Alarms				
Sorted by trucks across all firehalls				
1 truck	2.3	±0.7	2.1	36
2 trucks	4.1	±0.7	2.6	16
3 - 5 trucks	9.6	±7.4	8.9	8
Sorted by firehall				
Firehall No. 40 - 2 trucks	1.3	±0.5	0.7	9
Firehall No. 30 - 2 trucks	1.8	±1.2	1.2	6
Firehall No. 19 - 2 trucks	3.4	±1.9	1.5	5
Firehall No. 46 - 2 trucks	5.3	±12.7	5.1	3
Firehall No. 5 - 2 trucks	5.4	±4	3.2	5
Firehalls No. 30 and No. 40 - 2 trucks	1.5	±0.5	0.9	15
Firehalls No. 5 and No. 19 - 2 trucks	4.4	±1.9	2.6	10
DIESEL VEHICLES: Worst-case scenarios				
1 - 2 trucks (2-3 minutes)	9.4	±3.5	6	14
3 - 5 trucks (2-3 minutes)	10	±7.5	6	5
GASOLINE VEHICLES: Alarms				
1 car	18	±9.2	10	7
1 or 2 cars and 4 or 5 trucks	19.3	±46.8	18.8	3
TOOLS: Worst-case scenarios				
1 - 2 minutes	65	±26	52.3	18

to alarms were 110±27 ppm/min., 1.9±0.84 ppm/min. and 2.4±0.54 ppm/min., respectively. The subsequent decay of contaminants was three times more rapid if the doors were left open for a brief period than if they were closed immediately following the exit of fire trucks from the garages. The rate of decay of CO_2 with the doors open was 51±35 ppm/minute. With the doors left closed, the rate of decay was 16±14 ppm/min. ($p \leq 0.05$). Based on peak levels of 100 ppm CO_2 measured for 2-truck response to alarms (n=6), it is estimated that the gaseous components of diesel exhaust would to return to baseline levels in firehall garages if the doors were left open for approximately two minutes following the exit of the fire trucks. It is estimated that it would take approximately 6 minutes to achieve the same result with the doors closed.

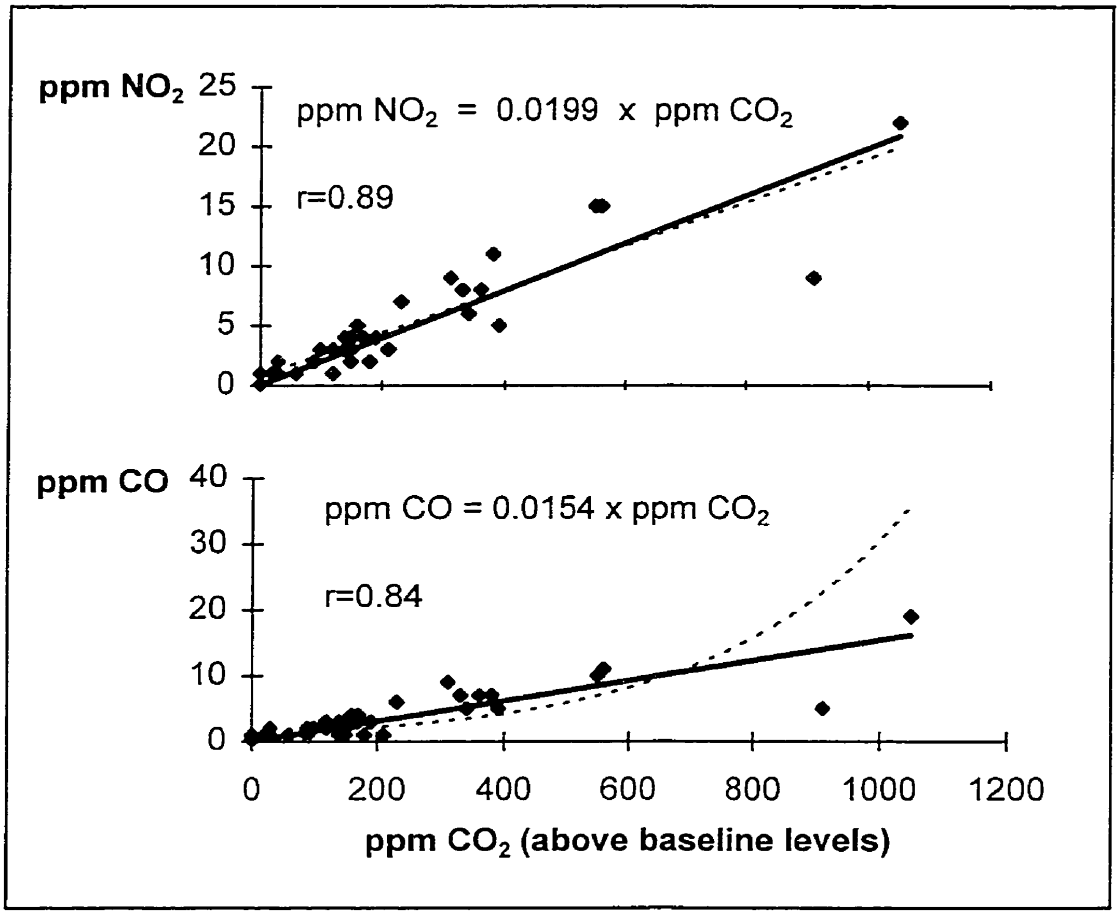
A strong correlation ($p \leq 0.001$) was found between measured CO_2, CO and NO_2 levels due to diesel emissions in firehall garages (Figure 9). Linear regression was statistically significant and was found to yield a better fit than exponential, polynomial or logarithmic models. The 95% confidence intervals for the ratios ppm NO_2/ppm CO_2, ppm CO/ppm CO_2 and ppm NO_2/ppm CO were 0.020±0.002, 0.015±0.002 and 1.22±0.07, respectively. The regression models predicted peak levels of 195 to 257 ppm CO_2 and 4.8 to 5.4 ppm NO_2 for the 4.1 ppm of CO found during 2-truck response to alarms. Peak levels of NO_2 measured for 2-truck response to alarms (n=6) was 2.2 ppm, lower than predicted by the regression model. Overestimation by the regression model was likely due to the fact the measured levels of CO were close to the instrumental detection limit of 1.0 ppm.

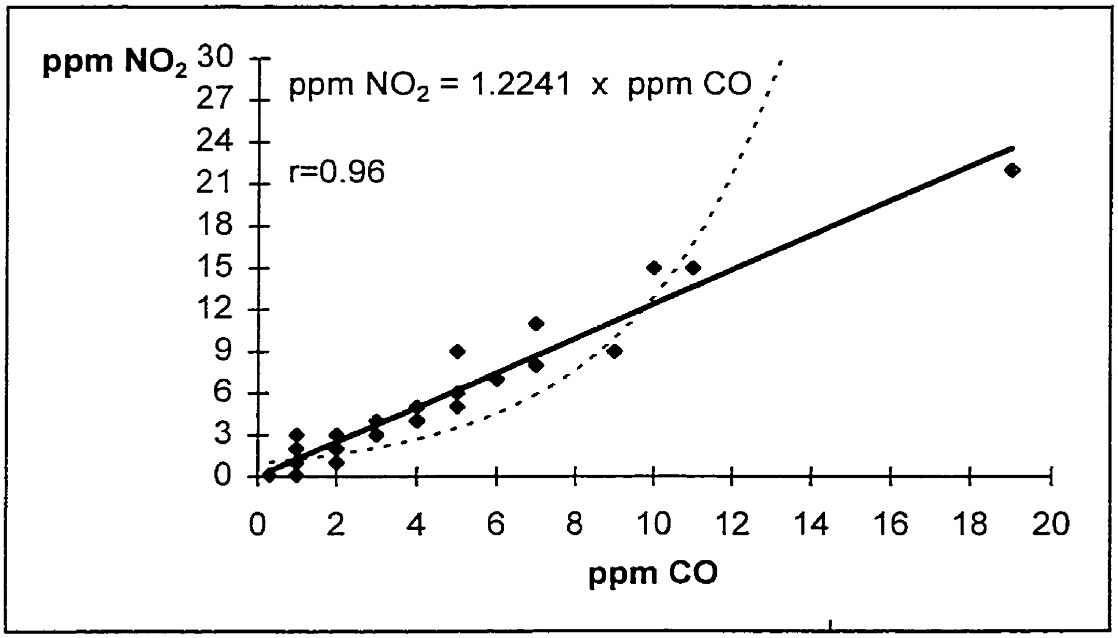
II. COMPRESSED BREATHING AIR CONTAMINATION

Contaminated compressed breathing air

Sampling of Montréal Fire Department compressed breathing air cylinders in March, 1993, revealed an arithmetic mean CO concentration of 60±38 ppm (95% CI) which exceeds the ceiling level established by the *Canadian CAN3-Z180.1-M85*

Figure 9. The graphs show the positive linear correlations between levels (ppm) of NO_2 and CO and those of CO_2 as well as the correlation between NO_2 levels and those of CO. These results indicate that the measurement of either CO or CO_2 could be used to estimate the levels of the other two contaminants. The solid lines describe the results of linear regression while the dotted lines show the application of exponential regression.


ppm NO$_2$
25
20
15
10
5
0
ppm NO$_2$ = 0.0199 x ppm CO$_2$
r=0.89
ppm CO
40
30
20
10
0
ppm CO = 0.0154 x ppm CO$_2$
r=0.84
0
200
400
600
800
1000
1200
ppm CO$_2$ (above baseline levels)


ppm NO$_2$
30
27
24
21
18
15
12
9
6
3
0
ppm NO$_2$ = 1.2241 x ppm CO
r=0.96
0
2
4
6
8
10
12
14
16
18
20
ppm CO

Standard on Compressed Breathing Air and Systems (Table 17). The mean concentrations and 95% confidence intervals of CO_2 and CH_4 were 747±207 ppm and 42±37 ppm, respectively, which also exceed the maximum allowed. Four of the other eight fire departments sampled showed carbon monoxide contamination of the compressed breathing air ranging from 1-27 ppm CO. The single sample from the diving equipment store revealed 1.0 ppm of CO. Quadruplicate testing on two of the samples using the Draeger™190-dataloging device yielded means of 28 ppm and 55 ppm with standard deviations of 6 ppm. One of the SCBA samples, which showed a concentration of 95 ppm CO using this instrument, was analyzed by an independent testing laboratory and was found to contain 250 ppm of CO, 17 ppm of water vapour, 926 ppm of CO_2 and elevated levels of methane and non-methane hydrocarbons. It also contained low levels (below the maximum allowable) of nitrous oxide, ethane/ethylene, acetylene, propane, propylene and traces of propyne, toluene and decane. The discrepancy between the levels of CO reported by the laboratory analysis and those found with the the Draeger™190-dataloging device is explained by the fact that the levels of CO present exceeded the calibration range of the latter instrument.

Analysis of the first six samples from the Bauer™ compressor showed no carbon monoxide contamination. It was only with repeated sampling over the course of three hours that contamination began to show up with a final sample giving a reading of 113 ppm CO. This compressor was removed from service and completely overhauled. The air purification system was also overhauled and all chemical cartridges were replaced. When operational again, the air was closely monitored and, initially, showed no evidence of contamination. However, carbon monoxide contamination began to appear after a few days at which point the compressor was permanently withdrawn from service.

Quality Analysis/Quality Control

Results of the QA/QC program are reported for the 42 month period from

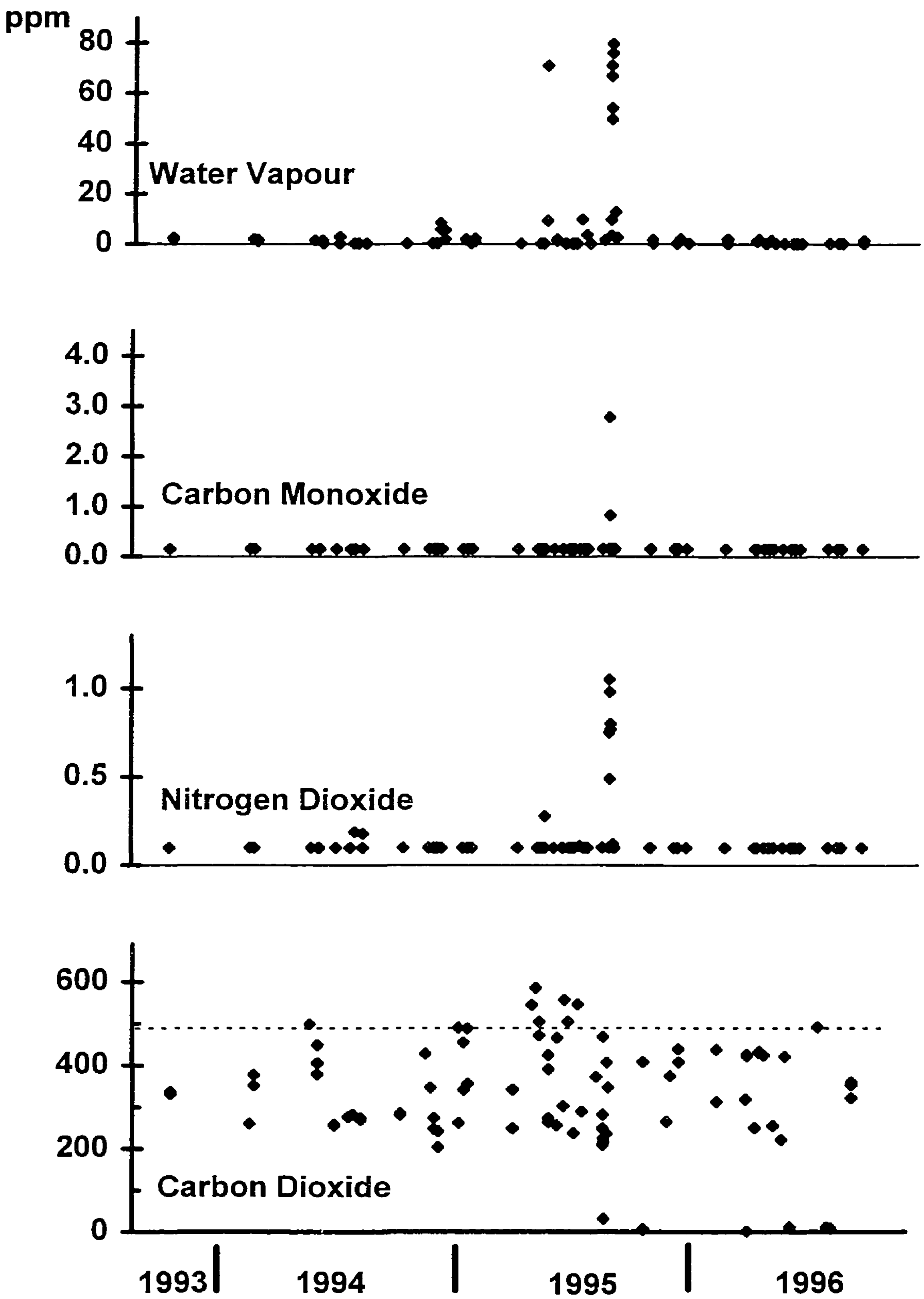
Table 17. Analysis of contaminated compressed breathing air

Location	Carbon monoxide				Carbon dioxide				Methane				Water	
	n	Range	Mean	SD	n	Range	Mean	SD	n	Range	Mean	SD	n	Mean
Mtl. Fire Dept. compressor	11	0-113	16	±33	1	-	430	-	1	-	8	-	-	-
Mtl. Fire Dept. SCBA's	16	0-250	60	±72	6	490-926	747	±197	5	8-77	42	±30	1	17
Mtl. Fire Dept. storage tanks	4	16-53	35	±15	2	510-530	520	±14	-	-	-	-	-	-
Total Mtl. samples	**31**		**47**	**±68**	**9**				**6**	**-**	**37**	**±30**	**1**	**17**
Other Fire Dept's SCBA's	8	0-27	4	± 9	-	-	-	-	-	-	-	-	-	-
SCUBA equip. store	1	-	1	-	-	-	-	-	-	-	-	-	-	-

[a] Values represent number of samples, levels and standard deviations in ppm (measured at atmospheric pressure) for samples analyzed in March, 1993.

August, 1993 to December, 1996 (Figure 10). Comparison of seven paired samples showed no difference in means between the City of Montréal laboratory and the independent testing laboratory for CO_2 or for water vapour levels at the 95% confidence level. Comparison of CO levels could not be made since the amounts present were less than the detection limits for both laboratories. The levels of the other contaminants analyzed were negligible. While there was no interlaboratory significant difference in variance for the analysis of CO_2, there was significantly greater variance in the levels of water vapour found by the City of Montréal laboratory. Analysis of variance (ANOVA) revealed no significant difference (at the 95% confidence level) between compressors in the levels of CO_2, CO or water vapour for the 75 samples analyzed by the City of Montréal laboratory. All test results from the four compressors were therefore treated as one data set together with the results of 16 samples analyzed by the independent testing laboratory. There was a positive correlation between the levels of water vapour and the levels of CO and NO_2, the correlation coefficients (*r*) being 0.5 and 0.93 respectively (Figure 10). There was also a positive correlation between the levels of water vapour and Freons™ (r=0.5). Since unusually elevated levels of water vapour were found during only two weeks of the 144 week sampling period, these 11 samples were deleted from the database for the purpose of calculating means and standard deviations (Table 18). Carbon monoxide, NO_2, Freon™ and NMOC were not found at levels exceeding 0.2, 0.1, 0.3 and 0.2 ppm, respectively, in the remaining 80 compressor air samples. The mean concentrations and 95% confidence intervals of CO_2, methane and N_2O were 359±22 ppm, 1.9±0.17 ppm and 0.3±0.03 ppm, respectively. The mean water vapour concentration, measured at atmospheric pressure, was 1.2±0.38 ppm. The distribution of water analysis results was not continuous, concentrations being $\leq$0.2 ppm in 51% of samples, between 1.0 and 1.9 ppm in 33% of samples and $\geq$2.3 ppm in 11% of samples (Figure 11). In all cases, the upper limit of the 95% CI was less than the maximum contaminant concentration established by the *Canadian CAN3-Z180.1-M85 Standard on*

Figure 10. Fourier transform infrared analysis (FTIR) of compressed breathing air obtained from four compressed breathing air quality compressors following implementation of new standard operating procedures and a QA/QC program. The dotted line shows the maximum allowable levels of CO_2. The data is derived from samples analyzed by C. Tirado of the City of Montréal Environmental Laboratory, Chemistry Section.



ppm
80
60
40
20
0
Water Vapour
4.0
3.0
2.0
1.0
0.0
Carbon Monoxide
1.0
0.5
0.0
Nitrogen Dioxide
600
400
200
0
Carbon Dioxide
1993
1994
1995
1996

Table 18. Quality control test results for compressed breathing air[a]

Quality control test results for compressed breathing air[a]

	CO	CO_2	NO_2	N_2O	Freon[d]	NMOC[e]	Methane	H_2O
Maximum allowed[b]	5	500	0.3	2.5	5	1/10 TLV[f]	25	2.3[g]
Detection limits[c]	0.054	0.64	0.039	0.012	0.008	0.058	0.052	0.293
Arithmetic mean	<0.2	359	<0.1	0.3	<0.3	<0.2	1.9	1.2
SD	-	±94	-	±0.14	-	-	±0.74	±1.70
95% CI	-	±22	-	±0.03	-	-	±0.17	±0.38
n	80	71	80	80	80	80	80	80

[a] Values represent levels in ppm (measured at atmospheric pressure from 1993 to 1996) following implementation of new operating procedures and a QA/QC program. Non-detected amounts were assigned a value equal to the method detection limit. Outliers were deleted from the database prior to calculation of means. See text for details.

[b] CSA CAN3-Z180.1-M85 Standard on Compressed Breathing Air and Systems. Values are ceiling levels, not to be exceeded at any time (CSA, 1985).

[c] Analytical method detection limits determined using the Québec Ministry of the Environment detection limit protocol (MENVIQ, 1993).

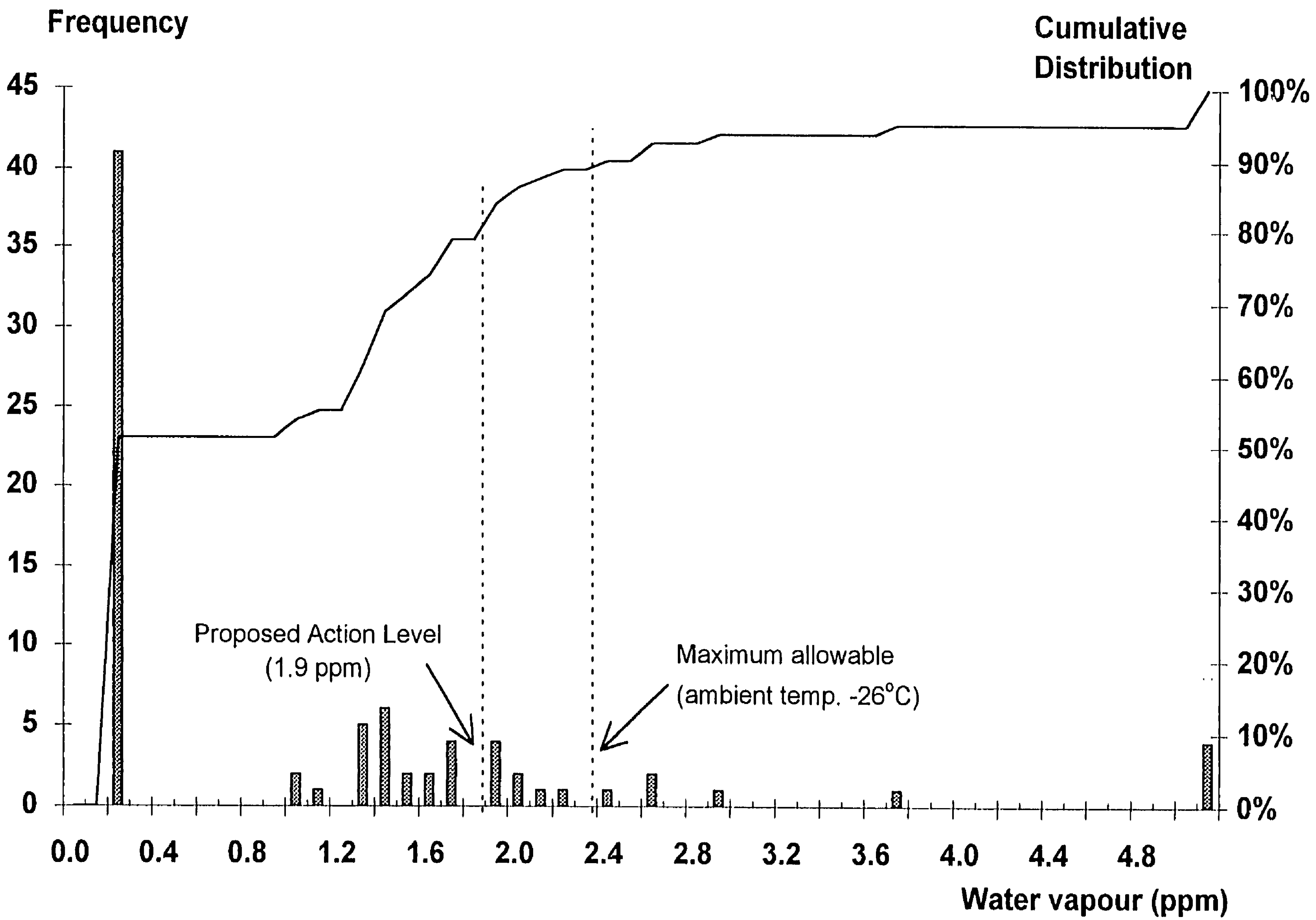
[d] Dichlorodifluoromethane (Freon12); Monochlorodifluoromethane (Freon22); Chlorofluoromethane (Freon13); 1,1,2-trichloro-1,2,2-trifluoroethane (Freon113).

[e] Non-methane organic compounds reported as ethane equivalents.

[f] TLV is the threshold limit value as currently documented by the American Conference of Government Industrial Hygienists.

[g] The Standard states that, "The pressure dew-point shall be 5°C below the ambient temperature." The value given is applicable to 2,216 psig breathing apparatus when the temperature is colder than -26°C.

Figure 11. The distribution of water vapour concentrations found in compressed breathing air samples (n=80) following implementation of new standard operating procedures and a QA/QC program for the Montréal Fire Department. The bars represent the number of samples at a given level of water vapour (in ppm) whereas the line represents the cumulative distribution (in percent) of the water vapour in the samples taken. The high levels occurring in 1995 are not included.


Frequency
Cumulative Distribution
45
40
35
30
25
20
15
10
5
0
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.8
Water vapour (ppm)
Proposed Action Level
(1.9 ppm)
Maximum allowable
(ambient temp. -26°C)

Compressed Breathing Air and Systems (CSA, 1985).

VOC's in compressor air were analyzed by the Summa™ canister method. Levels found were comparable to those seen in outdoor ambient air, the principal components present being isobutane, butane, 2-methylbutane, pentane and toluene (Figure 12A). In the case of firefighters working on ladder trucks, compressed breathing air was delivered to the mask through 25 m of NIOSH approved rubber hose and in the case of firefighters working in confined space entry the air was delivered through 100 m of hose. Sampling of this air, without prior purging, revealed traces (<100 ppb) of solvents such as dichloromethane, 1,1,1-trichloromethane, toluene and xylene (Figure 12B). Traces of carbon disulphide, methylene chloride and 2-isothiocyanato-2-methyl propane were also tentatively identified from samples analyzed in SCAN mode. These substances were present at extremely low levels however and concentrations of all VOC contaminants fell to less than 10 ppb when the hose was purged with compressed breathing air for approximately five minutes, the principal contaminants remaining being toluene and xylene (Figure 12C).

Freezing of compressed air breathing apparatus

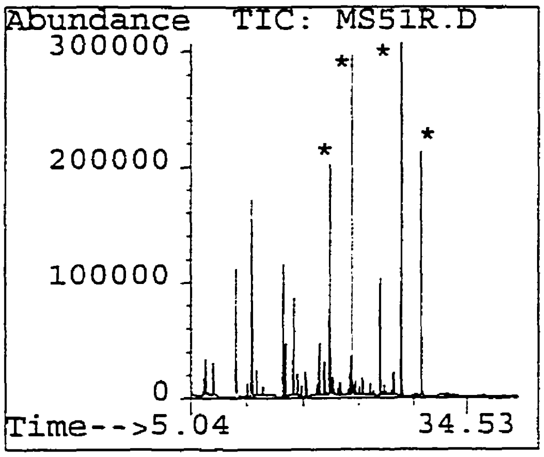
To facilitate the interpretation of the significance of water vapour contamination, the relationship was calculated between the ambient temperature at which a breathing apparatus regulator might freeze (i.e. the pressure dew-point) and the levels of water vapour in compressed air measured in ppm at atmospheric pressure (Figure 13). The mean measured water vapour concentration of 1.2 ppm corresponds to a pressure dew-point of -34 °C, equal to the *Canadian CAN3-Z180.1-M85 Standard on Compressed Breathing Air and Systems* requirement for use of a 2,216 psig SCBA at an ambient temperature of -29°C (CSA, 1985).

Estimation of COHb concentration from measured CO levels

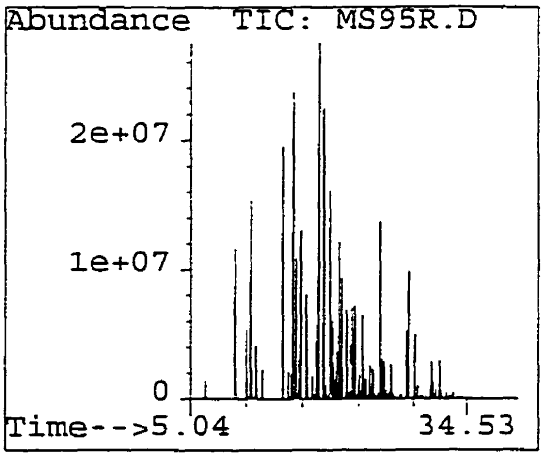
The CFK equation was applied to determine the relationship between

Figure 12. Chromatograms of 500 mL of undiluted, compressed breathing air samples analyzed by mass selective detector operated in the selective ion mode (SIM), showing detector response (abundance) vs. retention times (min.) for a: (A) air from a storage tank on a ladder truck; (B) air from a 90 m, NIOSH approved, rubber breathing hose without prior purging; and, (C) air from the same hose following purging. The low levels of toluene and xylene detected in purged air from the breathing hose may arise from the hose itself. Asterisks indicate the internal standards normally added to samples prior to analysis.

A.


Abundance
TIC: MS51R.D
300000
200000
100000
0
*
*
*
*
*
Time-->5.04
34.53

B.


Abundance
TIC: MS95R.D
2e+07
1e+07
0
Time-->5.04
34.53

C.

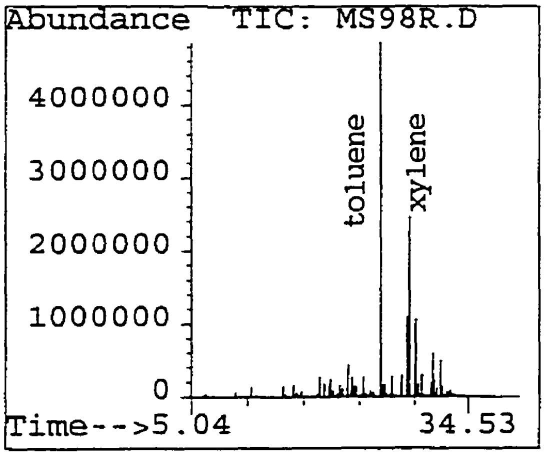
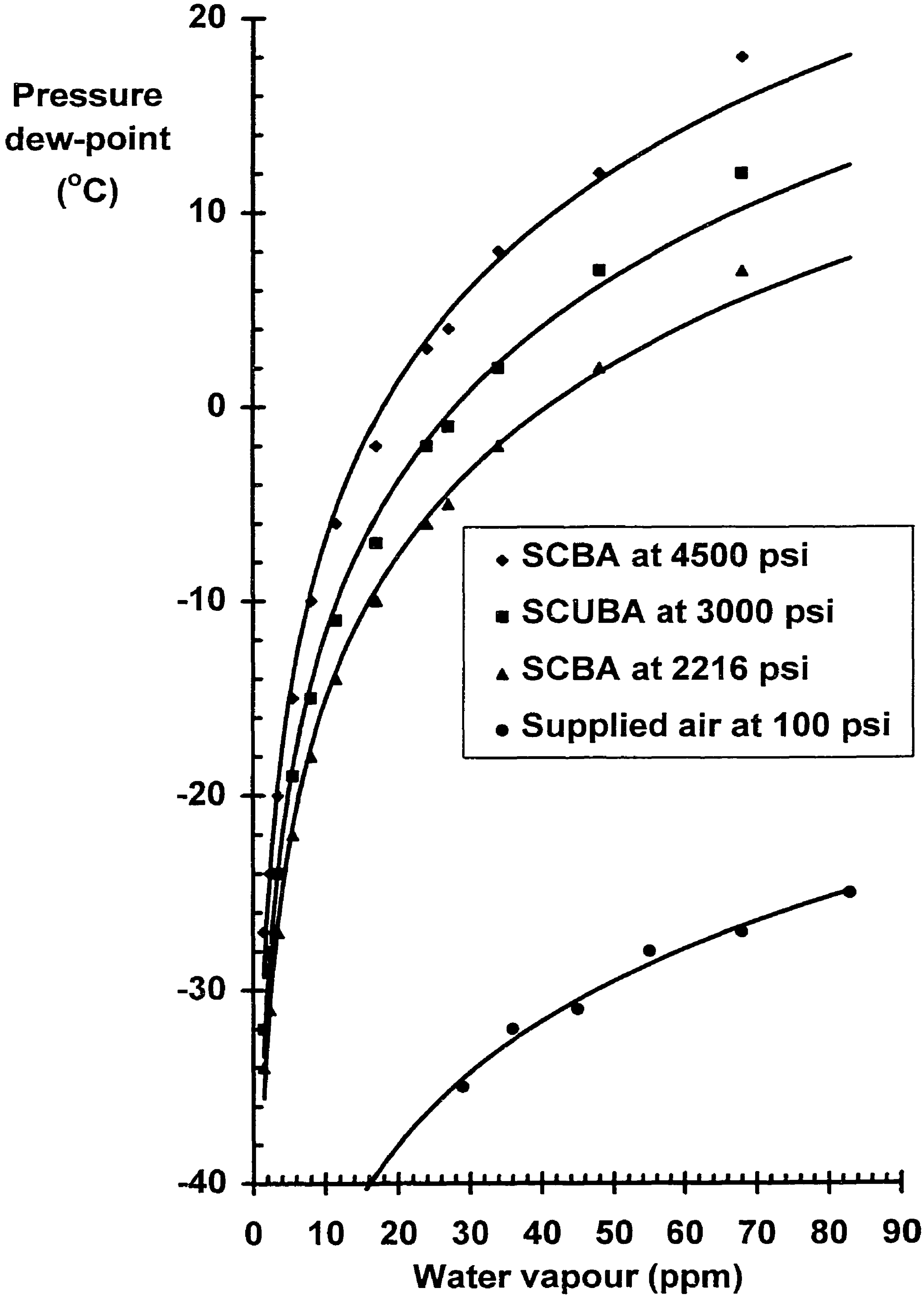

Abundance
TIC: MS98R.D
4000000
3000000
2000000
1000000
0
toluene
xylene
Time-->5.04
34.53

Figure 13. Ambient temperature at which an air regulator might freeze (equivalent to the pressure dew-point) as a function of water vapour levels found in compressed air measured at atmospheric pressure.


Pressure dew-point (°C)
20
10
0
-10
-20
-30
-40
0
10
20
30
40
50
60
70
80
90
Water vapour (ppm)
◆ SCBA at 4500 psi
■ SCUBA at 3000 psi
▲ SCBA at 2216 psi
● Supplied air at 100 psi

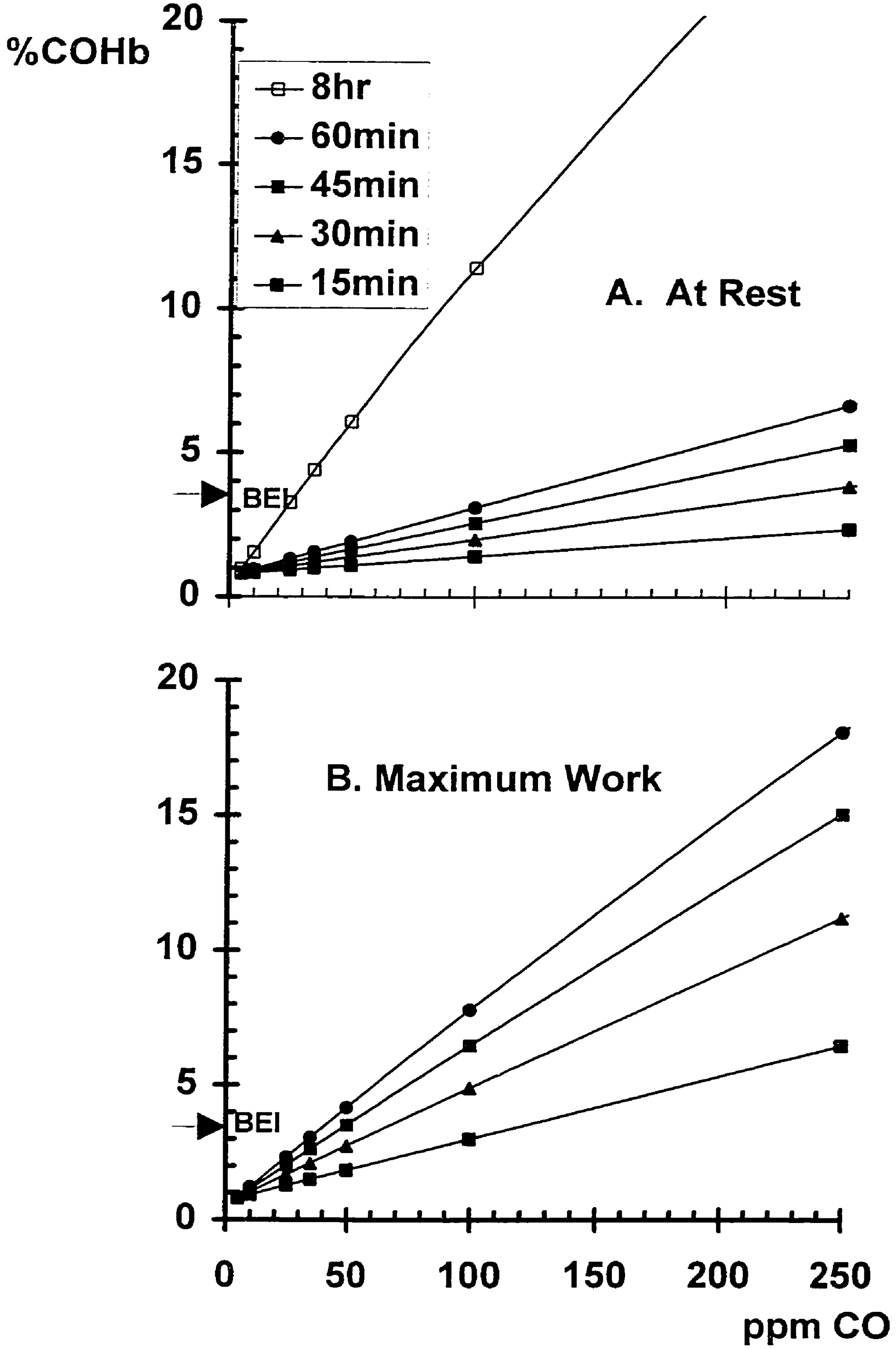
theoretical %COHb levels to measured levels of CO in air for nonsmokers at rest and at maximum work levels (Figure 14). In addition to the standard 8-hour exposure time, relationships were calculated for 15, 30, 45 and 60 minutes exposures corresponding to the use by firefighters of 1, 2, 3 or 4 SCBA cylinders, respectively. The derived relationships did not incorporate any safety factors and should not be used to determine emergency exposure levels. The *Canadian CAN3 180.1-M85 Standard on Compressed Breathing Air and Systems* sets 5 ppm as the maximum allowable concentration of CO. At this level, even under conditions of maximum work, the blood COHb will not rise significantly above baseline levels. Solution of the CFK equation for non-smokers at maximal work levels predicts that 3.5 %COHb will be attained after approximately 45 minutes exposure to 50 ppm CO (Figure 14A). Exposure to 250 ppm CO for 45 minutes at maximal work levels is predicted to result in a COHb level of 15% (Figure 14B).

III. ANALYSIS OF VOC's FOUND IN FIRES

A. THE MODIFIED EPA TO-14 METHOD VALIDATION

The EPA TO-14 method (EPA, 1988) describes the GC/MS analysis of ambient air samples collected in Summa™ canisters. For use in this study, the reliability of the analytical system was verified by repeated analysis of samples of prepared standard mixtures, blanks and ambient air samples, these being processed in the same manner as would be subsequently used for fire samples. The analytical method involved the addition of a fixed volume of an internal standard, via a sample loop, into the transfer lines carrying aliquots of the sample (Figure 4A). An aliquot was withdrawn from the canister containing the sample and analyzed by chromatographic separation of the components present in the sample. Peaks were identified by retention time and qualifier ion ratios. Compound identification was confirmed by selective ion monitoring (SIM) of two or three selected molecular ion fragments (m/z) characteristic of the mass spectrum of each

Figure 14. Solution of the CFK equation relating theoretical %COHb levels to measured levels of CO in air for nonsmokers at rest and at maximum work levels. These curves did not incorporated any safety factors and should not be used to determine emergency exposure levels. BEI indicates the Biological Exposure Index which is the limit recommended by the ACGIH.


%COHb
20
15
10
5
0
8hr
60min
45min
30min
15min
A. At Rest
BEI
B. Maximum Work
20
15
10
5
0
BEI
0
50
100
150
200
250
ppm CO

compound. This permitted the analysis of analytes eluting from the GC with identical retention times. The ratio of the integrated area of each target ion chromatographic peak to the integrated area of the internal standard chromatographic peak was computed for each analyte. The amount of target compound present in the sample was determined by comparison of each ratio to a 5-point calibration curve prepared by analyzing a standard calibration mixture in a manner identical to that used for the analysis of field samples. The standard mixture, prepared by Environment Canada for use in outdoor ambient air studies, was used for validation of the analytical method (Appendix 3). The mixture included all 40 of the TO-14 target compounds, 104 new target compounds, including a number of polar compounds and many olefins (alkenes).

Integration

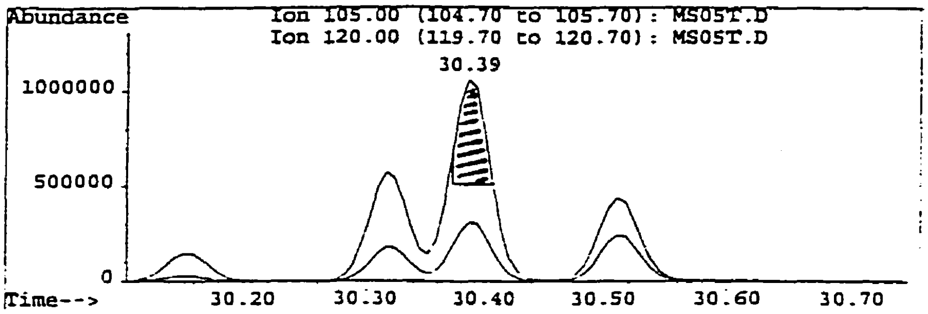
It was found that automated computer integration of selected ion chromatographic peaks was not reliable for all analytes, the peak area being underestimated by 38% on average. The size of each peak is proportional to the amount of analyte present and this is calculated by the software based upon integration of the area of the peak. The horizontal and vertical lines drawn under the peak show the area that was actually calculated during automated computer integration and it can be seen that the peak areas for 4-ethyltoluene, benzene and styrene were under-estimated by approximately 25%-70% (Figure 15). Consequently, automated computer integration of chromatographic peaks was not used in this study, all peak areas being calculated by computer assisted manual integration.

Co-eluting compounds

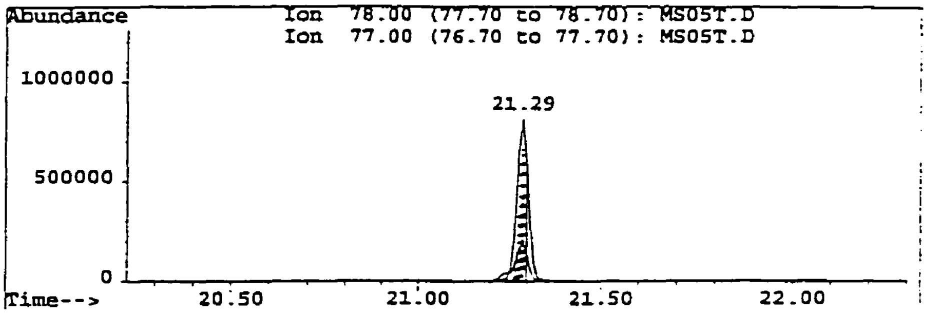
Compounds which co-eluted from the gas chromatograph and which were correctly identified by the software included: cyclohexene and 3-methylhexane; trichloroethene and 1-heptene; bromotrichloromethane and 2,3,4-trimethylpentane; cis-1,2-dimethylcyclohexane and chlorobenzene-d_5; 1,4-dichlorobutane and styrene;

Figure 15. Chromatograms (detector response-abundance vs. retention times-min.) showing the automated computer integration (hatched area) for 4-ethyltoluene (A), benzene (B) and styrene (C). The concentrations of these chemicals were underestimated by approximately 25% to 70%.

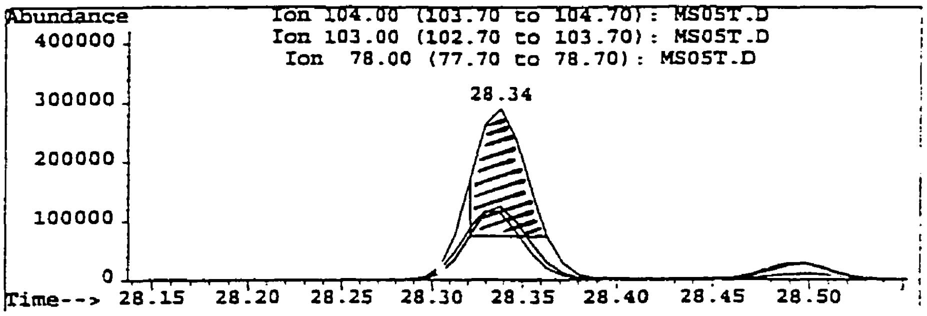
A.


Abundance
Ion 105.00 (104.70 to 105.70): MS05T.D
Ion 120.00 (119.70 to 120.70): MS05T.D
30.39
1000000
500000
0
Time-->
30.20
30.30
30.40
30.50
30.60
30.70

B.


Abundance
Ion 78.00 (77.70 to 78.70): MS05T.D
Ion 77.00 (76.70 to 77.70): MS05T.D
21.29
1000000
500000
0
Time-->
20.50
21.00
21.50
22.00

C.


Abundance
Ion 104.00 (103.70 to 104.70): MS05T.D
Ion 103.00 (102.70 to 103.70): MS05T.D
Ion 78.00 (77.70 to 78.70): MS05T.D
28.34
400000
300000
200000
100000
0
Time-->
28.15
28.20
28.25
28.30
28.35
28.40
28.45
28.50

tert-butylbenzene and 1,2,4-trimethylbenzene; 1,3-dichlorobenzene and 1,4-dichlorobenzene; sec-butylbenzene and 1,2,3-trimethylbenzene. Automated computer identification of chromatographic peaks was not reliable in the case of all co-eluting compounds. This was the case with the following pairs of compounds: trans-2-butene and 2,2-dimethylpropane; 2-methylhexane and 2,3-dimethylpentane; 2,4-dimethylhexane and cis/trans-1,3-dichloropropene; octane and trans-1,2-dimethylcyclohexane; 1,1,2,2-tetrachloroethane and o-xylene and 1-nonene; 3-ethyltoluene and 4-ethyltoluene; 1,3-diethylbenzene and 1,4-diethylbenzene. However, the use of retention times and characteristic mass spectral ion fragments did allow accurate manual identification of these co-eluting compounds.

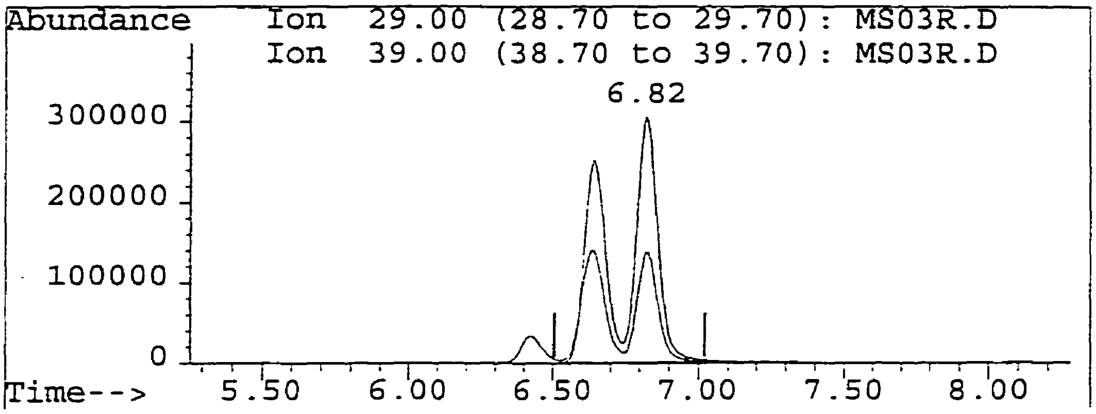
Peak splitting

Early eluting analytes (particularly propane, Freon22™, Freon12™, chloromethane, isobutane and vinyl chloride which eluted between approximately six and 11 minutes) sometimes exhibited splitting of the chromatographic peak (Figure 16). It appeared that this was due to immersion of the trap too deeply into the cryogen during collection of sample aliquots in the pre-concentrator (Figure 4A). The integrated areas of these split peaks were manually added together for calculation of the corrected amount of analyte present in the sample.

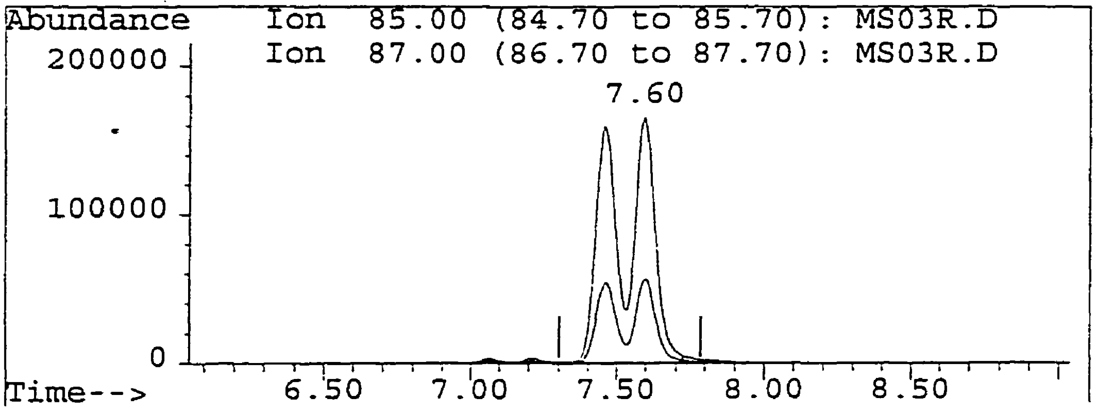
Propyne, which eluted at approximately 8.0 minutes, was treated as above for split peaks (Figure 17A). However, unlike the previously mentioned substances, the phenomena appeared exclusively in chromatograms obtained from field samples and not in chromatograms obtained from samples of standard mixtures prepared in the laboratory. Also, its appearance did not depend upon the level of cryogen in the pre-concentrator. This suggested that these peaks corresponded to two different substances. Propyne, present in the standard mixture, produced an asymmetrical peak at 8.28 minutes, the degree of tailing of the target ion being 2.6. Its acquired mass spectrum matched the NIST (1992) library mass spectra for propyne. Another similar chromatographic peak, eluting approximately 0.15

Figure 16. Chromatograms of propane (A), Freon22™ (B), Freon12™ (C), chloromethane (D) and isobutane (E) showing split peaks arising from an artefact due to the immersion of the tubing too deeply into the liquid oxygen. The integrated areas of both peaks were added together.

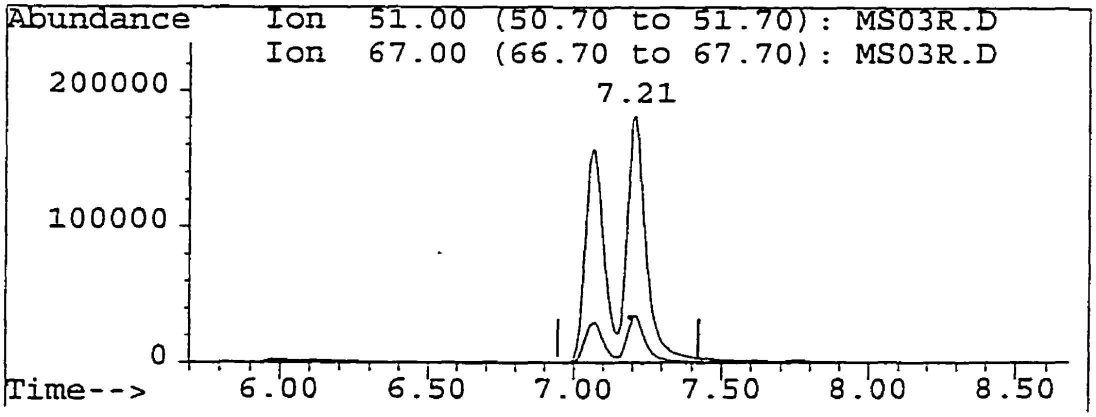
A.


Abundance
Ion 29.00 (28.70 to 29.70): MS03R.D
Ion 39.00 (38.70 to 39.70): MS03R.D
6.82
300000
200000
100000
0
Time-->
5.50
6.00
6.50
7.00
7.50
8.00

B.

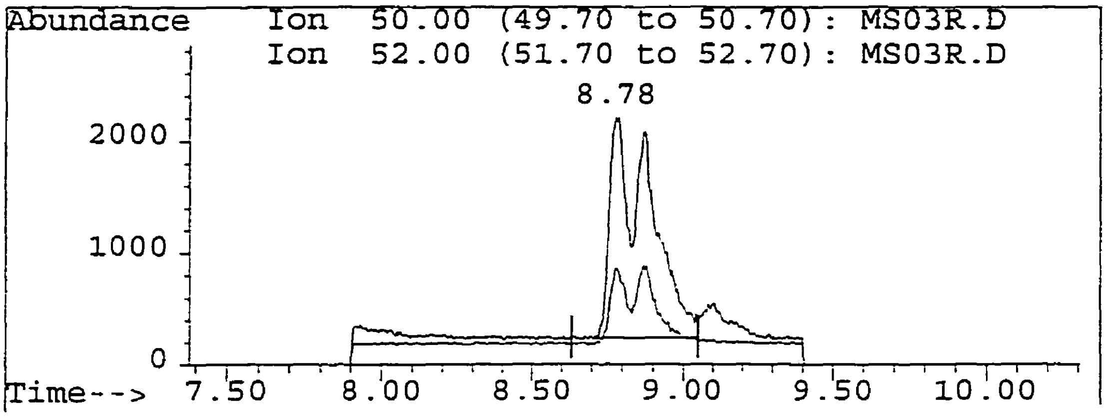

Abundance
Ion 85.00 (84.70 to 85.70): MS03R.D
Ion 87.00 (86.70 to 87.70): MS03R.D
7.60
200000
100000
0
Time-->
6.50
7.00
7.50
8.00
8.50

C.


Abundance
Ion 51.00 (50.70 to 51.70): MS03R.D
Ion 67.00 (66.70 to 67.70): MS03R.D
7.21
200000
100000
0
Time-->
6.00
6.50
7.00
7.50
8.00
8.50

6b

D.


Abundance
Ion 50.00 (49.70 to 50.70): MS03R.D
Ion 52.00 (51.70 to 52.70): MS03R.D
8.78
2000
1000
0
Time-->
7.50
8.00
8.50
9.00
9.50
10.00

E.

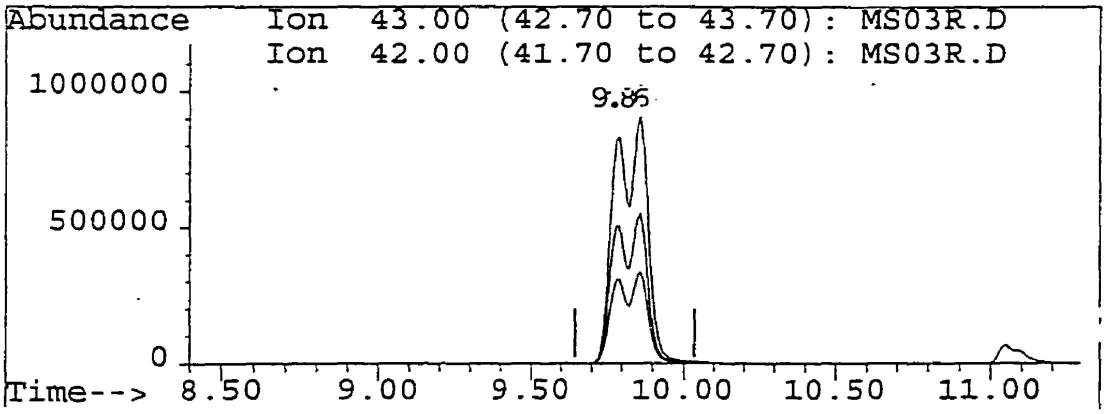
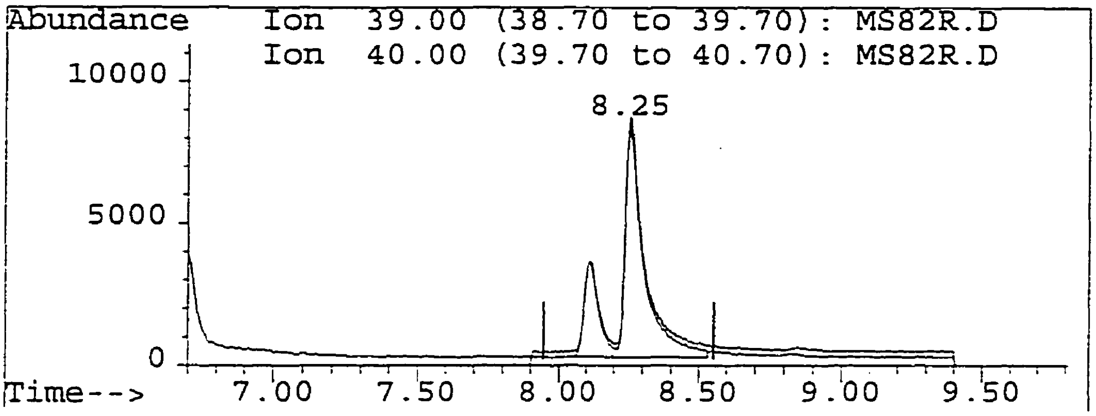
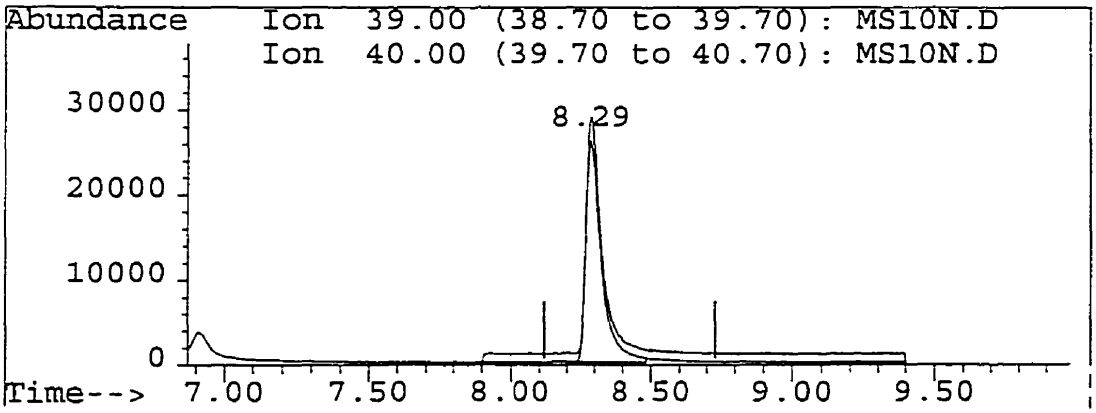

Abundance
Ion 43.00 (42.70 to 43.70): MS03R.D
Ion 42.00 (41.70 to 42.70): MS03R.D
1000000
9.85
500000
0
Time-->
8.50
9.00
9.50
10.00
10.50
11.00

Figure 17. Chromatograms of (A) propyne detected in a field sample from a fire and (B) from a standard mixture. The split peaks in the former may constitute a mixture of the two isomers, propadiene and propyne. The integrated peak areas were added together and reported as propyne.

A.


Abundance
Ion 39.00 (38.70 to 39.70): MS82R.D
Ion 40.00 (39.70 to 40.70): MS82R.D
10000
5000
0
8.25
Time-->
7.00
7.50
8.00
8.50
9.00
9.50

B.


Abundance
Ion 39.00 (38.70 to 39.70): MS10N.D
Ion 40.00 (39.70 to 40.70): MS10N.D
30000
20000
10000
0
8.29
Time-->
7.00
7.50
8.00
8.50
9.00
9.50

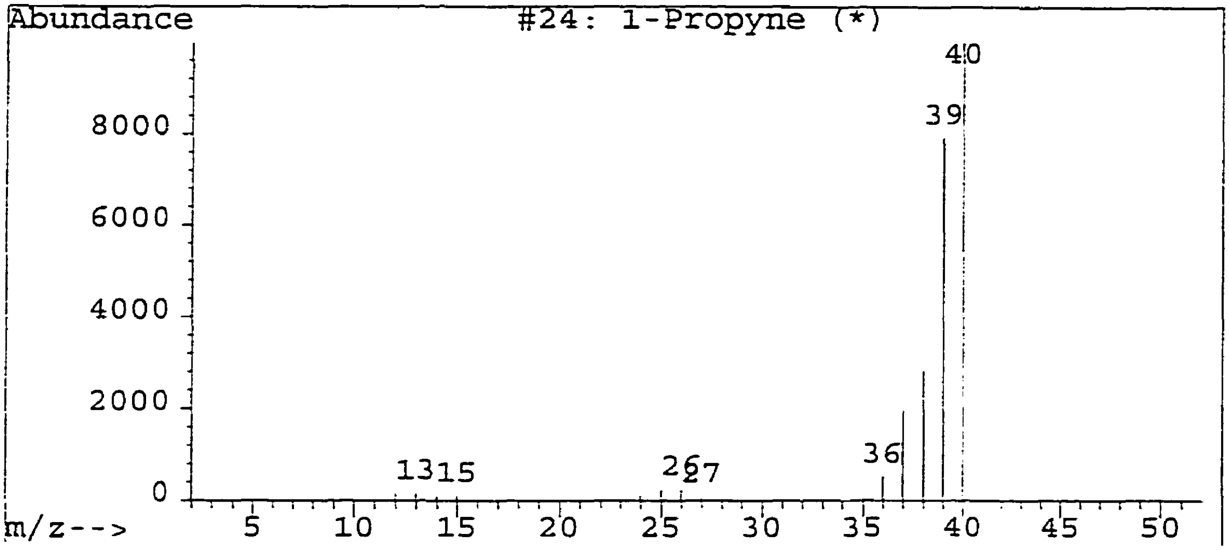
minutes ahead of it, was observed in samples obtained from both outdoor ambient air and fire atmospheres but not in the prepared standard mixture (Figure 17B). Its mass spectrum was identical to that exhibited in the major propyne peak. Although the two peaks were added together during quantification, the total being reported as propyne, it is possible that the earlier eluting peak was propadiene since standards of propadiene and propyne have very similar mass spectra (Figures 18A and 18B). Propadiene may be a separate, stable component present in field samples along with propyne, as is shown in Figures 19A and 19B, respectively. Alternatively, propadiene and propyne isomers may have arisen as a result of their reaction with free radicals known to exist in the atmosphere.

Retention times

The range of retention times, from 5 minutes to 38 minutes, was divided into 27 time "windows" during which the mass selective detector monitored different groups of selected molecular ion fragments corresponding to the analyte target and qualifier ions selected for each group. The average shift in retention times (±0.11 min.) of internal standards observed over a 6-month period was better than the TO-15 (1997) technical accpetance criteria of ±0.33 minutes and the ±0.5 minutes over 24 hours required by the U.S. EPA (1991). Due to the large number of target compounds, some of the chromatographic peaks eluted very close to the edge of their respective "windows". Consequently, it was necessary to periodically update the computerized data acquisition method controlling the mass selective detector to compensate for shifts in the chromatographic retention times. The data analysis software was also updated to compensate for shifts in retention times. Expected retention times were corrected to within ±0.02 minutes, exceeding the EPA (1994) and TO-15 (1997) technical acceptance criteria of ±0.06 min.

Figure 18. Library mass spectra for (A) propyne and (B) propadiene obtained from NIST (1992).

A.


Abundance
#24: 1-Propyne (*)
8000
6000
4000
2000
0
m/z-->
5
10
15
20
25
30
35
40
45
50
13
15
26
27
36
39
40

B.

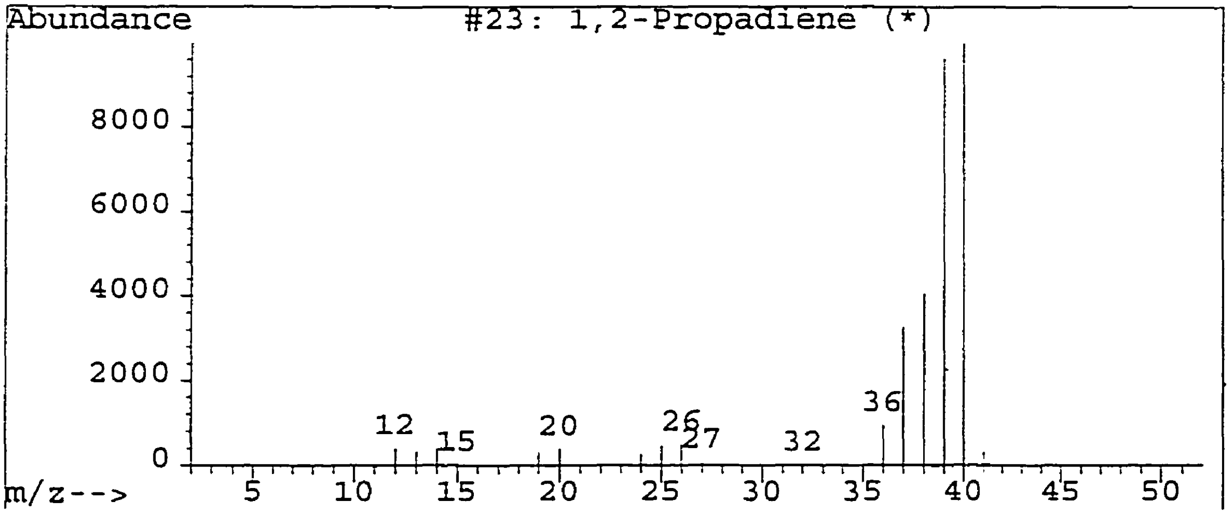
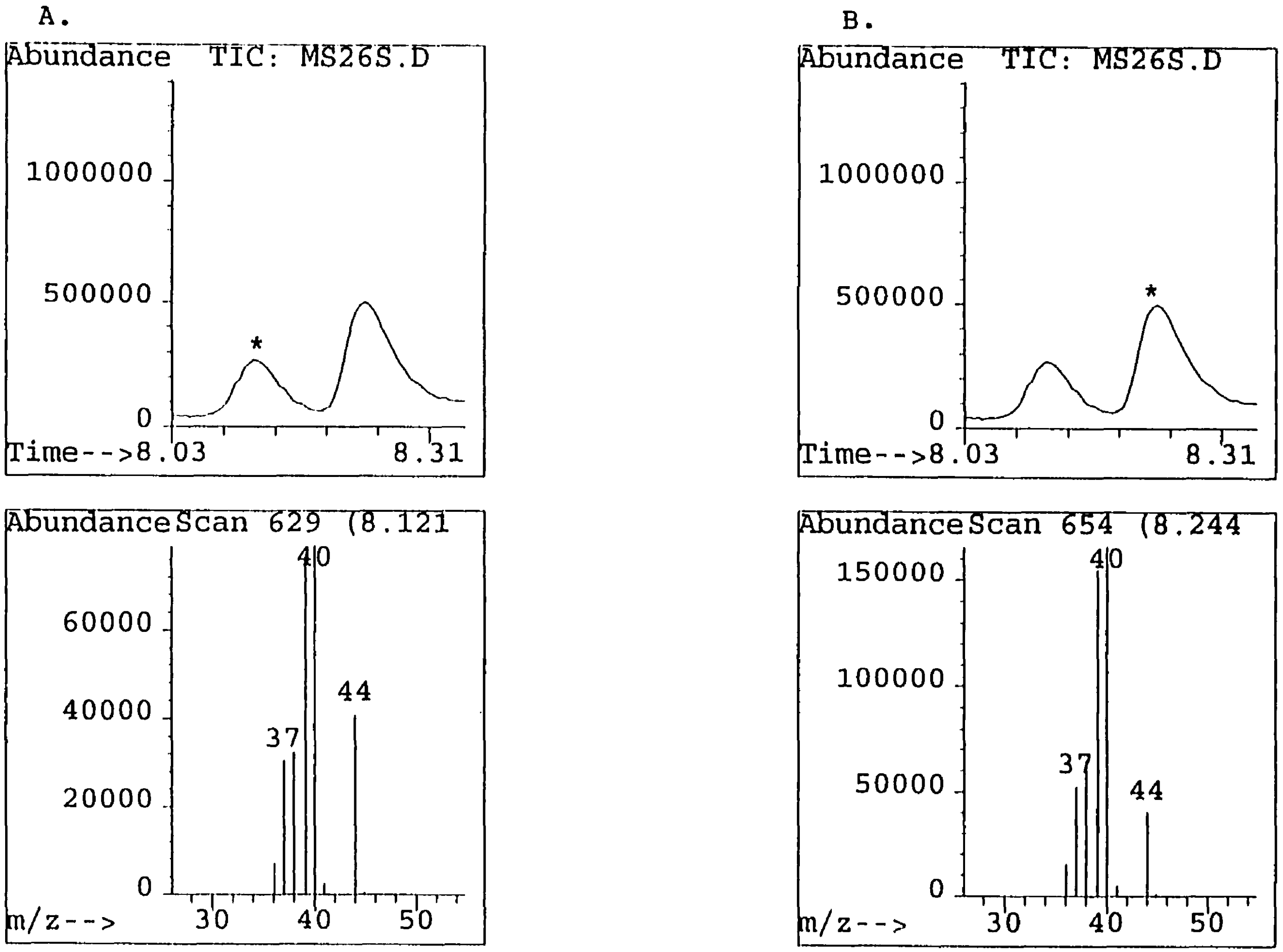

Abundance
#23: 1,2-Propadiene (*)
8000
6000
4000
2000
0
m/z-->
5
10
15
20
25
30
35
40
45
50
12
15
20
26
27
32
36

Figure 19. Chromatograms of propyne (A) and suspected propadiene (B) from fire samples. The upper panels show the individual chromatograms while the lower panels show the mass spectrograms for the peaks indicated by the asterisks. The similar spectra do not permit differentiation between the chemicals.


A.
Abundance TIC: MS26S.D
1000000
500000
0
*
Time-->8.03
8.31
Abundance Scan 629 (8.121
60000
40000
20000
0
40
37
44
m/z-->
30
40
50
B.
Abundance TIC: MS26S.D
1000000
500000
0
*
Time-->8.03
8.31
Abundance Scan 654 (8.244
150000
100000
50000
0
40
37
44
m/z-->
30
40
50

Calibration curves

GC/MS analytical calibration curves in the range of 0.5 ng to 20 ng were prepared for each of 144 target compounds from 250, 500, 750, 100 and 1250 mL aliquots of the standard instrument calibration mixture. Since air was withdrawn from the sample canister at 25 mL/min. (controlled by a mass flow controller), the required volume was adjusted by varying the delivery time, assisted by a stop-watch. These linear 5-point calibration curves were forced through the origin and the internal standard method was used for quantification. The average relative standard deviation (rsd) of calibration curve response factors was 19%. This was better than the TO-15 (1997) technical acceptance criteria and the U.S. EPA requirement of ±30% (EPA, 1991). Due to the initial pressure surge when opening the canister, the mass flow controller took a few seconds to stabilize. This introduced a small error in the actual volume of air delivered to the system. The alternative procedure would be to add an instrument in-line which would measure the actual volume of air delivered to the system. Since, for volumes $\geq$ 250 mL, the calibration curves obtained using the stop-watch method satisfied the data quality objectives, this additional, costly, in-line instrument was not necessary. The average *method sensitivity*, described by the rate of change in instrument response to the change in analyte concentration (slope), was 0.74 (SD=±0.09). The mass spectrometer was tuned weekly and the continuing validity of the calibration curves was checked daily.

The results achieved for the 5-point analytical calibration curves were excellent, correlation coefficients exceeding the 99% confidence level critical value of 0.959 for 79 target compounds. The average correlation coefficient for all 144 target compounds was 0.916 (SD=±0.13), exceeding the 95% confidence level critical value of 0.878. Calibration curves meeting this criteria (p<0.05) were not consistently obtained in the case of 31 of the target compounds (in order of decreasing confidence: cyclohexene, dibromomethane, dibromochloromethane, bromotrichloromethane, tetrachloroethene, cis-2-heptene, trans-1,4-

dimethylcyclohexane, 2-ethyl-1-butene, 1-butyne, trans-3-heptene, cis-2-octene, 1-nonene, 1,4-dichlorobutane, trans-2-pentene, cis-2-pentene, 4-methyl-1-pentene, 1-heptene, cis-3-heptene, hexachlorobutadiene, cis-2-hexene, 1-hexene/2-methyl-1-pentene, 1-methylcyclohexene, trans-4-methyl-2-pentene, 1-octene, 3-methyl-1-pentene, bromoform, 1-decene, isoprene, styrene and 1,1,2-trichloroethane).

The upper limit of each calibration curve was determined by the point at which linearity fell off due to suppression of the signal by water. Dry air passed through the Teflon™ tubing over the dryer successfully removed the water from all injected samples except those of high volume. As larger aliquots were introduced, the amount of water which found its way into the pre-concentrator increased. Eventually, enough water was present at injection to suppress the GC signal, generally in the region roughly between benzene and toluene, and the analytical results were invalid for the target compounds eluted in this region. It was determined that an aliquot of 1250 mL of humidified air could be trapped at a rate of 25 mL/min without suppressing the GC signal. In addition to the water problem introduced by excessively long collection times, some of the more unstable compounds were lost in the pre-concentrator. This was seen, for example, with some of the olefins, where the linearity of the calibration curve fell off at approximately 50 minutes collection time. The upper limit of the calibration curves was set at 50 minutes collection time, or 1250 mL of sample.

It was found that the calibration curves deviated significantly from linearity at the low end when the sample collection time was less than 10 minutes. This may be due to a slow response of the mass flow controller to the initial pressure surge in the line when the canister was first opened. This resulted in an underestimation of the volume and a systematic error and positive deviation at the lower end of the calibration curve. The pressure surge was minimized by opening the evacuated lines to air prior to sample collection. Since it was not possible (given the equipment available) to measure the volume of air actually delivered to the pre-concentrator, the lower limit of calibration was determined by the point at which there was deviation from linearity due to the inaccurate sample volume. This was found to be 250 mL collected at 25 mL/min. for 10 minutes.

The mass flow controller took 10 to 15 seconds to recover from the pressure surge at the beginning of sample pre-concentration. This caused an error in the total sample volume and accounted, in part, for the failure of the calibration curve to pass through the origin. An attempt was made to further minimize this problem by using a needle valve on the canister to reduce the initial high flow. Unfortunately, the needle valve (probably the Viton™ O-ring) was an active site for a number of calibration compounds in the olefin category. The correlation coefficients for these compounds varied generally from 0.3 to 0.7. Isoprene and styrene, in particular, disappeared altogether. When the needle valve was removed, these compounds were recovered satisfactorily. The latter situation was chosen in order to obtain an improved response of the olefins rather than increased precision of the sample volume. Since excellent correlation coefficients were obtained when the linear regression is forced through the origin, this compromise did not adversely affect the quality of the data.

Accuracy

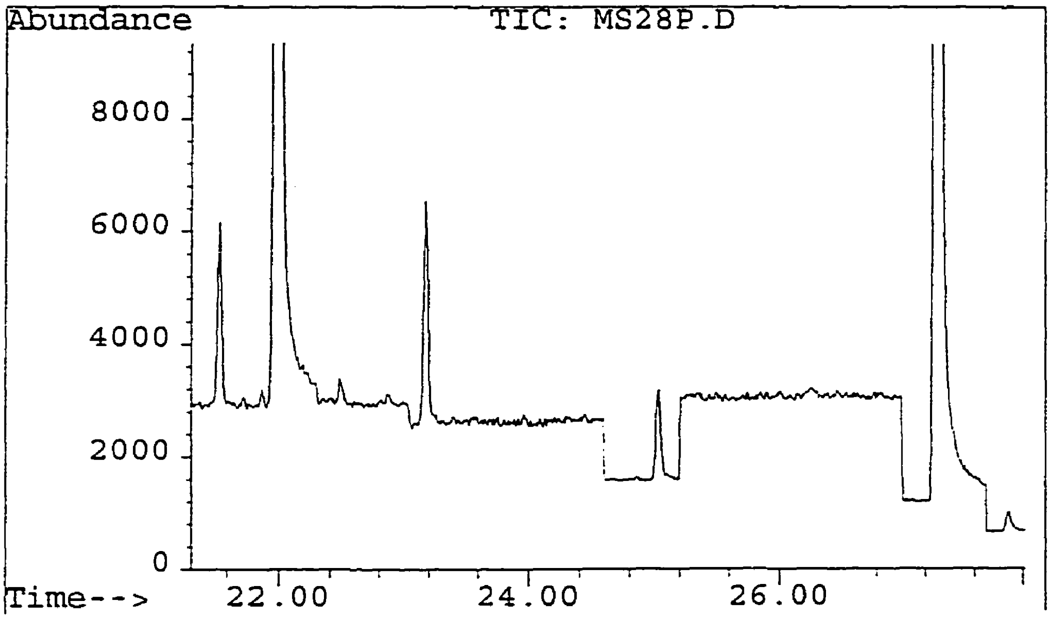
The average analytical accuracy for the quantification of the 144 target compounds was ±15% (determined by analysis of 11 instrument calibration samples over a period of six weeks using 3 sets of updated calibration curves). Six compounds (2-methyl-1-butene, cis-2-octene, cis-2-heptene, trans-1,4-dimethylcyclohexane, 1-decent and bromoform) were quantified with an error higher than 30% due to poor reproducibility of the peak areas for these compounds. However, this was an insignificant source of error in the present study, these six compounds accounting for less then 0.3% of the total VOC's found in fire samples. It may be that these substances occupy adsorption sites on the walls of the Summa™ canister the Nafion™ dryer, the pre-concentrator, valves or transfer lines. However, the observed discrepancies were particularly evident when the canister pressure was less than 20 psig as a result of withdrawal of aliquots over time. This suggests that these substances may be stable in the standard mixture for a shorter period of time than the others. The average analytical accuracy was ±17.8% (SD=±6.9%) for 16 target compounds (propane, 2,2-dimethylbutane, 2,3-dimethylbutane, 3-methylpentane, hexane, cyclohexane, 2,3-dimethylpentane, cyclohexane, 2,3-dimethylpentane, 2,2,4-trimethylpentane, methylcyclohexane, 2,3,4-trimethylpentane, 2-methylheptane, ethylbenzene, m/p-xylene, o-xylene and isopropylbenzene) present at a nominal concentration of 2 ppb in a round-robyn *Photochemical Assessment Monitoring Stations* (PAMS) proficiency test canister (ALM041274, test #PF940804). The average analytical accuracy was ±5.3% (SD=±2.9%) for 10 NIST traceable standards (isobutane, butane, pentane, 2-methylpentane, hexane, benzene, toluene, octane, 1,2,4-trimethylbenzene and undecane) present in a U.S. EPA audit canister (ALM041274), concentrations ranging from 0.2 ppb to 10 ppb. Quadruplicate analysis of an NIST standard mixture, from which 0.645 mL of sample was delivered to the pre-concentrator via a sample loop, resulted in a mean analytical error of ±5% for the target compounds propane, benzene, toluene and chlorobenzene present at a nominal concentration of 10 ppm. These results exceed the U.S. EPA (1991) and TO-15 (1997) method requirements for an audit accuracy of ±30%.

Instrument Sensitivity

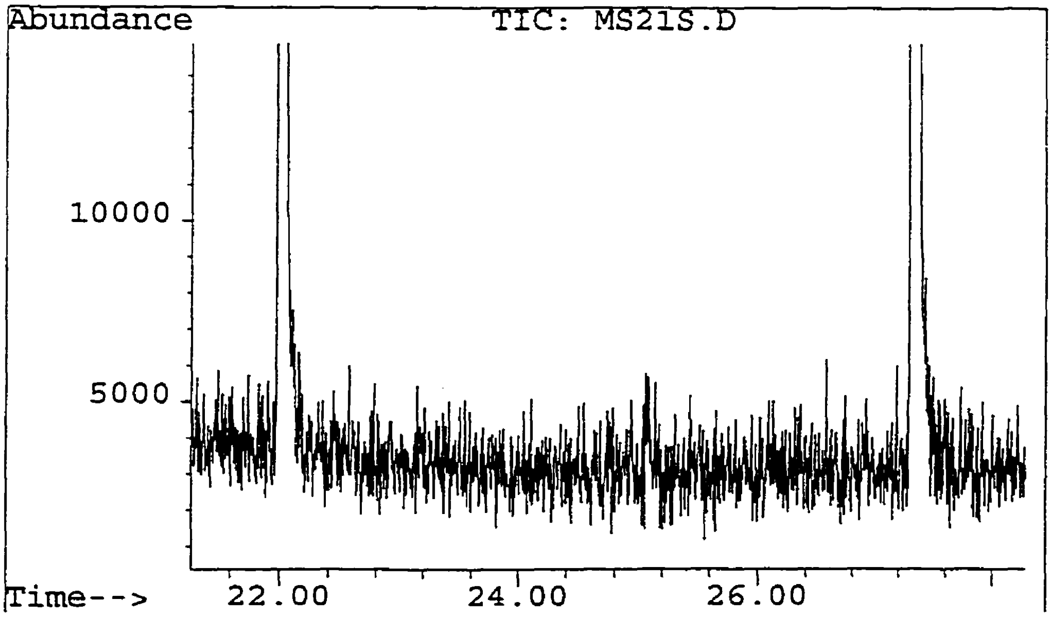
The standard deviation of the system noise was a measure of the lower limit of the system's analytical capabilities and was used to determine when a signal could be properly distinguished from background noise. Some ions were noisier than others, and background noise varied from one acquisition window to the next since different ions were being monitored in each window. A 10-fold decrease in noise was achieved when the GC/MS was operated in SIM mode (Figure 20A) rather than in SCAN mode (Figure 20B). This was made possible by virtue of the longer MS dwell times achieved as a result of the restricted number of molecular ion

Figure 20. Instrument sensitivity (noise) observed in while operating the GC/MSD in (A) the selected ion monitoring (SIM), and (B) the total ion (SCAN) modes, respectively. The sensitivity is increased approximately 10-fold by operating the GC/MSD in SIM mode because of the monitoring of a few selected ions whereas in the SCAN mode all (total) ions are being detected.

A.


Abundance
TIC: MS28P.D
8000
6000
4000
2000
0
Time-->
22.00
24.00
26.00

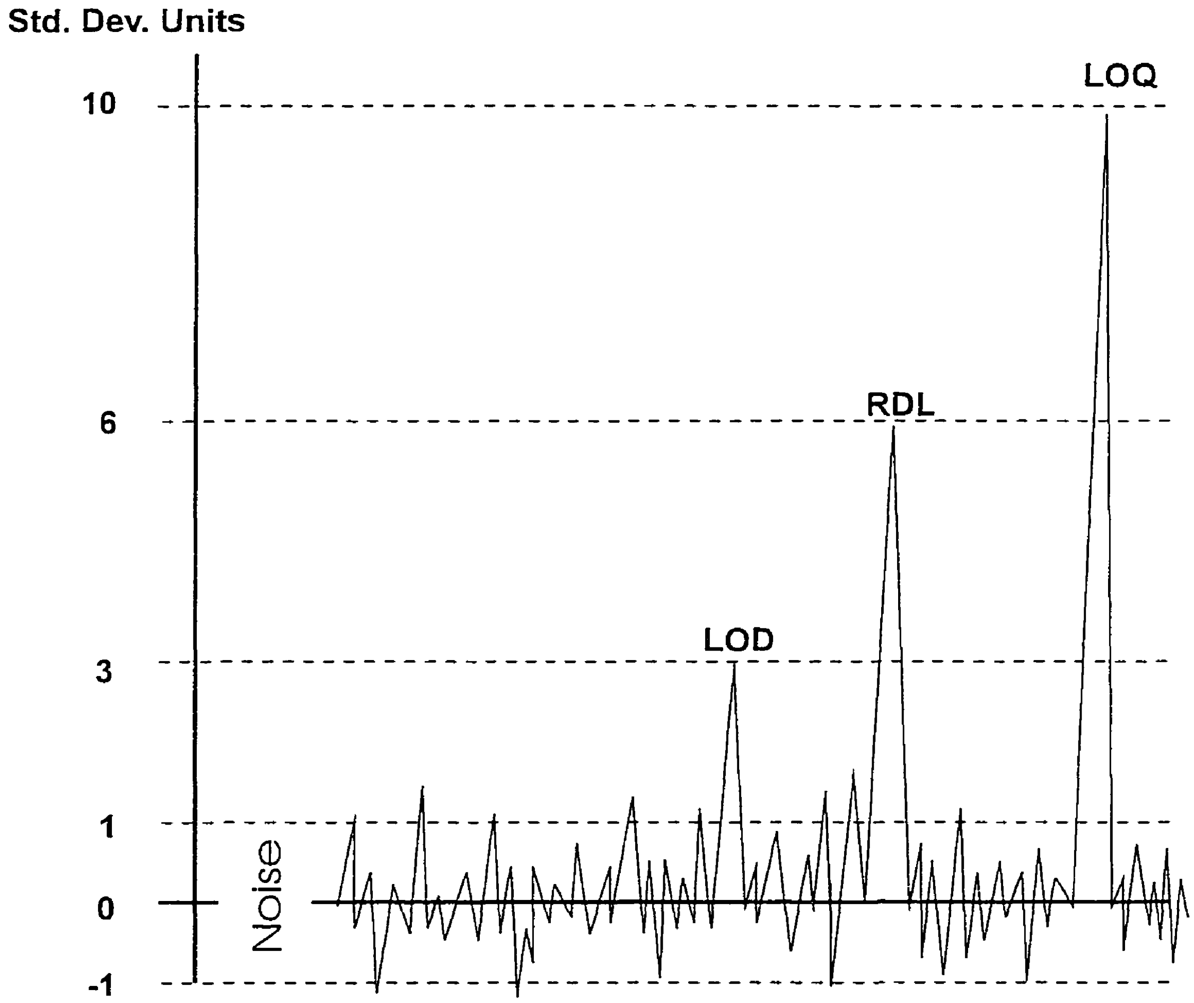
B.


Abundance
TIC: MS21S.D
10000
5000
Time-->
22.00
24.00
26.00

fragments (m/z) which were monitored at one time. Instrument sensitivity in the SIM mode was determined by integration of the baseline noise adjacent to each of the 144 target compound peaks in 10 mL samples of the instrument calibration mixture. The limits of detection are described diagrammatically in Figure 21 as they related to baseline noise.

The average baseline noise signal (N) reflected the random measurement variability and was found to be equivalent to an average 0.0018 ng (SD=±0.0018) for the 144 target compounds. The average limit of detection (LOD=3xSD) was 0.0054 ng (*p*=0.001) for the 144 target compounds. This represents a 0.1% (α) chance of a Type I error of reporting a false positive and a 0.1% (β) chance of a Type II error of reporting a false negative. The average LOD achieved was 1000 times lower than the LOD of 5 ppb required by the U.S. EPA (1991). To determine if the fire matrix would significantly affect the LOD, the SD of the baseline noise was determined as above using samples collected at fires. Application of the F-test found no significant difference, at the 95% confidence level, between the variances of the noise signals produced when analyzing instrument calibration mixtures and fire samples. The reliable detection limit (RDL= 6xSD) was 0.011 ng (0.005 ppb) for the 144 target compounds, representing the lowest analyte concentration that could be reliably detected at the 99% confidence level. Other authors have referred to this as the detection limit (DL) but this terminology has fallen into disfavour because it may lead to confusion (Currie, 1988). The limit of quantification (LOQ=10xSD) was 0.018 ng (0.01 ppb) for the 144 target compounds, which represents an uncertainty of ±30% in the measured value of the LOQ at the 99.9% confidence level. The average method detection limit (MDL=3xSD) was determined by analyzing replicate samples of the standard mixture where the concentration of the target compounds was within a factor of approximately five of the expected MDL. The U.S. EPA (1991) requirement for a MDL $\leq$5 ppb was confirmed for 103 target compounds. The U.S. EPA has established method limits of quantification (MLOQ) of 2 to 5 ppb, depending on the compound, for 40 of the substances which

Figure 21. A schematic diagram showing the various limits of detection/quantification as defined for GC analysis. LOD - average limit of detection equal to three times the standard deviation (SD) of the level of the noise signal. RLD - reliable limit of detection equal to 6 x SD of the noise signal. LOQ - limit of quantification equal to 10 x SD of the noise signal.

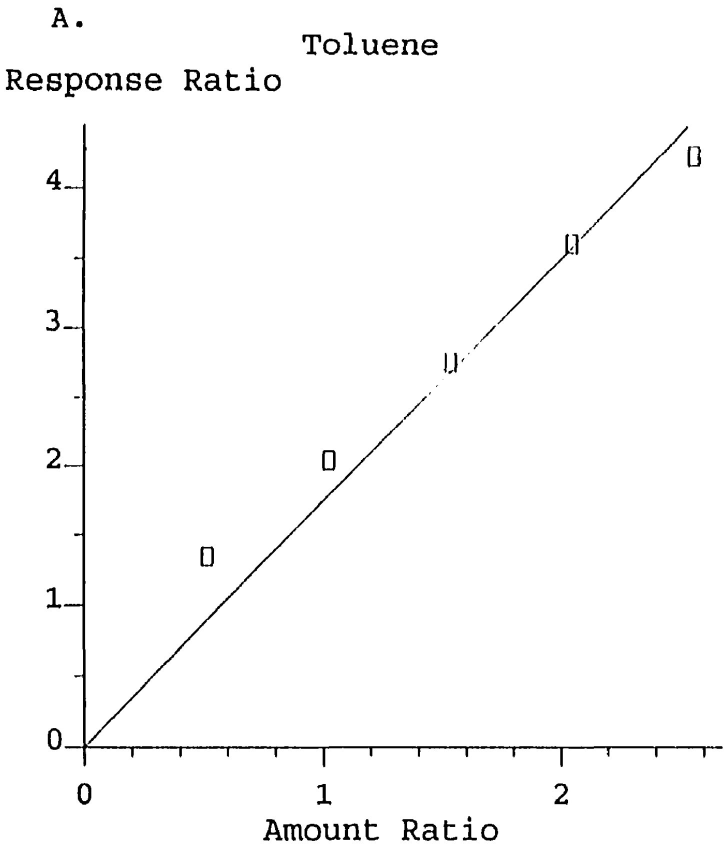

Std. Dev. Units
10
6
3
1
0
-1
Noise
LOD
RDL
LOQ

were present in the standard mixture. An MLOQ ≤5 ppb was confirmed for 74 of the compounds present in the mixture. Higher MLOQ's (15 to 25 ppb) were found for the later-eluting or semi-volatile substances including 1,3-diethylbenzene, indane, 1,3-diethylbenzene, 1,4-diethylbenzene, n-butylbenzene, 1,2-diethylbenzene, undecane, 1,2,4-trichlorobenzene, naphthalene, dodecane, hexachlorobutadiene and hexylbenzene.

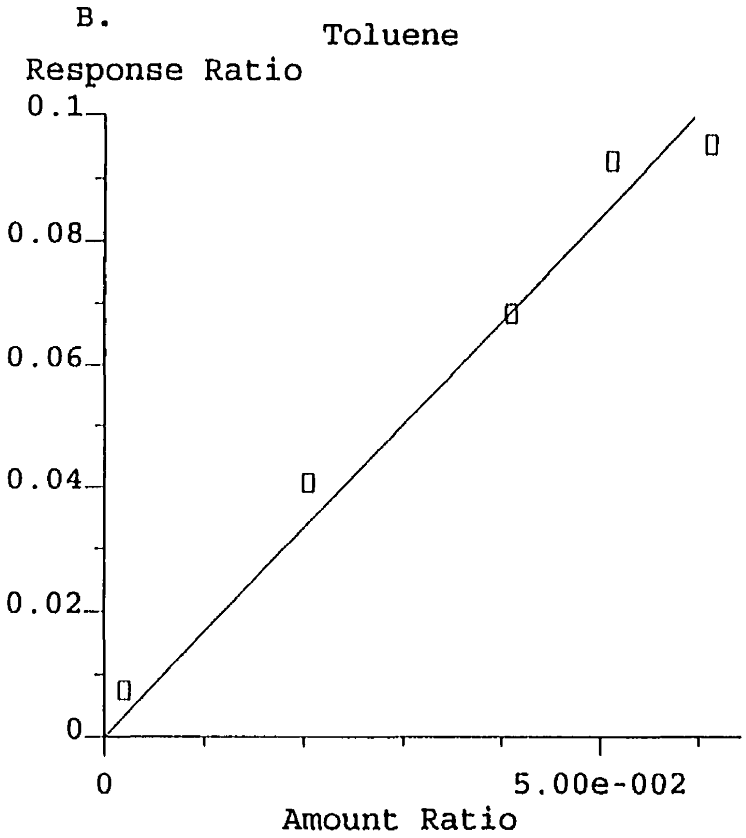
Linearity

Linearity was found to extend below the lower limit of the calibration curves. The 5-point linear calibration curves were extrapolated to 0.04 times their lower limit for the determination of unknown samples in the range of the LOQ (Figure 22A). Thirty-five compounds were quantified with better than 30% accuracy from replicate analysis of 10 mL aliquots (n=3) of the instrument calibration mixture, the average standard deviation being ±0.02 ng. Benzene and toluene, for example, were determined from 0.081 ng samples with an accuracy of 6% (SD=±0.013 ng) and 1% (SD=±0.0094 ng), respectively. A new set of calibration curves for analyte concentrations in the range of 0.01 ng to 0.5 ng were prepared from 1 mL, 10 mL, 20 mL, 25 mL and 30 mL aliquots of the instrument calibration mixture (Figure 22B). The accuracy and precision of these calibration curves prepared for these extremely low levels was surprisingly good. The average relative standard deviation (rsd) of the response factors increased from 19% to 28% and the average calibration curve correlation coefficient decreased to 0.90 from 0.92. Twenty-three compounds, present in 10 mL of the instrument calibration mixture, were quantified with better than 30% accuracy. Analytical accuracy and precision were confirmed at the LOQ of 0.02 ng to 0.2 ng, depending on the analyte. The calibration curves for toluene, for example, had similar slopes when prepared in the normal range of concentrations and near the MDL (1.61 ppb and 1.69 ppb, respectively). Their correlation coefficients were 0.999 and 0.982, respectively.

Figure 22. The linearity of the relationship between concentration and detector response (response ratio of toluene/internal standard) for toluene in (A) the instrument calibration range corresponding to concentrations expected in diluted samples and, (B) 250-fold lower levels.



Resp Ratio = 1.75e+000 * Amt
Corr Coef = 0.998



Resp Ratio = 1.69e+000 * Amt
Corr Coef = 0.982

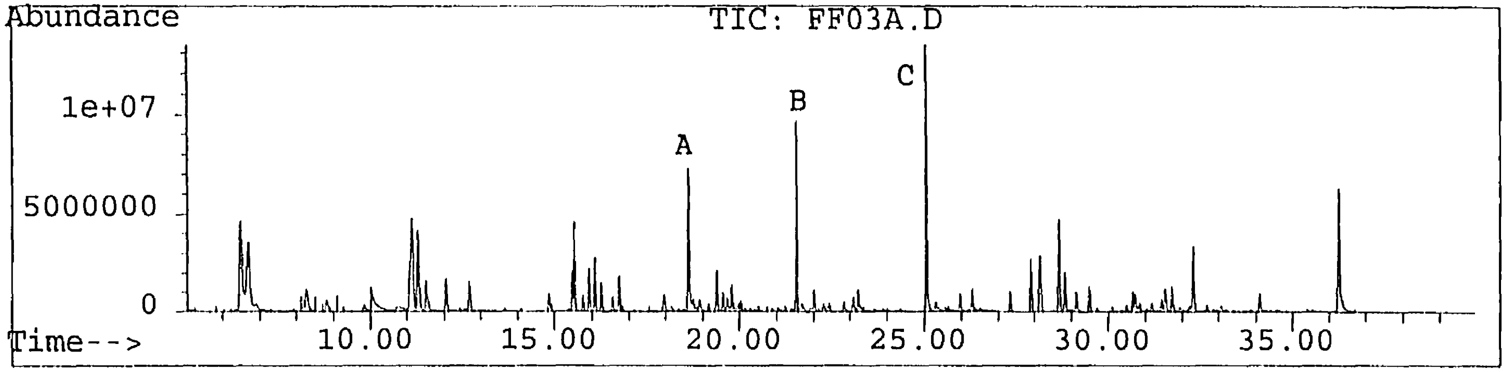
Theoretically, very low levels of VOC's present in ambient air could be concentrated by passing large sample volumes through the cryogenic pre-concentrator thereby bringing them up to the instrumental detection limit. In practice, this strategy was limited to approximately 1500 litres of air due to the inability of the Nafion™ dryer to remove larger amounts of water, the quantity of which increased with increasing volumes of air leading to ice blockage of the cryogenic pre-concentrator. Analysis of 500 mL aliquots resulted in mass abundance counts less than approximately 500,000.

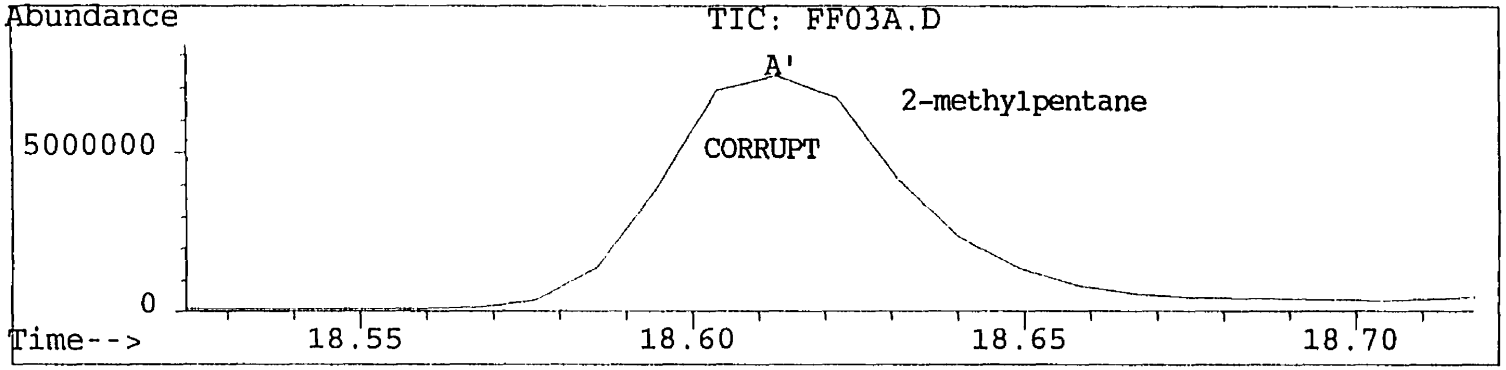
Fire samples, collected at sub-atmospheric pressure, were pressurized to 40 psig in order to permit sample collection in the cryogenic pre-concentrator. This resulted in a dilution factor of approximately 3-fold. Linearity of the mass selective detector response fell off at high concentrations due to detector saturation. Figure 23, for example, shows corruption of the 2-methylpentane, benzene and toluene peaks from a 125 mL aliquot of a fire sample when their concentration exceeded approximately 6,000,000 mass abundance counts. Analysis of 1 mL to 10 mL aliquots of diluted samples generally resulted in mass abundance counts less than 2,000,000. The total range of linearity for the analysis of air samples was approximately 0.02 ppb to 100 ppm. The upper limit can be extended by sequential dilutions of samples containing levels of target compounds above 100 ppm.

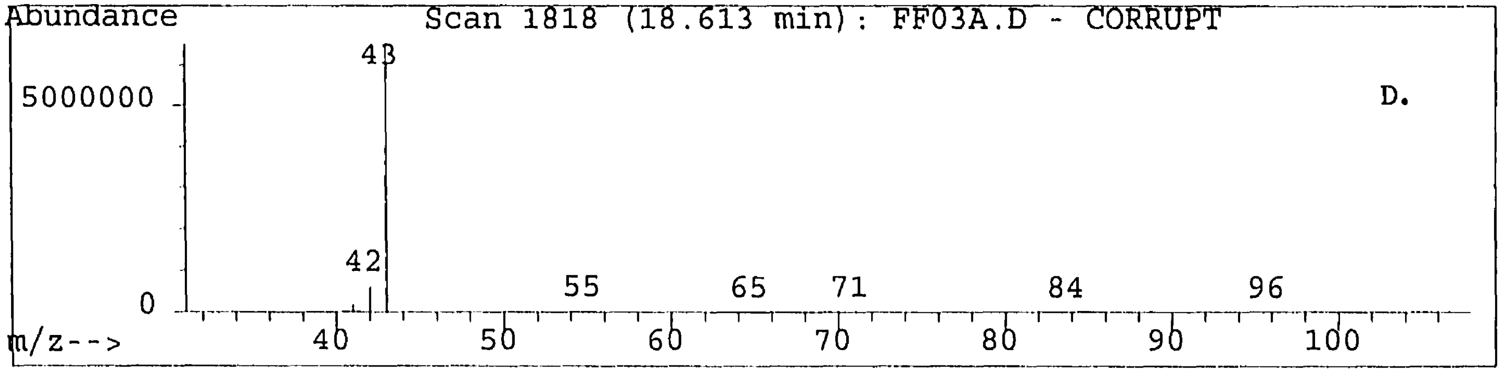
Analytical precision

The average intra-day precision of the area counts for the four internal standards was ±3% rsd. The average inter-day precision of the internal standards (1,4-difluorobenzene, chlorobenzene-d5 and 1-bromo-4-fluorobenzene) observed over a period of 8 months was ±22% rsd. This was much better than the ±40% required by the U.S. EPA (1991) and by the TO-15 (1997) method. The inter-day precision for bromochloromethane was unacceptably high (rsd=±43%) and this internal standard was not used for quantification. The area counts of internal standards added to sample canisters matched the area counts of

Figure 23. A chromatogram showing the saturation of the mass selective detector by the ion fragments from 2-methylpentane (A), benzene (B) and toluene (C) when the concentrations of these exceeds approximately 6,000,000 abundance counts. Such corrupted peaks can be found only by checking each suspect peak manually (A' and D).


Abundance
TIC: FF03A.D
1e+07
5000000
0
A
B
C
Time-->
10.00
15.00
20.00
25.00
30.00
35.00


Abundance
TIC: FF03A.D
A'
2-methylpentane
CORRUPT
5000000
0
Time-->
18.55
18.60
18.65
18.70


Abundance
Scan 1818 (18.613 min): FF03A.D - CORRUPT
43
D.
5000000
42
55
65
71
84
96
0
m/z-->
40
50
60
70
80
90
100

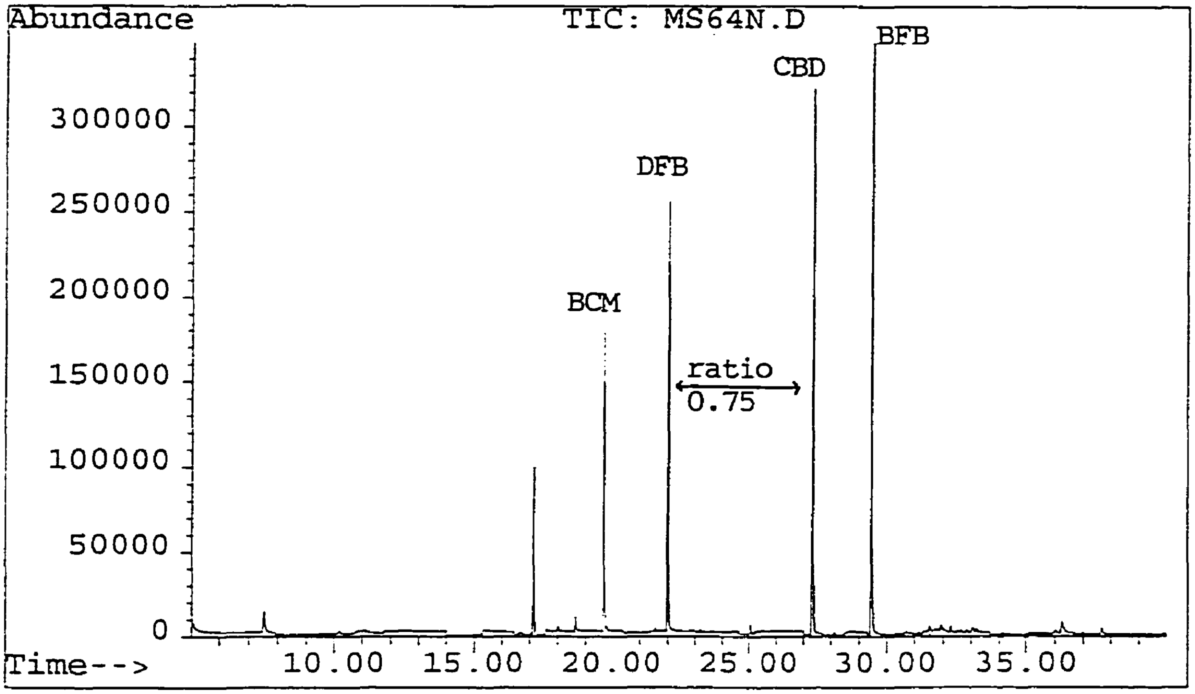
internal standards added to standard samples used in the preparation of calibration curves to within ±10%. Deviations from this criteria were due to baseline changes resulting from the effects of water in the GC/MS which had not been removed by the Nafion™ dryer. The MS signals for compounds eluting between approximately 17 and 27 minutes were suppressed in the presence of water, including the internal standards bromochloromethane and 1,4-difluorobenzene. The ratio of 1,4-difluorobenzene to chlorobenzene-d_5 area counts in the absence of water was approximately 0.75 (Figure 24A). In samples where signals were suppressed, this ratio decreased to approximately 0.5 (Figure 24B). In such cases, only the later eluting compounds, unaffected by the presence of water, could be quantified. One set of calibration curves were normally used for the quantification of samples over a period of one or two weeks, the average intra- and inter-day instrumental precision for the quantification of the 144 target compounds being ±8% rsd and ±15% rsd, respectively. The "best-case" measure of replicate precision quoted by the U.S. EPA (1991) was ±7% for replicate standard mixture samples at the 10 ppb level. A more conservative value (±25%) was quoted for replicate analysis of "real world" canister samples from *Toxic Air Monitoring Stations* (TAMS) and *Urban Air Toxics Monitoring Program* (UATMP) networks and for the TO-15 (1997) method.

Contamination

Leakage of air into the GC/MS system resulted in the appearance of numerous sharp spikes (Figure 25A), recognizable by their triangular shape (Figure 25B) and characteristic molecular ion fragment of 29 amu (Figure 25C). This problem was avoided by the use of firmly fitting Swagelok™ connectors between transfer lines and periodic replacement of O-rings in the GC/MS. Given the low nanogram level working range of the analytical method, contamination of the system could easily become a major problem. Analytical system contamination was monitored by running 500 mL samples of three different types of blanks: (1) *System air blanks* detected contamination in the Nafion™ dryer, pre-concentrator, valves, transfer lines

Figure 24. Chromatograms of "air blank" samples containing internal standards bromochloromethane (BCM), 1,4-difluorobenzene (DFB), chlorobenzene-d5 (CBD) and 1-bromo-4-fluorobenzene (BFB) showing the normal pattern (A) and that when the sample has been contaminated with water (B), causing elevation of the baseline leading to the suppression of peaks.

A.


Abundance
TIC: MS64N.D
300000
250000
200000
150000
100000
50000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
BCM
DFB
CBD
BFB
ratio
0.75

B.

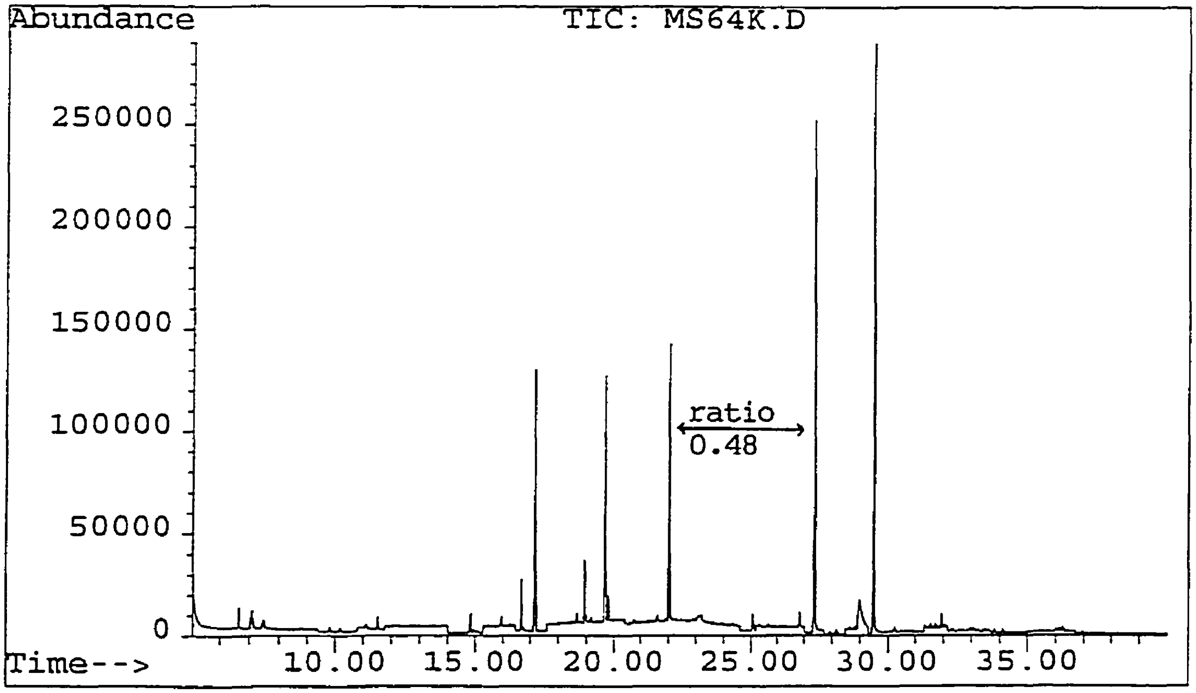
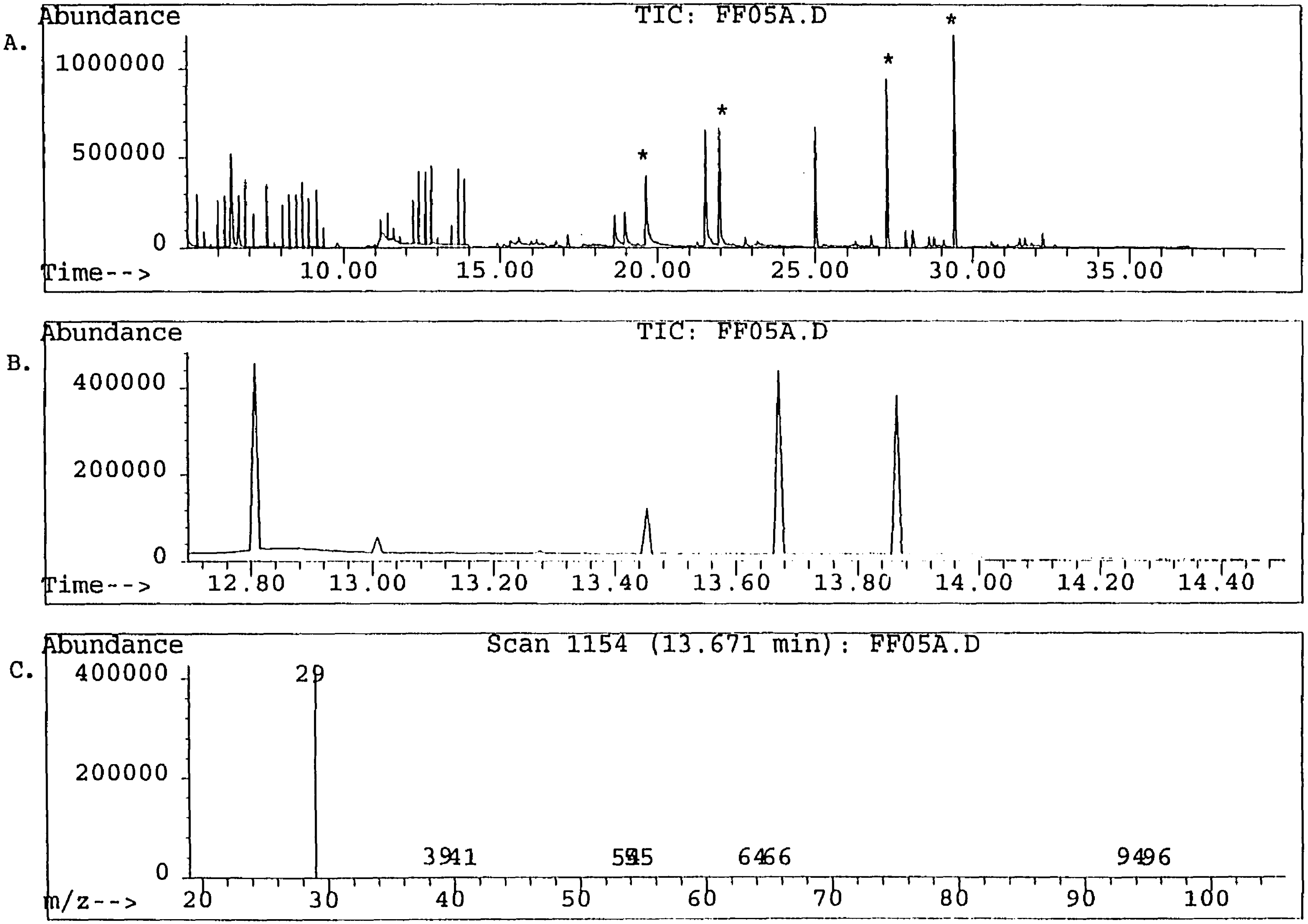

Abundance
TIC: MS64K.D
250000
200000
150000
100000
50000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
ratio
0.48

Figure 25. Chromatogram of a system blank where air has leaked into the system causing the appearance of numerous sharp spikes (A). The region from 12 to 15 minutes retention time has been magnified (B) to show the characteristic triangular shape of these extraneous spikes which appear when the 29^+ ion fragment is monitored (C). Asterisks indicate the internal standards normally added to samples prior to analysis.


A.
Abundance
TIC: FF05A.D
1000000
500000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*
B.
Abundance
TIC: FF05A.D
400000
200000
0
Time-->
12.80
13.00
13.20
13.40
13.60
13.80
14.00
14.20
14.40
C.
Abundance
Scan 1154 (13.671 min): FF05A.D
400000
200000
0
29
3941
5355
6466
9496
m/z-->
20
30
40
50
60
70
80
90
100

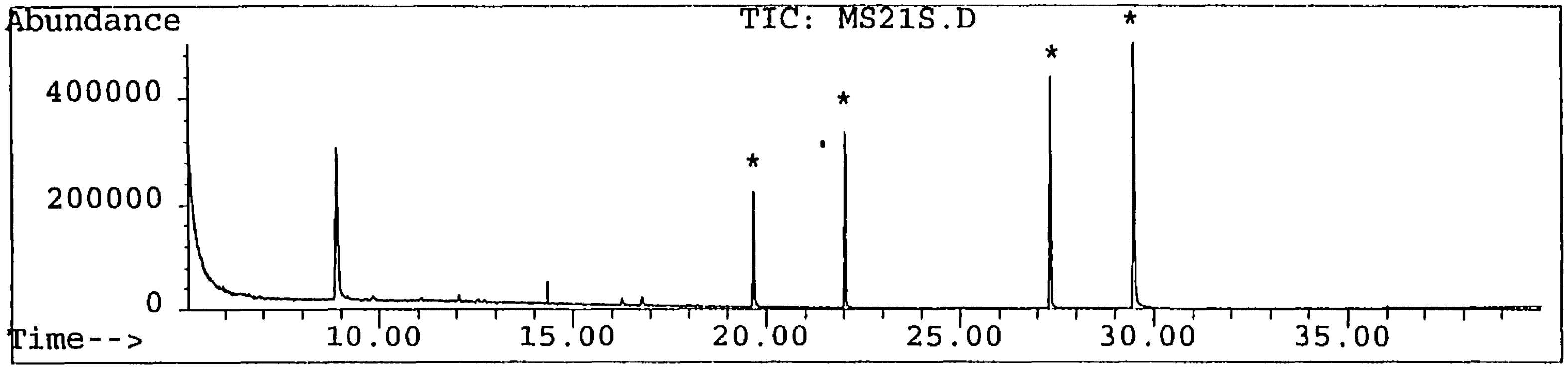
and GC/MS; (2) *Helium blanks* detected contamination in the GC/MS only; (3) *Clean canister blanks* detected contamination in the interface between the canister and the pre-concentrator, the pre-concentrator itself and the GC/MS. Figure 26 shows different types of blanks analyzed to monitor potential contamination in different parts of the sampling/analytical system. The flat baseline and minimum number and size of peaks seen in a SCAN of a *system air blank* following the all night stand-by at 150°C of the equipment indicates that the system was very clean (Figure 26A). One major peak, found at 9.4 minutes retention time, did not interfere with sample analysis because its molecular ions were not monitored when the GC-MS was operated in SIM mode (Figure 26B). Comparison of its mass spectrum with spectra in the NIST (1992) mass spectral library matched that of silane with 80% confidence. It is likely that this arose from the dimethyldichlorosilane treated glass wool plugs used in the cryogenic trap. A *helium blank* revealed contamination located in the GC/MS only. Changes in the baseline were highly magnified because there was little or no contamination to cause production of a signal in the mass selective detector (Figure 26C). A change in the height of the baseline corresponded to a change in the group of selected molecular ion fragments which were monitored for a given range or "window" of retention times. Analyses of *clean canister blanks* following runs of standard mixtures and fire samples revealed little or no contamination resulting from carry-over of analytes from one sample to the next (Figures 26D and 26E, respectively). The one compound which did sometimes cause problems, resolved by running one or more blanks, was naphthalene which eluted at approximately 36.2 minutes.

Canister cleaning

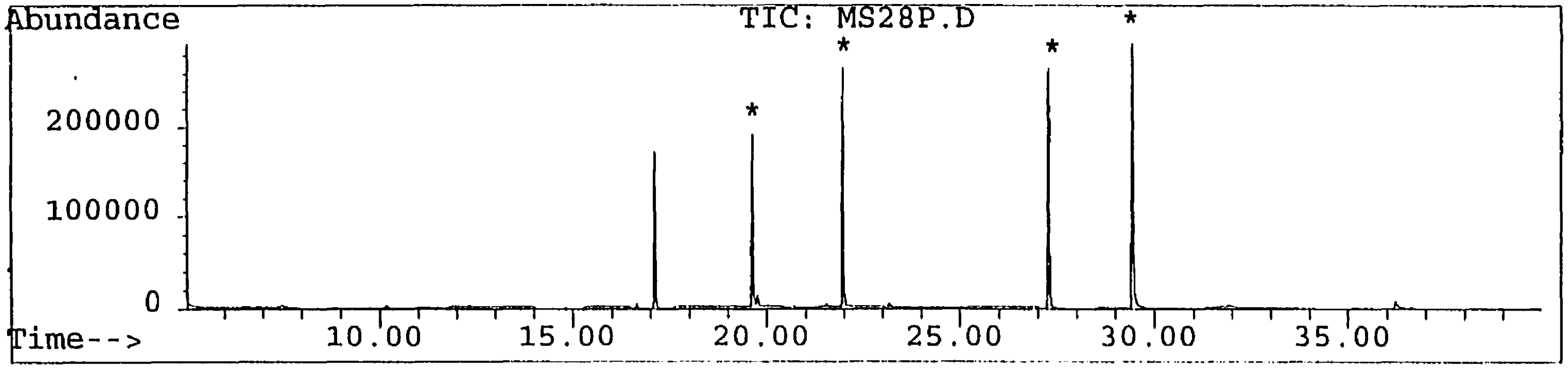
Canisters used exclusively for ambient sampling of low levels of air pollution were cleaned in an automated vacuum oven overnight. Since canisters used for sampling of fire atmospheres were exposed to much higher levels of contamination and, potentially to much dirtier air due to the presence of smoke and soot, such

Figure 26. Chromatograms showing the results of analysis of canister blanks run in: (A) SCAN mode after overnight standby; (B) SIM mode after overnight standby; (C) SIM mode after analysis of a standard mixture; (D) SIM mode after a varsol fire sample; and, (E) a system helium blank run in SIM mode. Asterisks indicate the internal standards normally added to samples prior to analysis.

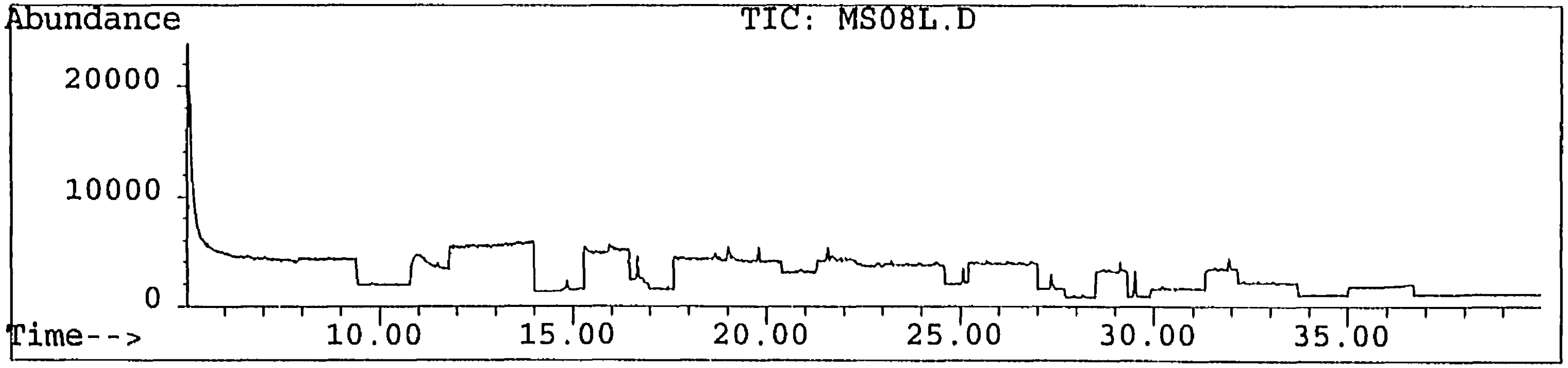
A.


Abundance
TIC: MS21S.D
400000
200000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*
*

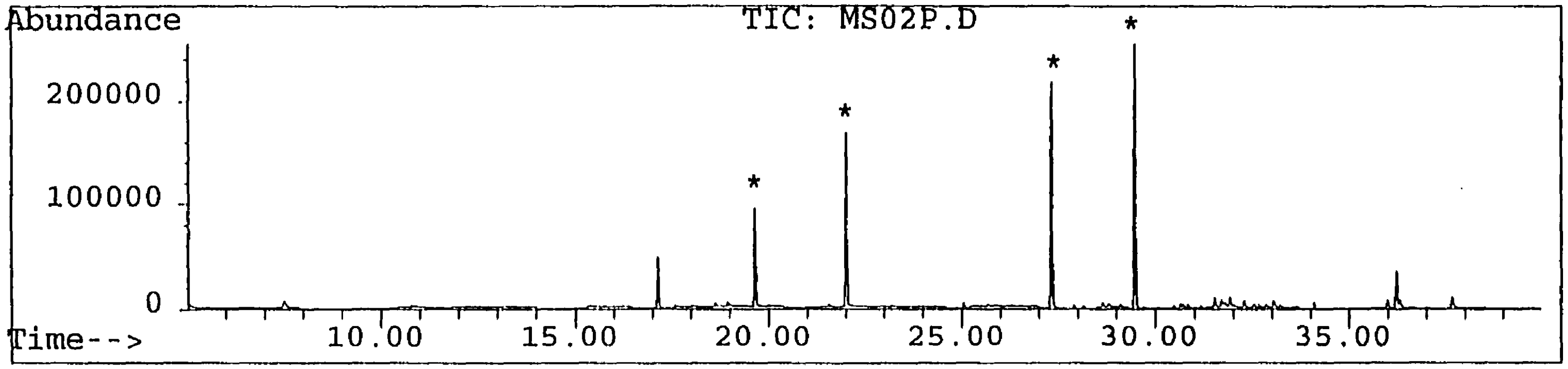
B.


Abundance
TIC: MS28P.D
200000
100000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*
*

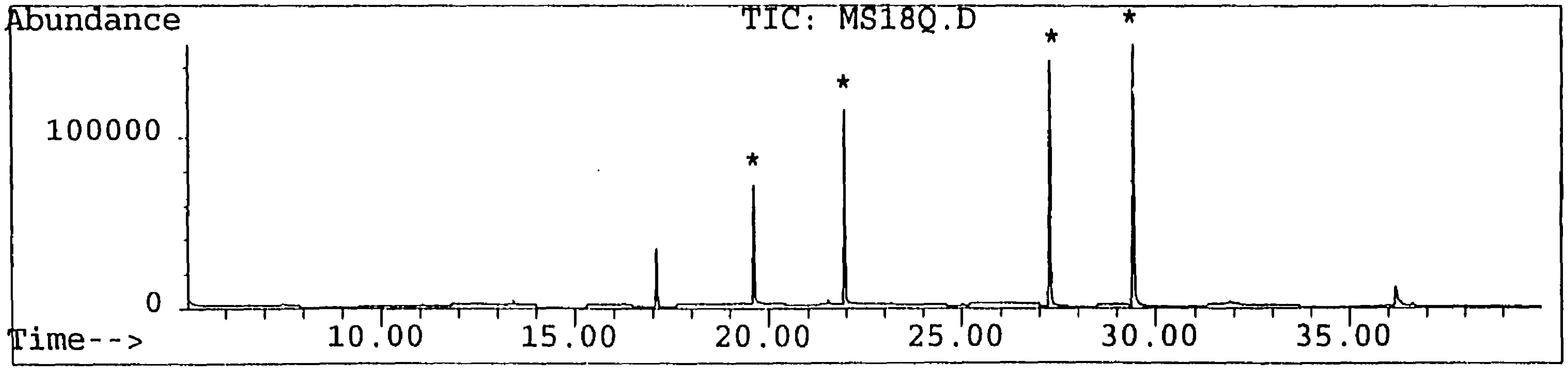
C.


Abundance
TIC: MS08L.D
20000
10000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

D.


Abundance
TIC: MS02P.D
200000
100000
0
*
*
*
*
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

E.

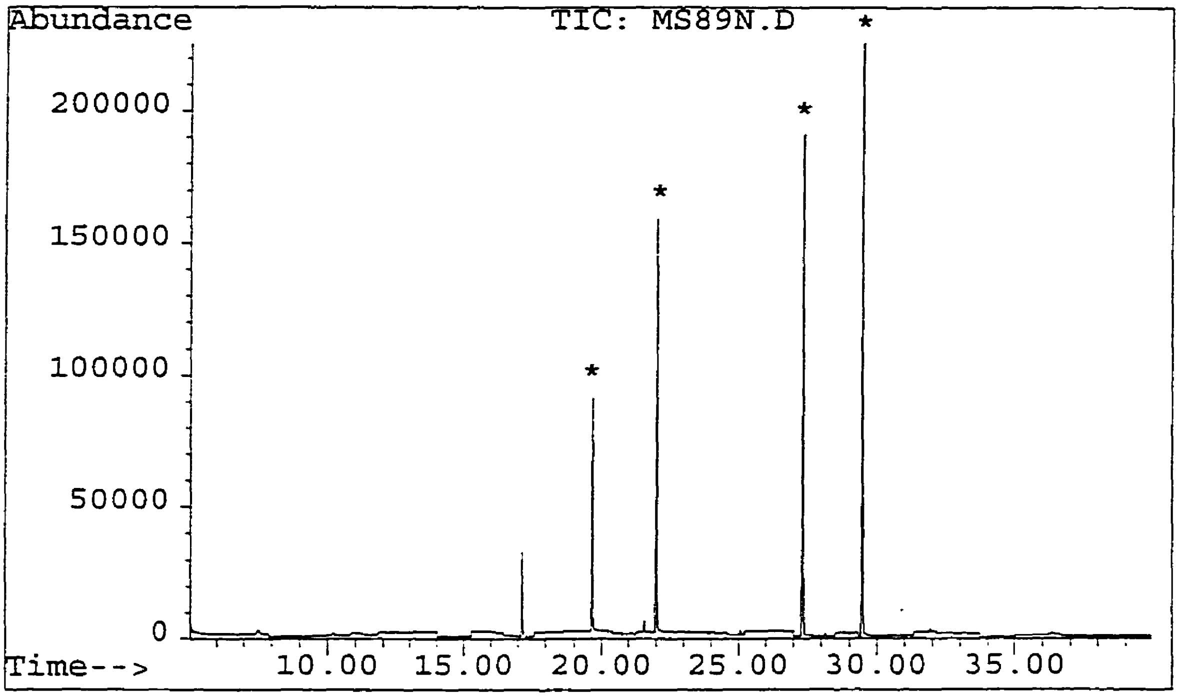

Abundance
TIC: MS18Q.D
100000
0
*
*
*
*
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

canisters were first evacuated manually and baked with a heat gun prior to overnight cleaning. Cleaned fire canisters were filled with purified humid air and left to equilibrate for one week or longer. A 500 mL aliquot of this air was analyzed by GC/MS (Figure 27A). In general, the results obtained from these blanks were as good as or better than those obtained for ambient air canisters which had undergone cleaning only in the automated vacuum oven (Figure 27B). Total VOC's found in 500 mL aliquots of dilution air taken from cleaned fire canisters was 5.4 ng (SD=±3.5 ng) or 2 ppb. This was better than the U.S. EPA (1991) requirement that analysis of method blanks result in no target compound at or above the U.S. EPA limit of quantification of 2 to 5 ppb, depending on the compound (EPA, 1991). Quantities found were less than or equal to the actual instrumental LOQ (0.02 ng) for 114 of the 144 target compounds and none were present in amounts greater than 1.0 ng (2 ppb). Naphthalene, styrene and 1,4-dichlorobenzene were the most problematic contaminants, levels found being 0.6 ng (SD=±0.5 ng), 0.5 ng (SD=±0.6 ng) and 0.1 ng (SD=±0.1 ng), respectively. Other detected contaminants included (in decreasing order of importance) Freon12™, 2-methyl pentane, Freon113™, dichloromethane, toluene, Freon114™, hexane and Freon122™, the source of these contaminants being the laboratory and system air. Analysis of fire samples was based on much smaller aliquots (1 mL or 10 mL) than those used for method blank determinations. The contribution of blank values to the amounts of analytes found in fire samples was negligible and no corrections were made to total values.

Occasionally a canister was found where the above cleaning procedures were unsuccessful (Figure 28A). In such cases, the canisters were successfully cleaned by rinsing with a weak hydrochloric acid solution, baking under steam pressure for three hours, followed by evacuating and baking with the heat gun, and then analyzed following cleaning again in the automated vacuum oven (Figure 28B). There was the possibility that, even with the aggressive cleaning procedure described, canister contamination might arise as a result of desorption of analytes from the canister walls. Re-analysis of purified humid air following one week

Figure 27. The re-use of canisters is dependent upon the ability to clean and/or remove any residuals from the previous sample. Chromatogram A shows results for a fire canister cleaned by manual evacuation, baking with a heat gun prior to overnight cleaning in an oven with automated repeat filling and evacuation of air. Chromatogram B is an ambient air canister cleaned only by the automated oven. Asterisks indicate the internal standards normally added to samples prior to analysis.

A.


Abundance
TIC: MS89N.D
200000
150000
100000
50000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*

B.

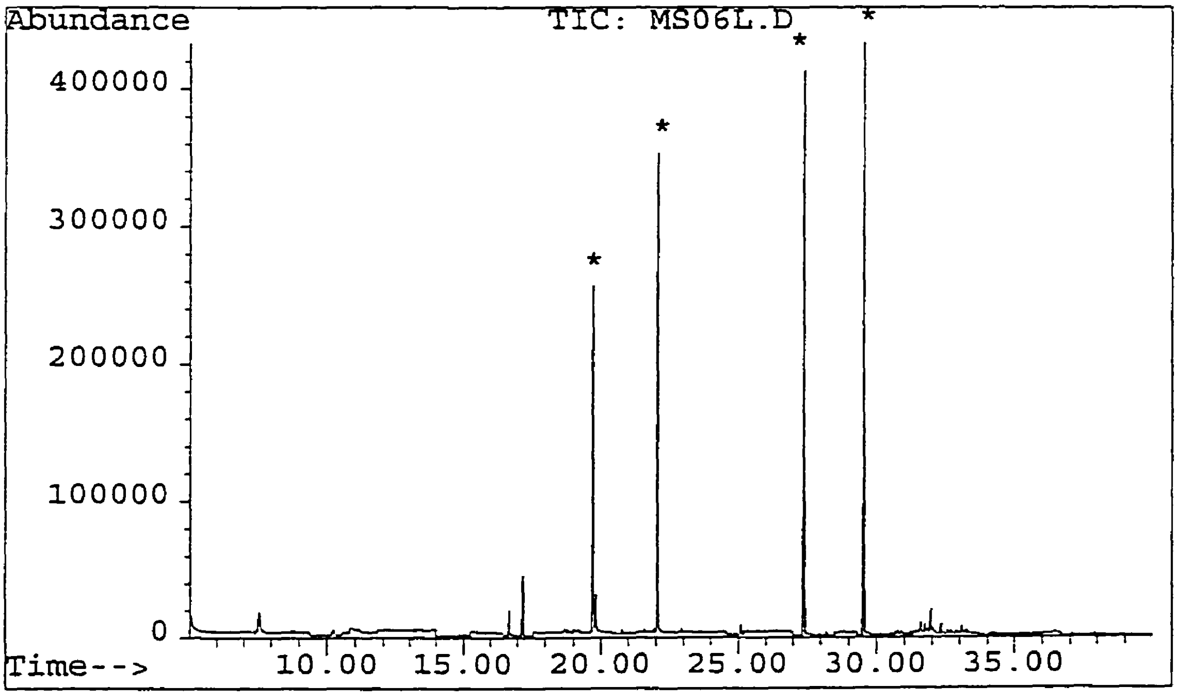
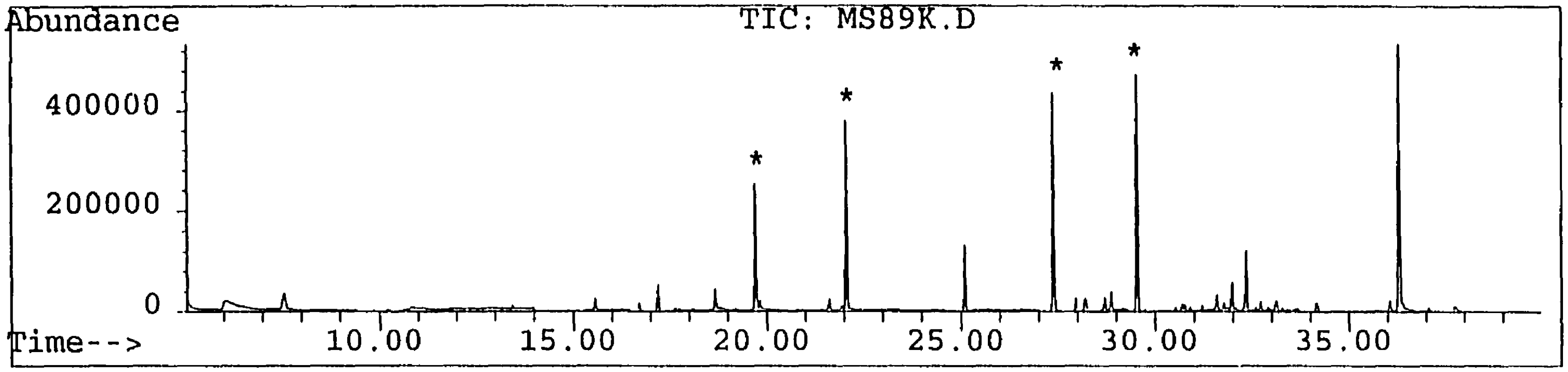
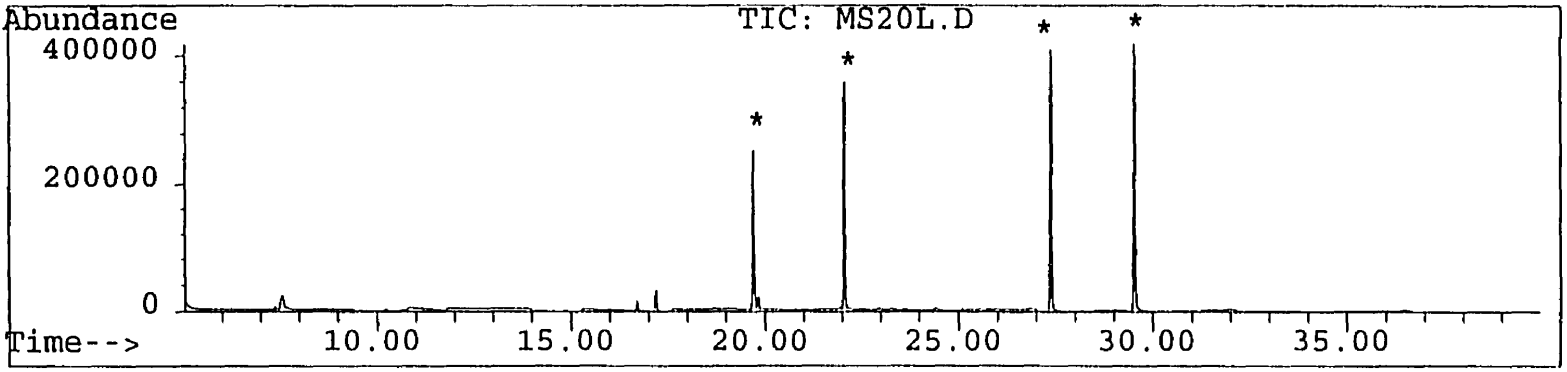

Abundance
TIC: MS06L.D
400000
300000
200000
100000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*

Figure 28. Chromatograms of canisters showing, (A) contamination after normal cleaning procedures, (B) decontamination after rinsing with a weak hydrochloric acid solution, baking under steam pressure for three hours followed by a repetition of the normal cleaning procedure (C) cleanliness verified one week later. Asterisks indicate the internal standards normally added to samples prior to analysis.

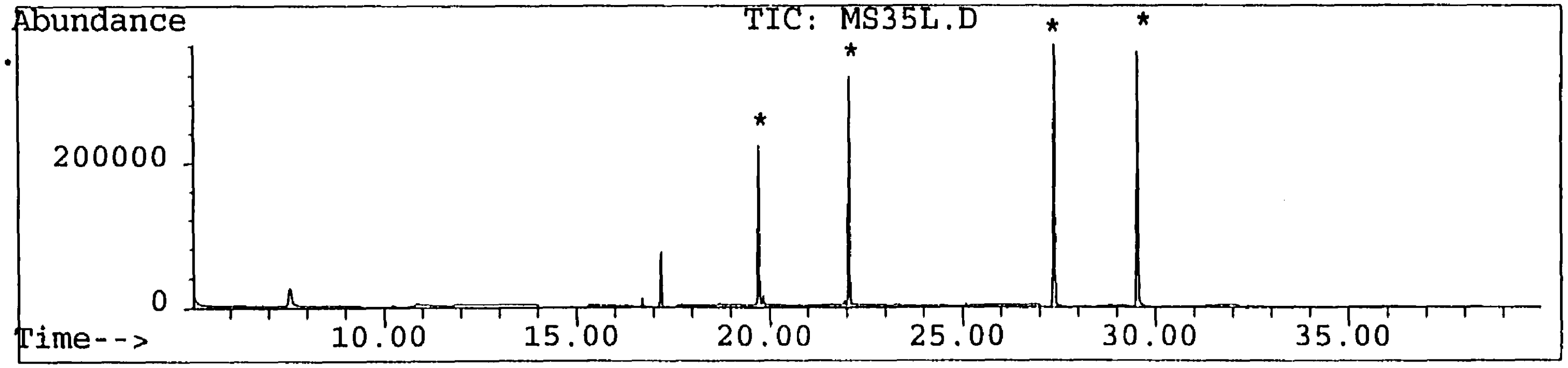
A.


Abundance
TIC: MS89K.D
400000
200000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*

B.


Abundance
TIC: MS20L.D
400000
200000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*

C.


Abundance
TIC: MS35L.D
200000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
*
*
*
*

of storage in this canister did not reveal this to be the case (Figure 28C).

Canister adsorption/desorption

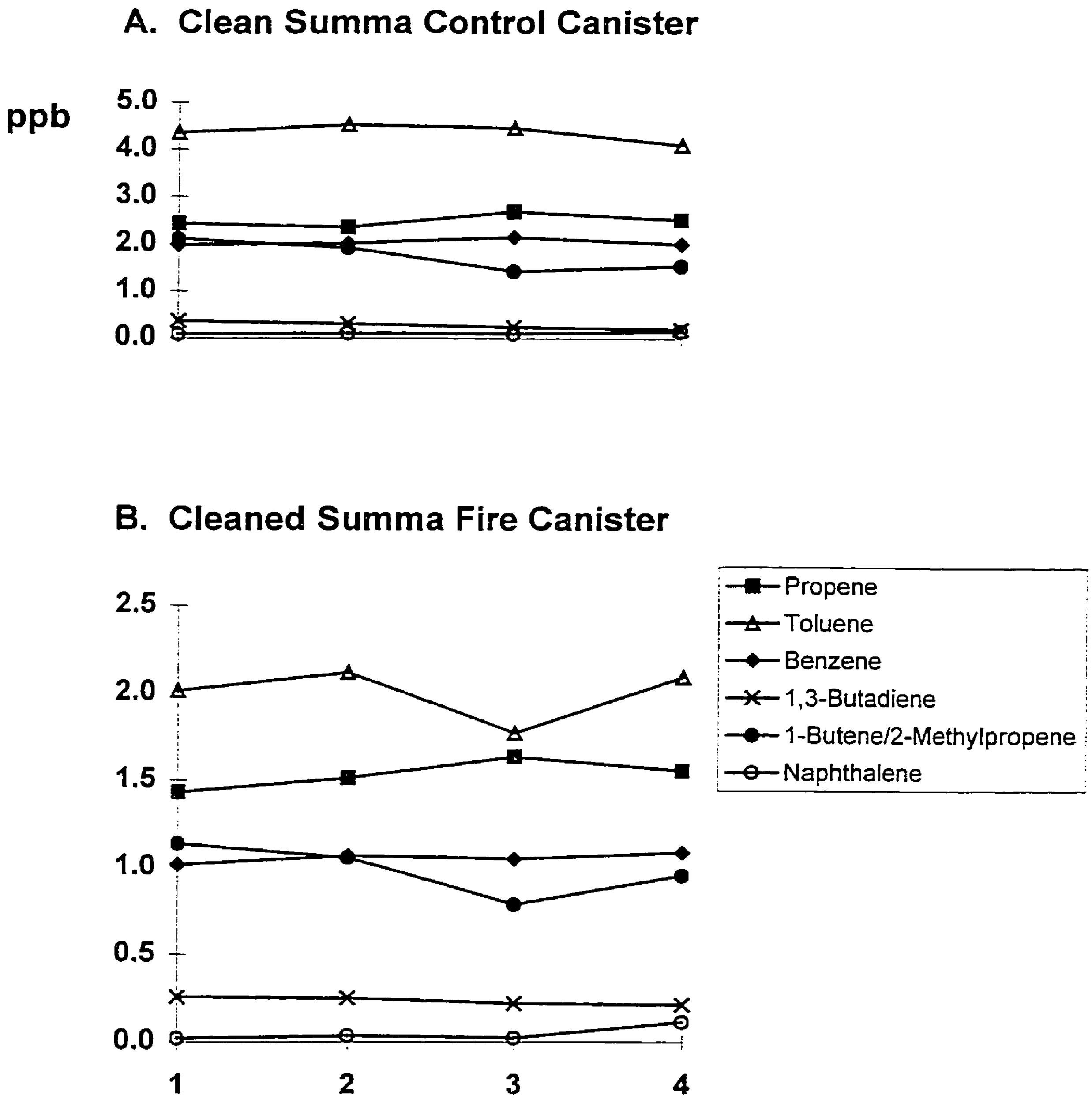
The possible adsorption of analytes onto the inner walls of the Summa™ canisters was monitored by repeated analysis of low level samples. Outdoor air samples were collected on different days over a 24-hour period in downtown Ottawa (Canada). The first sample was collected in a thoroughly cleaned Summa™ canister which had been used previously for sampling of highly polluted fire atmospheres. The second sample was collected into a cleaned Summa™ canister which had previously been used exclusively for the collection of outdoor ambient air. Total VOC's found were 28 ppb (SD=±0.95 ppb) and 57 ppb (SD=±0.90 ppb), respectively. There were no trends showing a gain or loss of VOC's and there was no significant difference in variance, at the 95% confidence level, between samples stored in a previously cleaned fire canister (Figure 29A) and samples stored in an ambient air canister (Figure 29B) over a 3-month period. The stability of low levels of VOC's found in outdoor ambient air samples confirmed that there was no significant adsorption or desorption of analytes onto the walls of the Summa™ canisters.

Fire analysis standard calibration mixture

A survey sample from a 10-minute experimental fire of burning gasoline and wood was collected in a Summa™ canister. An aliquot was withdrawn from the canister and the components were separated by gas chromatography with the mass selective detector operated in SCAN mode (Figure 30A). The total mass spectrum was obtained for each of the resulting peaks and identified by comparison with spectra found in the NIST (1992) mass spectral library. The products of combustion were found to be a complex mixture of alkanes and alkenes resembling the pollutants found in city, outdoor, ambient air, supporting the conclusion that outdoor pollution is largely the result of the burning of combustible materials such as wood

Figure 29. The stability of selected chemicals found in urban ambient air collected into (A) a clean Summa™ canister and (B) a thoroughly cleaned canister that had been used to collect a fire sample. No significant changes were noted in the concentrations of the chemicals following analysis.

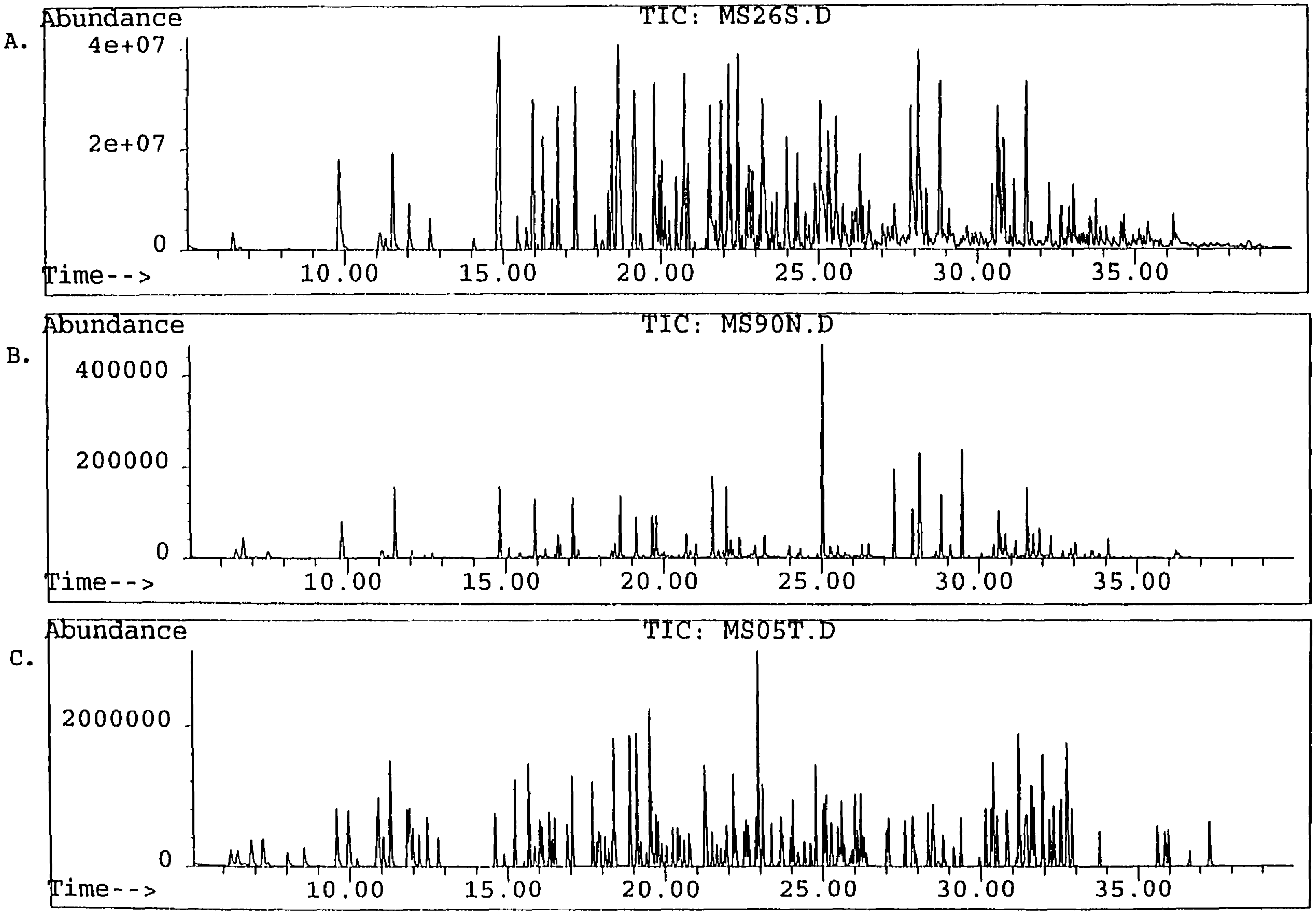
29



A. Clean Summa Control Canister

B. Cleaned Summa Fire Canister

Figure 30. Chromatograms of (A) a wood/gasoline fire sample, (B) an ambient air sample and (C) a standard mixture, illustrating that compounds found in both of the air samples were also present in the 144-compound standard calibration mixture.


A.
Abundance
TIC: MS26S.D
4e+07
2e+07
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
B.
Abundance
TIC: MS90N.D
400000
200000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
C.
Abundance
TIC: MS05T.D
2000000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

and fossil fuels (Figure 30B). This same standard mixture of 144 chemicals was used for the fire studies. As can be seen, the components in the standard mixture covered the spectrum, molecular masses (114-258 amu) and retention times (6-38 min) of components detected in fire samples (Figure 30C). These substances included alkanes and alkenes having three to 10 carbon atoms, halogen-substituted compounds and lighter weight semi-volatile compounds such as naphthalene.

Fire sample stability

Potentially highly polluted and reactive fire samples were found to be very stable in Summa™ canisters. Fire samples, where the concentration of VOC's was approximately 1500-fold higher than that found in outdoor ambient air, were found to be surprisingly stable. Figure 31 shows the results of repeated analysis of VOC's in Summa™ canisters for six compounds over a period of six months. Total VOC's found were 49 ppm (SD=±0.6 ppm). There were no trends showing a gain or loss of individual, representative analytes over this sample storage period.

Canister Filling and Dilution

The Matheson™ flow meter, used for calibration of flow controllers attached to Summa™ canisters, was itself calibrated, quadruplicate readings being taken with a electronic Gilibrator™ bubble meter used as a primary standard (Figure 32). It was found that Millaflow™ mechanical flow controllers could be adjusted to maintain a constant flow rate (±10%) for sampling periods of 15 to 40 minutes during which time, the evacuated canisters filled to approximately one half their volume (Figure 33). Due to their weight and cumbersomeness when attached to Summa™ canisters on the firefighters' belt, the flow controllers were not consistently used for the collection of fire samples, samples being obtained only with the use of the sintered filter. Such canisters filled to atmospheric pressure within a few seconds of opening the canister valve.

Field samples were diluted by pressurizing them in the laboratory to 30 psig

Figure 31. The stability of selected chemicals from a fire sample stored in a Summa™ canisters, the analyses being done repeatedly for a period of six months. No significant changes in chemical concentrations were observed in this time period.

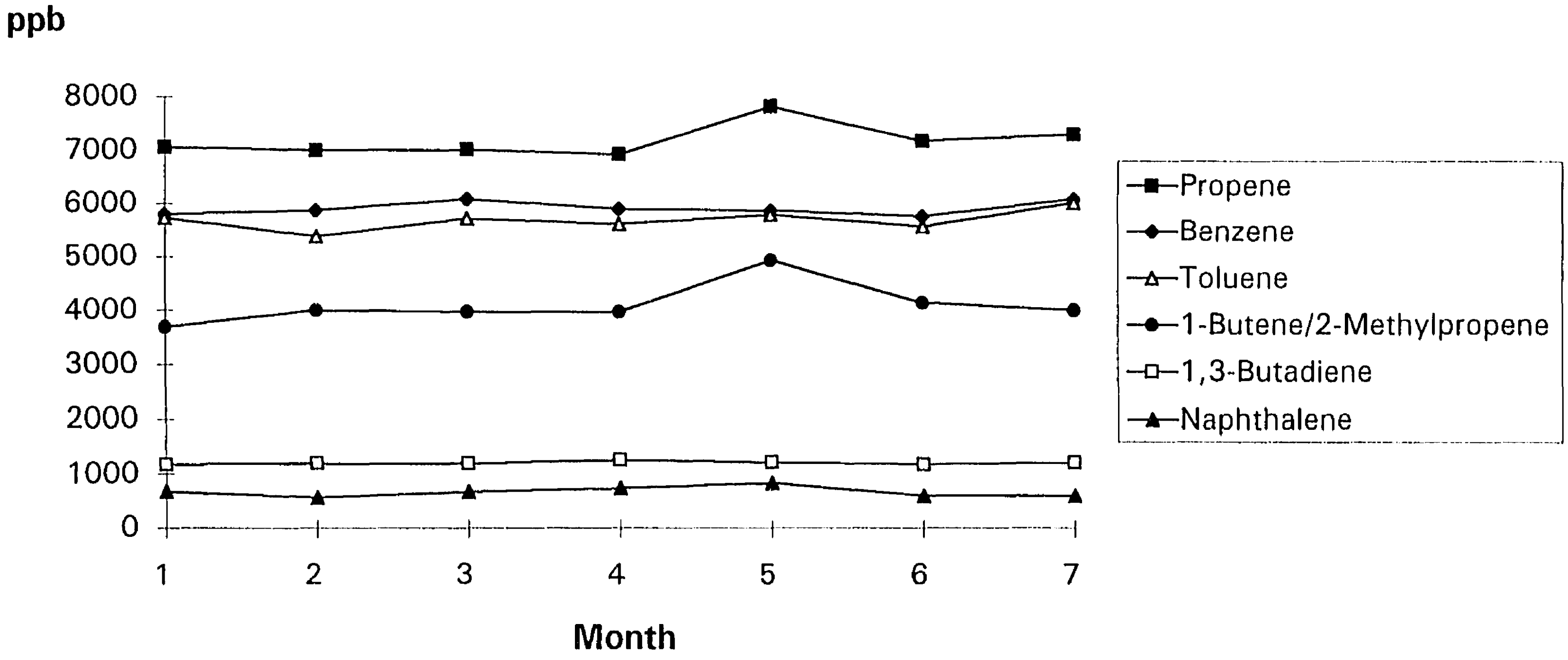

ppb
8000
7000
6000
5000
4000
3000
2000
1000
0
1
2
3
4
5
6
7
Month
Propene
Benzene
Toluene
1-Butene/2-Methylpropene
1,3-Butadiene
Naphthalene

Figure 32. Calibration of Matheson™ mass flow meters for the ranges of (A) 0-10 mL/min, and (B) 0-100 mL/min. against a Gilibrator™ soap-film bubble electronic flow meter, showing linearity over the rates of flow.

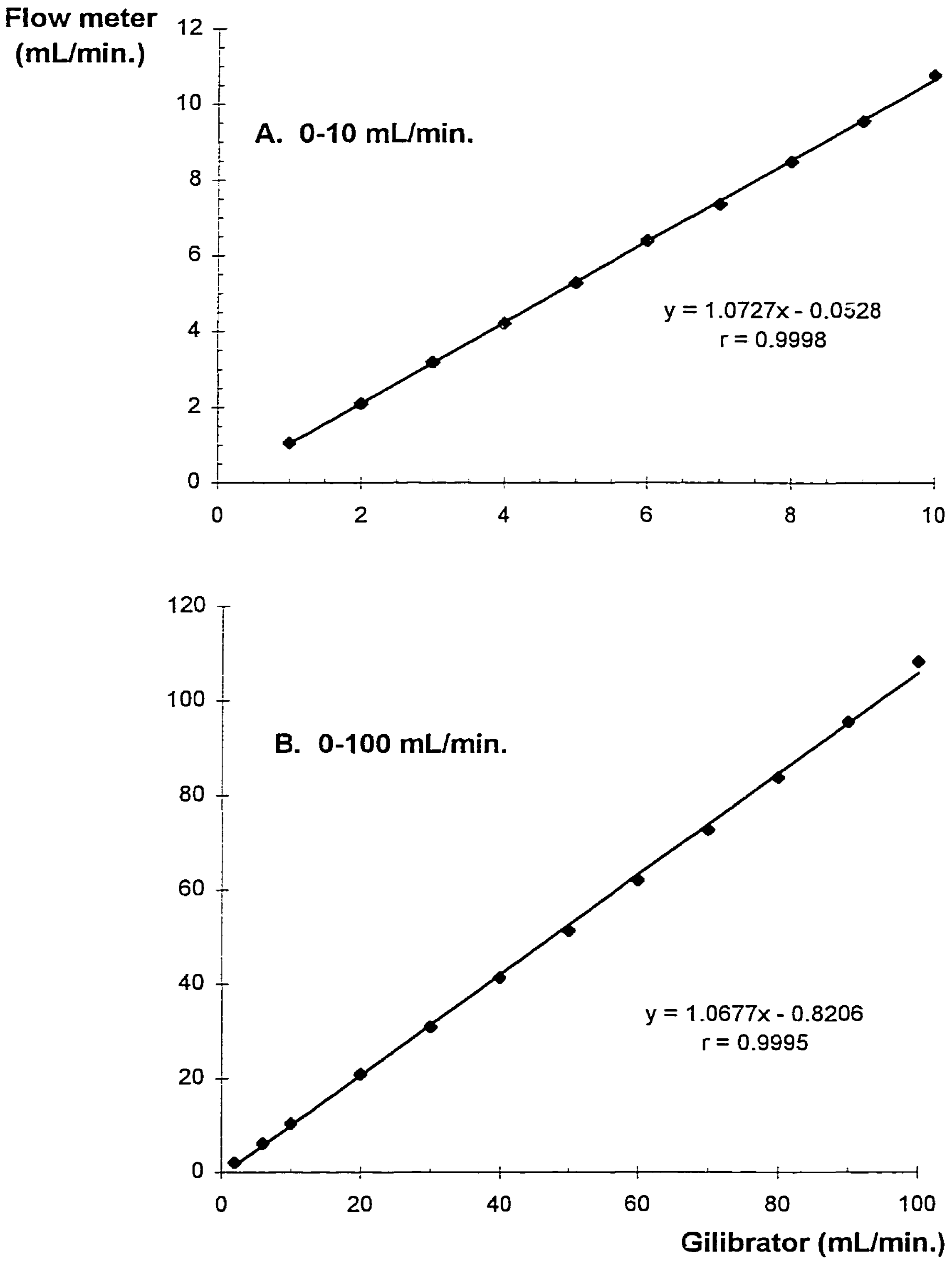
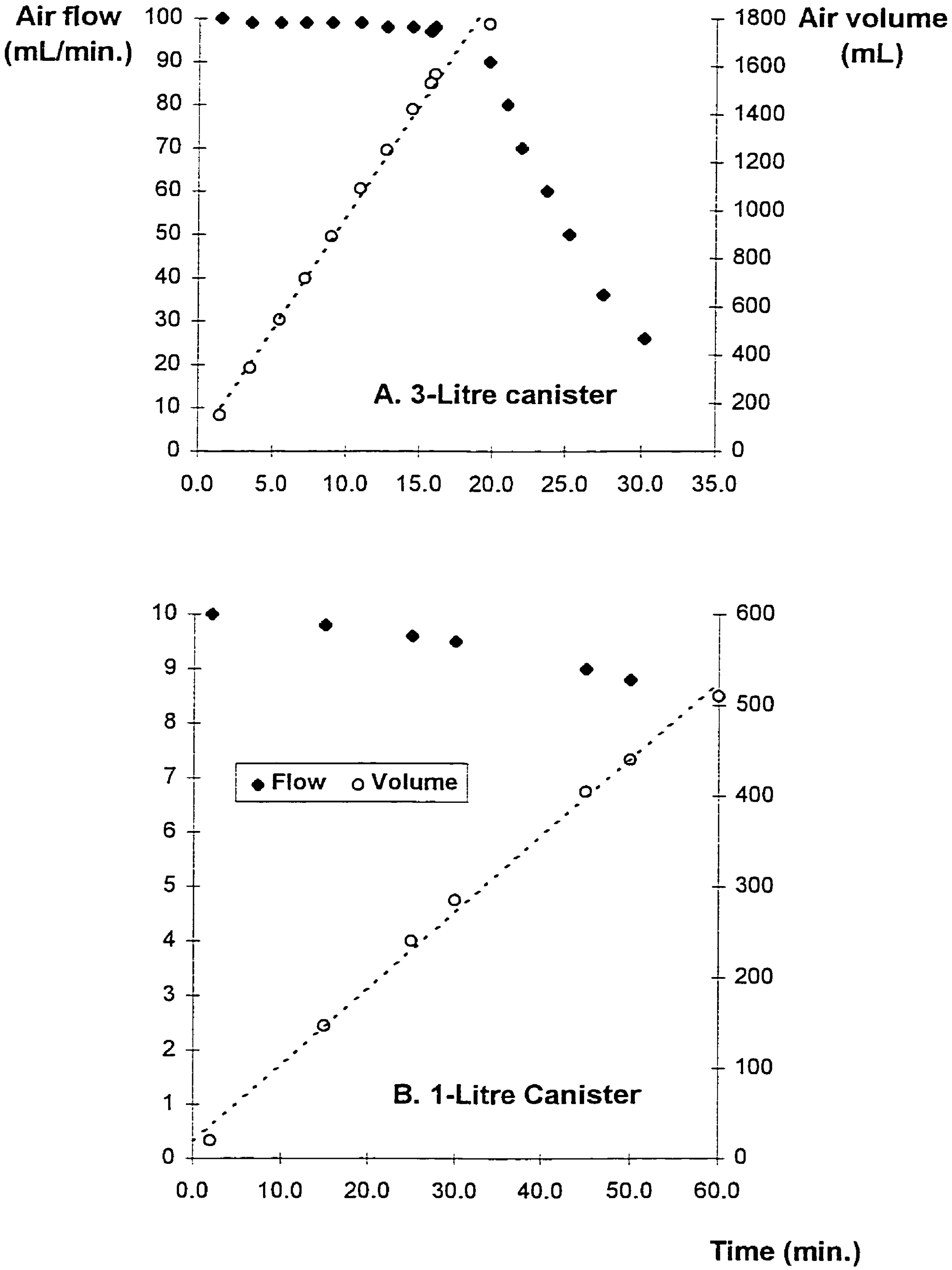

Flow meter (mL/min.)
A. 0-10 mL/min.
y = 1.0727x - 0.0528
r = 0.9998
0
2
4
6
8
10
12
0
2
4
6
8
10
B. 0-100 mL/min.
y = 1.0677x - 0.8206
r = 0.9995
0
20
40
60
80
100
120
0
20
40
60
80
100
Gilibrator (mL/min.)

Figure 33. Calibration of Matheson™ mechanical flow controllers fitted to (A) 3-litre and (B) 1-litre evacuated Summa™ canisters showing constant flow rates maintained over the expected 15-minute sampling periods.


Air flow (mL/min.)
100
90
80
70
60
50
40
30
20
10
0
1800
1600
1400
1200
1000
800
600
400
200
0
Air volume (mL)
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
A. 3-Litre canister
10
9
8
7
6
5
4
3
2
1
0
600
500
400
300
200
100
0
◆ Flow ○ Volume
B. 1-Litre Canister
0.0
10.0
20.0
30.0
40.0
50.0
60.0
Time (min.)

with purified humid air. A pressurized sample was necessary in order to be able to withdraw aliquots from the canister. Dilution with purified air lowered, by a factor of three to ten, the concentration of target compounds which were expected to be present at levels exceeding the calibration range of the method. Dilution factors, at STP were calculated based on the initial sample pressure and the final dilution pressure of the canisters. Flow rate and fill time were used as a cross check of calculations. The relationship between canister pressure and volume was determined by filling evacuated 1- and 3-litre Summa™ canisters with purified humid air at STP until reaching a final pressure of 30 psig. The fill rate, 200.0 ml/min., was controlled by a Matheson™ mass flow controller and time and pressure were recorded at regular intervals. The times determined from three successive fillings were used to calculate the volume of air delivered for different canister pressures. The relationship between canister volume and pressure was found by linear regression, separate graphs being plotted for pressures above and below atmospheric pressure (Figure 34). Correlation coefficients were greater than or equal to 0.999 in all cases and the regression equations found were:

Under vacuum:	1-Litre canisters	mL = 35.78 x mm Hg + 1019
	3-Litre canisters	mL = 94.48 x mm Hg + 2704
	6-Litre canisters	mL = 202.3 x mm Hg + 5804
Above atmospheric pressure:	1-Litre canisters	mL = 66.25 x psi + 1031
	3-Litre canisters	mL = 198.60 x psi + 2697
	6-Litre canisters	mL = 419 x psi + 5804

Sampling precision

The sources of variability (described by the overall method precision of ±23%) of the modified U.S. EPA TO-14 method when used for the analysis of VOC's found in municipal structural fires, are summarized schematically in Figure 35. Four components of the sampling precision were investigated: (1) the precision attributable to the sampling device itself; (2) the variability attributable to sampling of experimental fires canisters; (3) the variability attributable to sampling

Figure 34. Graphs showing the linear relationships of volume vs. pressure for (A) 3-litre and (B) 1-litre Summa™ canisters during pressurization with dilution air.

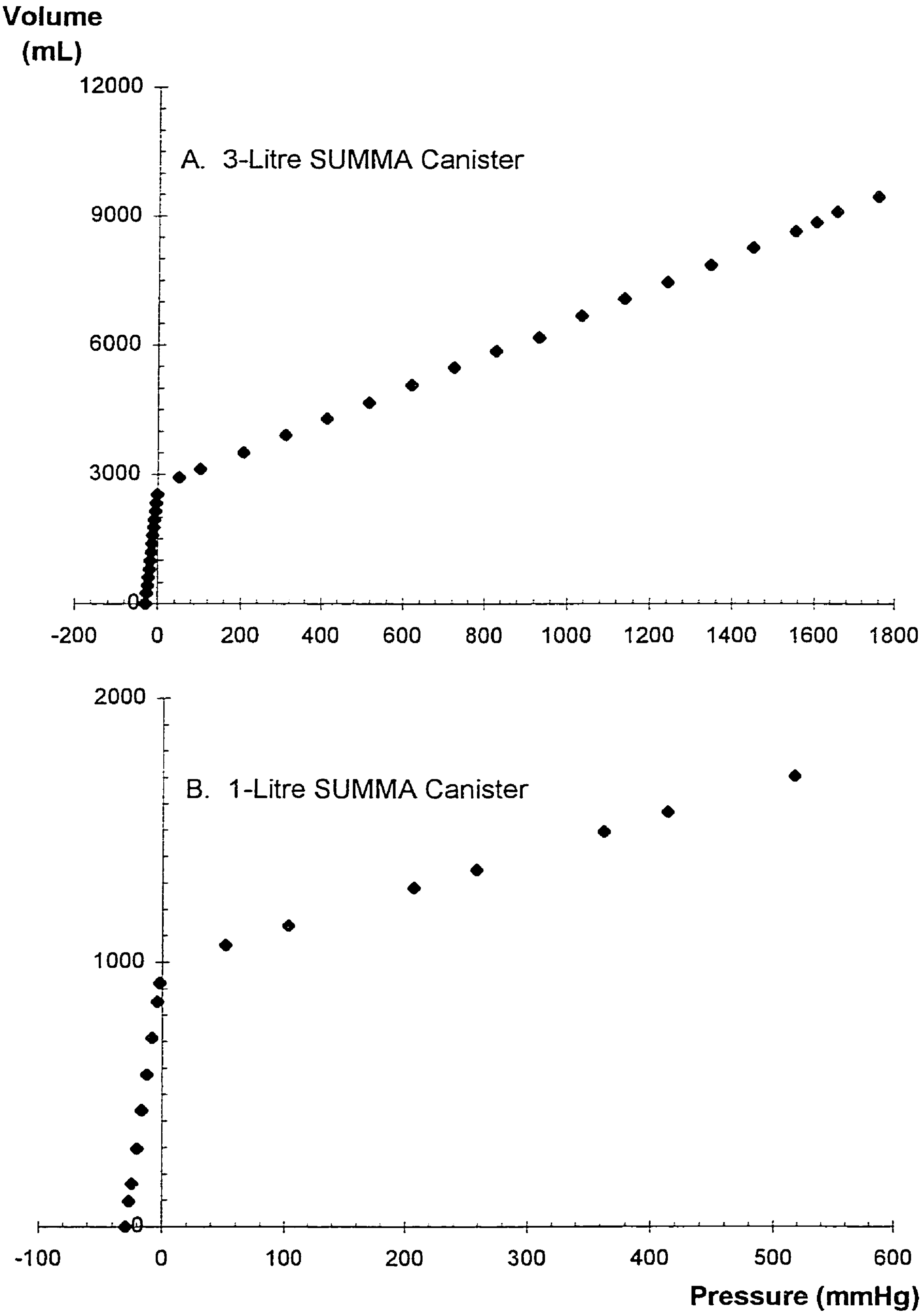
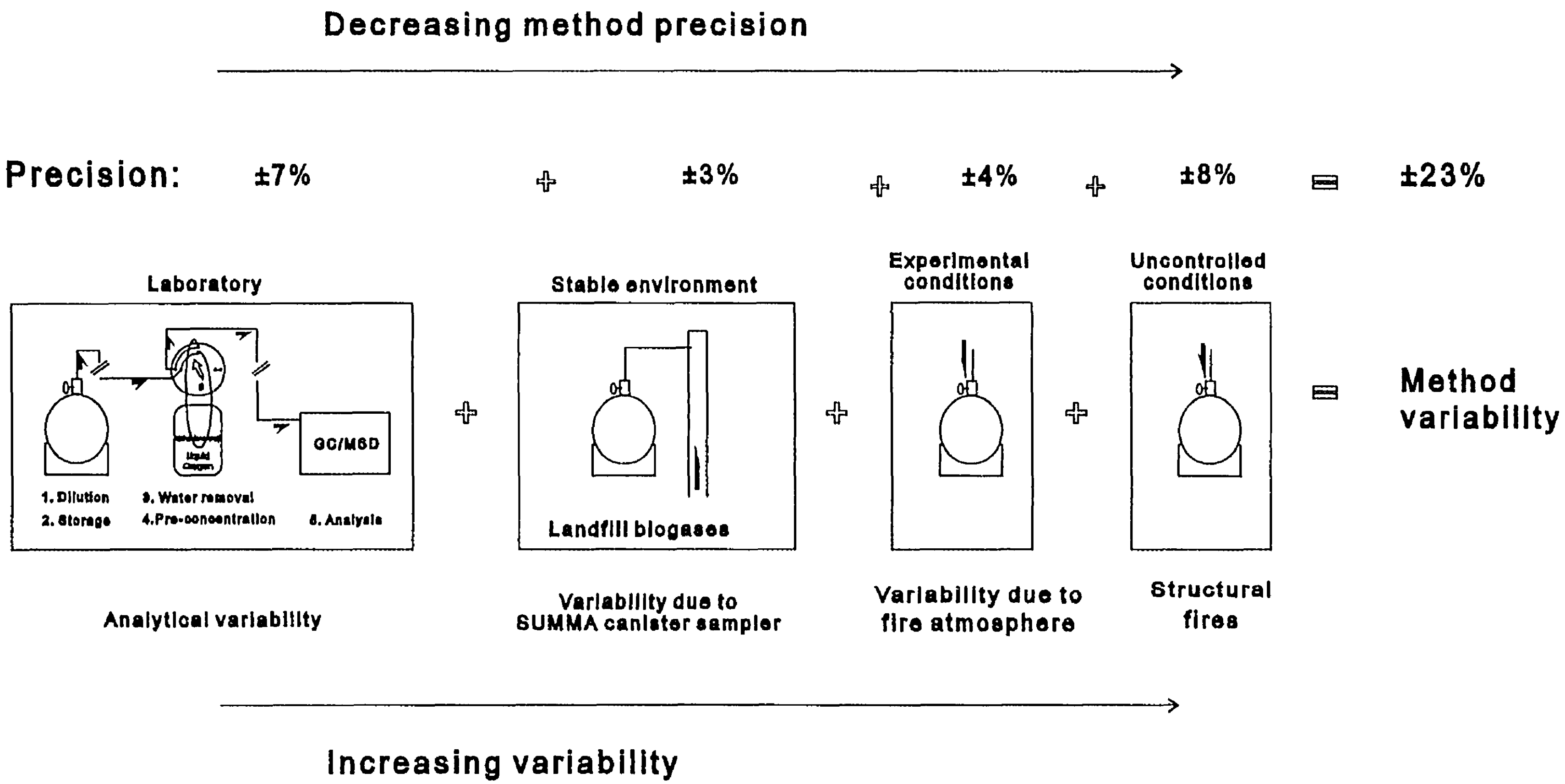

Volume
(mL)
12000
9000
6000
3000
0
A. 3-Litre SUMMA Canister
-200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
1000
0
B. 1-Litre SUMMA Canister
-100
0
100
200
300
400
500
600
Pressure (mmHg)

Figure 35. Components of potential variability in a method for the analysis of VOC's in fire samples including that attributed to analytical instrumentation, Summa™ canister sampling, to the dynamics of a fire under controlled and uncontrolled conditions. Calculated estimates of variability from all sources are no greater than ±23%. See text, pages 162-166 for details of calculations.



Decreasing method precision

Precision: ±7% + ±3% + ±4% + ±8% = ±23%

Laboratory + Stable environment + Experimental conditions + Uncontrolled conditions = Method variability

Analytical variability

Variability due to SUMMA canister sampler

Variability due to fire atmosphere

Structural fires

Increasing variability

real-life municipal fires; and (4) the variability attributable to the use of 1-litre canisters instead of the standard 3-litre canisters normally used in ambient air studies. To evaluate the precision of the Summa™ canister sampler, field samples were taken from an environment which was expected to show little variability over time. The landfill gas (LFG) collector pipe at a municipal sanitary landfill site was chosen for this purpose because the levels and spectrum of VOC's found in LFG were similar to those exhibited in fire samples. An increase in sampling variability was expected for fire atmospheres due to the rapidly changing dynamics of fires, including changes in combustion products with time, temperature changes leading to air movement and atmospheric chemical reactions between combustion products. A further increase in sampling variability might be expected in structural fires due to different materials, different rates of burning and different combustion products as well as firefighter intervention.

The use of the Summa™ canister sampling device was not found to be an important source of error for the measurement of VOC's in field samples. It was known that the range and levels of VOC's found in LFG were comparable to those found in fire samples. Unlike fire atmospheres, however, there was little variability in the concentration of VOC's over time, making the analysis of landfill samples ideal for the evaluation of the magnitude of the error attributable to the Summa™ canister sampler. Summa™ canister samples were collected in duplicate (n=10) by Environment Canada personnel from the header of a gas collection system just before the suction fan at a municipal waste landfill site. The paired Student's *t*-test and the F-test found no significant differences in means or variances between the duplicate landfill samples and the average precision of the determinations was ±11% rsd, exceeding the previously determined intra-day analytical precision by 3%.

Summa™ canister samples were collected in 1-litre canisters at the same time marks on different days but under identical experimental conditions by firefighters at experimental fires burning varsol. The paired Student's *t*-test and the

F-test found no significant differences in means or variances between these fire samples. The precision of these determinations, estimated at ±15% rsd, exceeded that found for the landfill site samples. The additional 4% error found under experimental fire conditions was attributed to air movements and to the changing dynamics of the fire atmospheres due to chemical reactions.

Replicate sampling of a municipal structural fire with three 1-litre Summa™ canisters and three 3-litre canisters (placed next to each other and opened within 30 seconds of each other) showed no difference in variability between the 1-litre and the 3-litre canisters (Table 19). The precision of these determinations, estimated at ±23%, exceeded that found for the experimental fires. It was concluded that the increased number of variables in structural fires where samples were collected under non-experimental conditions introduced an additional error of approximately 8%. The overall method precision of ±23% rsd found when sampling fires is an average for all 144 target compounds. In the case of the 14 compounds which will subsequently be shown to be of importance in municipal fires (propene, benzene, the xylenes, 1-butene + 2-methylpropene, toluene, propane, 1,3-butadiene, 2-methylbutane, ethylbenzene, naphthalene, styrene, cyclopentene, 1-methylcyclopentene and isopropylbenzene), the mean sampling precision was estimated to be ±12% rsd (Table 19).

Table 19. Method precision when sampling municipal structural fires

	1-Litre Canisters (n=3)		3-Litre Canisters (n=3)	
	Mean ± SD (ppm)	% rsd	Mean ± SD (ppm)	% rsd
Total VOC's (144 cpds)	41 ±9	±22%	53 ±13	±24%
Total selected VOC's (14 cpds)	22 ±3	±13%	28 ±3	±11%

B. EXPERIMENTAL FIRES

1. Qualitative Analysis

Experimental fires were burned in one corner of an enclosed, concrete basement (9 x 9 x 2.2 metres) of an abandoned, two-storey brick house as is shown in Figure 36, a fire being set with cardboard material. Two people wearing SCBA's (Figure 37) remained in the basement during the experiments while a third remained outside to signal the time marks. A light was located on the ceiling in the corner opposite the fire and Summa™ canisters were placed below this light, approximately one metre above the floor. The area was ventilated for approximately 15 minutes prior to experiments, at which point a field blank was collected. Experimental fires were allowed to burn for 15 minutes during which time smoke progressively filled the room. Figure 38 shows the experimental set-up used for a fire burning spruce wood pallets, including the ceiling light and the position of canisters for sampling. "Grab" samples (canisters filling to atmospheric pressure in approximately 20 seconds) were collected at the 2-, 5-, 10- and 15-minute time marks following ignition of the fire. Photographs of both the fire and the light were taken simultaneously with the collection of ambient air into Summa™ canisters at the 2-, 5-, 10- and 15-minute time marks for all 15 experimental fires. The entire area was ventilated and washed down with water from a fire hose following the experiment, at which point a final sample was collected.

Analysis of field blanks revealed approximately 100 ppb total VOC's, half of which was accounted for by the later-eluting or semi-volatile compounds (dodecane, undecane, decane and nonane) and isoprene. The remaining VOC's found did not exceed 1 ppb to 3 ppb. These substances would likely have arisen from the residue of experimental fires burned previously in that building. Although their concentration was approximately three times that found in outdoor ambient air, background levels were well below the ppm levels observed in experimental fires.

Figure 36. An experimental fire constructed of cardboard boxes (A), ignited in an enclosed space (B) in a cement basement of an abandoned brick house. Photographs were taken and Summa™ canister samples were collected at 2, 5, 10 and 15 minutes after ignition.

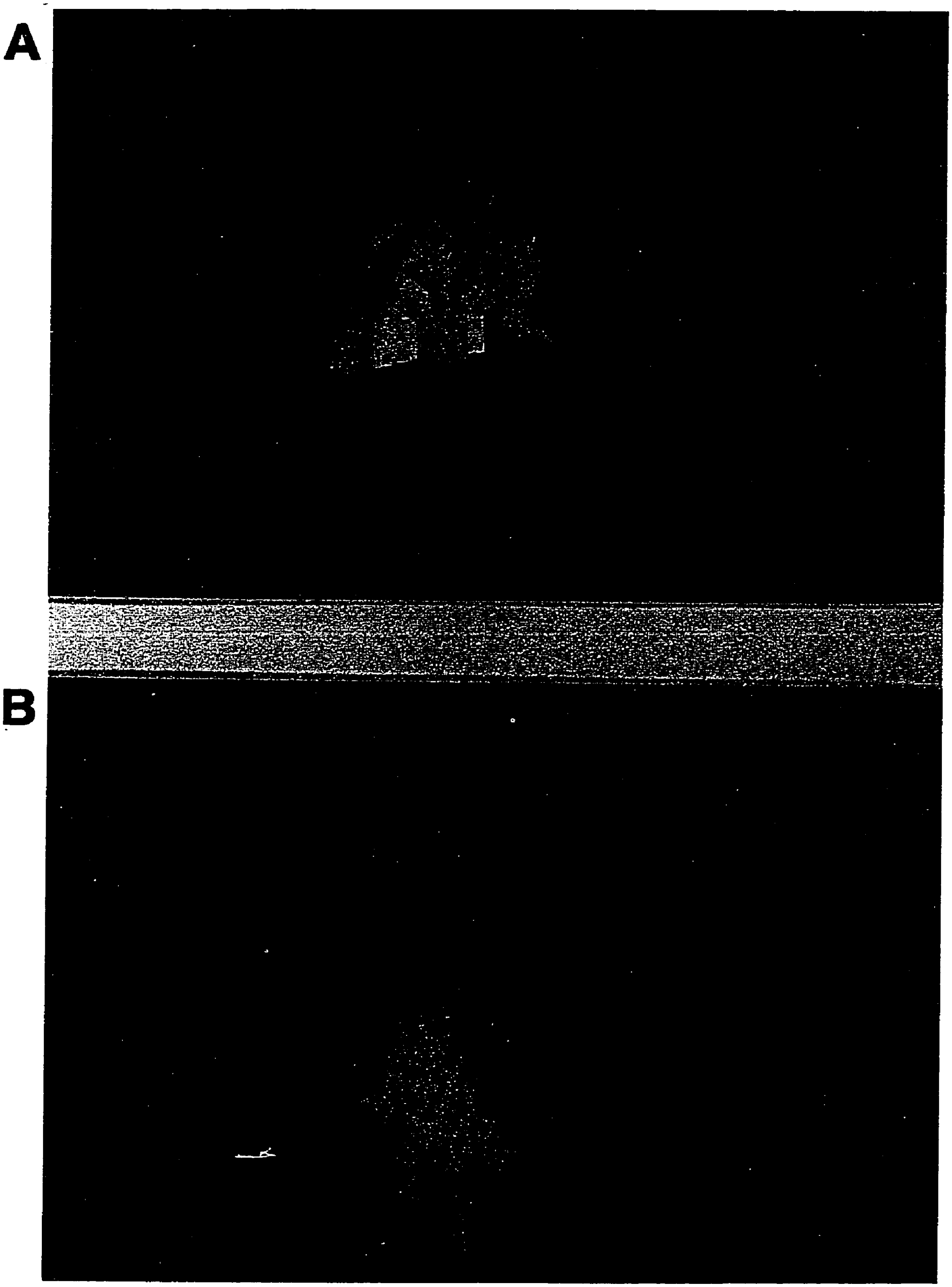

A
B

Figure 37. The equipment worn by firefighters collecting the samples during the experimental fires included bunker suits, protective helmets and self-contained-breathing-apparatus (SCBA).

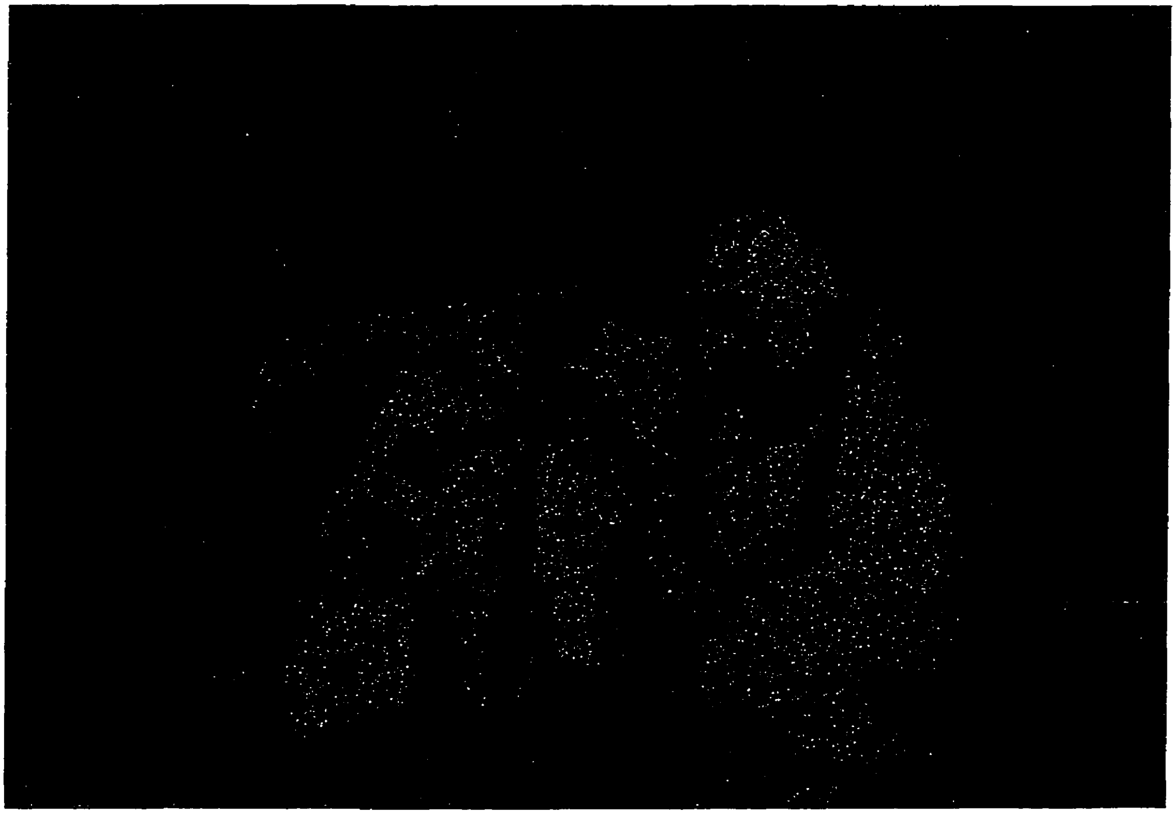


Figure 38. An experimental fire of spruce wood pallets (panels A and B), showing the density of the smoke as measured by the intensity of the light from a 60-Watt light bulb suspended from the ceiling, shown in panel C.

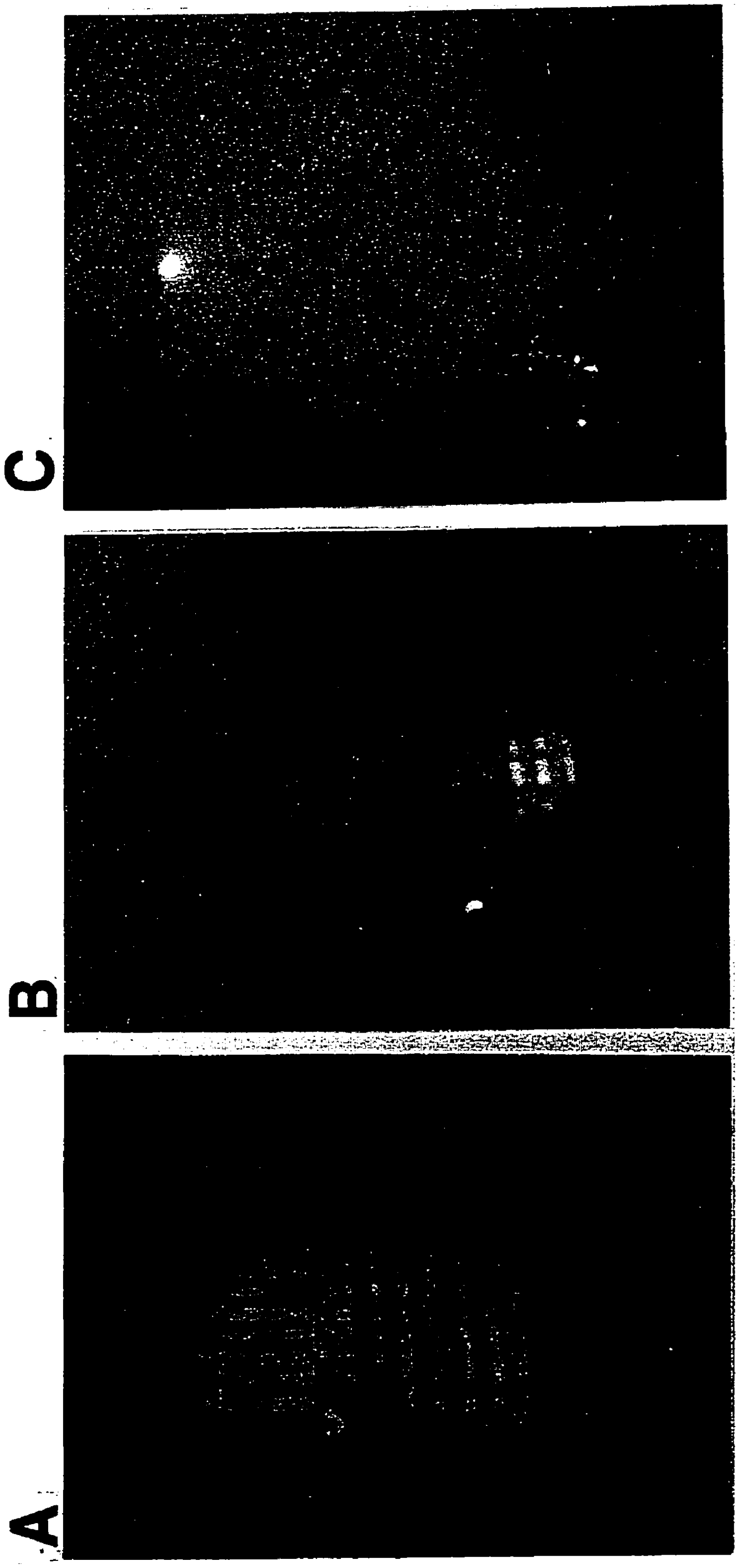

C
B
A

Figure 39 shows how the smoke, from a fire burning rigid, white foam insulation, progressively filled the room, the highest concentration being, initially, near the ceiling. Clear air at the 2-minute mark below a thickening layer of smoke in Figure 39C is a graphic illustration of why people are advised to keep their head low, crawling on their hands and knees, when exiting a burning building. Thick smoke from the burning, liquified foam completely filled the room after approximately three minutes. The progression of a rapidly burning gasoline fire and the associated smoke is illustrated by a series of paired photographs in Figures 40 and 41. The photographs show the density of the smoke around the fire and near the ceiling at five minutes (Figure 40) and at 10 minutes (Figure 41), eventually obscuring the light by 15 minutes following ignition of the fire.

Time-related appearance and disappearance of the products of combustion was observed in samples collected at all of the experimental fires. This is illustrated in Figure 42 with the chromatograms obtained from samples collected at the 5-, 10-, and 15-minute time marks at the same gasoline fire depicted in Figures 40 and 41. Initially, samples exhibited a higher concentration of the more volatile components such as the butanes, butenes and pentanes. Typically, the relative quantities of these substances decreased with time while that of the less volatile substances, notably naphthalene, increased.

Combustion products from different materials commonly found in municipal structural fires displayed a mixture of components. Figure 43 shows the chromatograms obtained from samples collected at the 10-minute mark for five different experimental fires ignited with spruce wood, a mattress, gasoline, varsol and white foam insulation. Several common peaks were observed for all of these combustible materials. To facilitate visual comparisons, these chromatograms were derived using CorelDraw™ v4.0 software, the internal standard peaks being removed to simplify them (Figure 44). Although the pattern of peaks seen (chromatographic "fingerprint") varied from one material to another, similarity in the nature of the combustion products generated by different materials was demonstrated by the

Figure 39. An experimental fire of solid, rigid, white foam insulation showing the initial stage (A), the burning of the melted foam (B), and the generation of layered smoke, that closest to the ceiling obscuring the light (C) at two minutes after ignition.

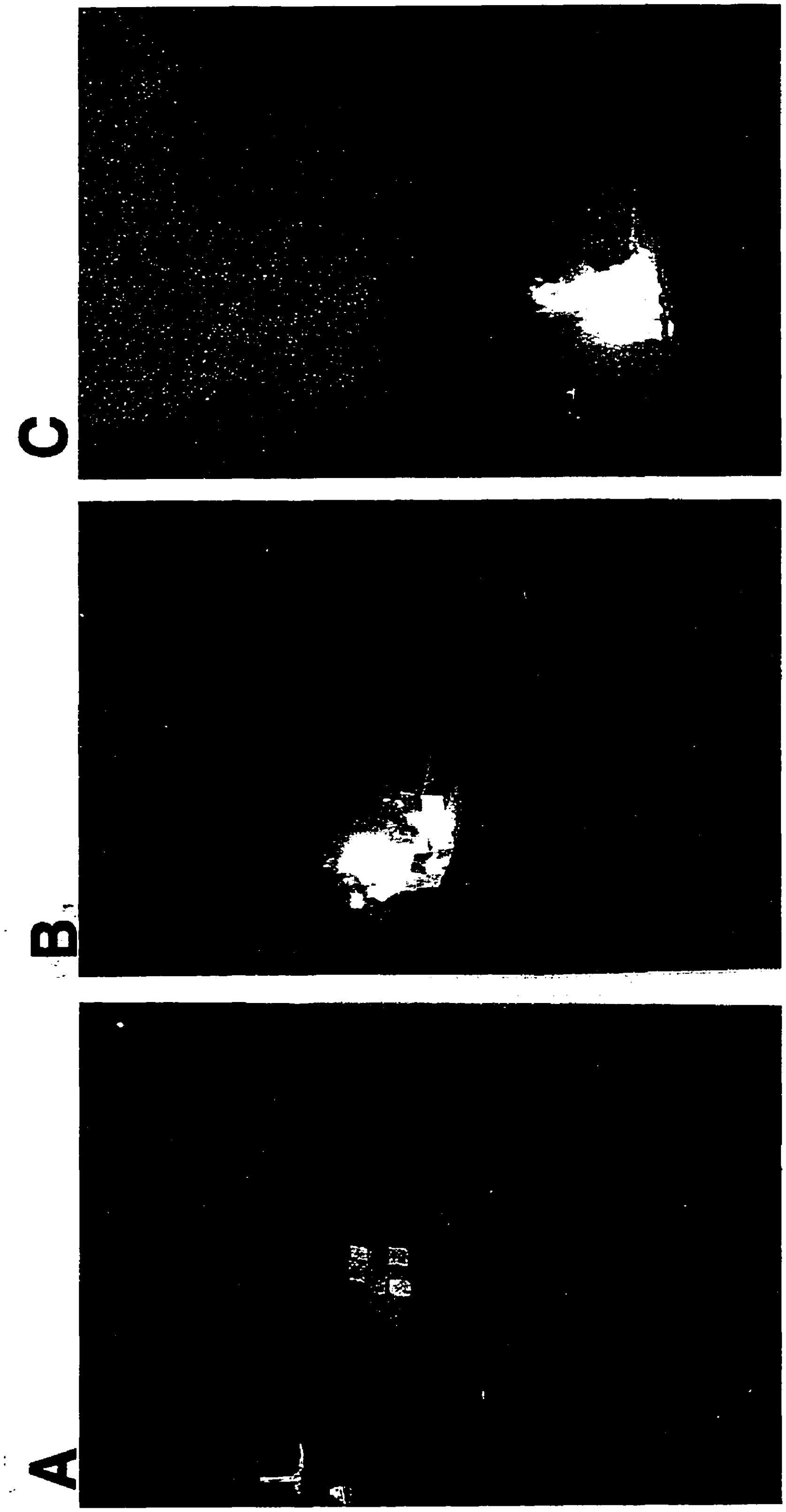

A
B
C

Figure 40. An experimental fire of gasoline (A) and the smoke produced (B) at five minutes after ignition, the smoke density almost obscuring the light.

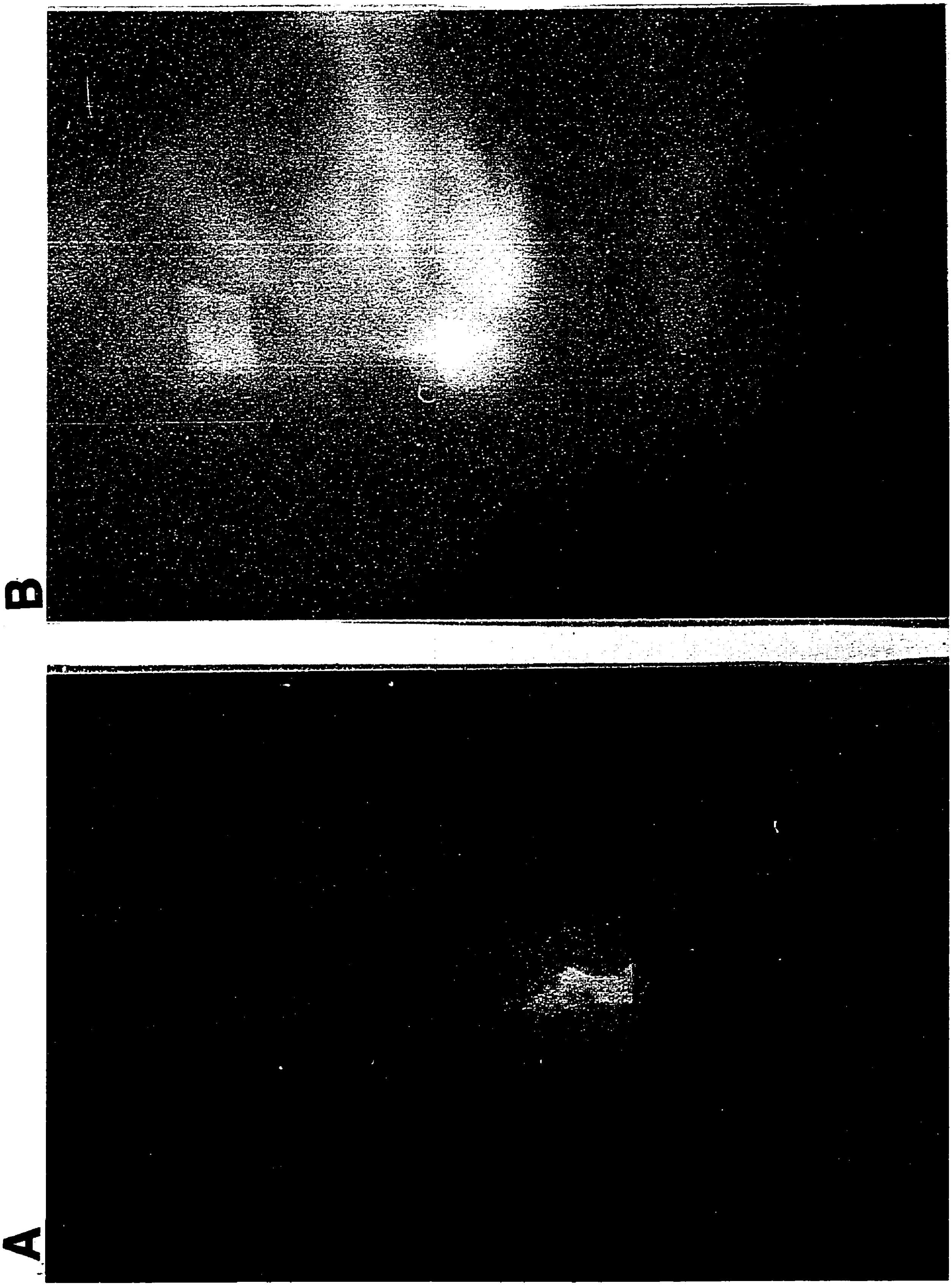

A
B

Figure 41. An experimental fire of gasoline (A) and the smoke produced (B) at 10 minutes after ignition, the light being totally obscured by smoke.

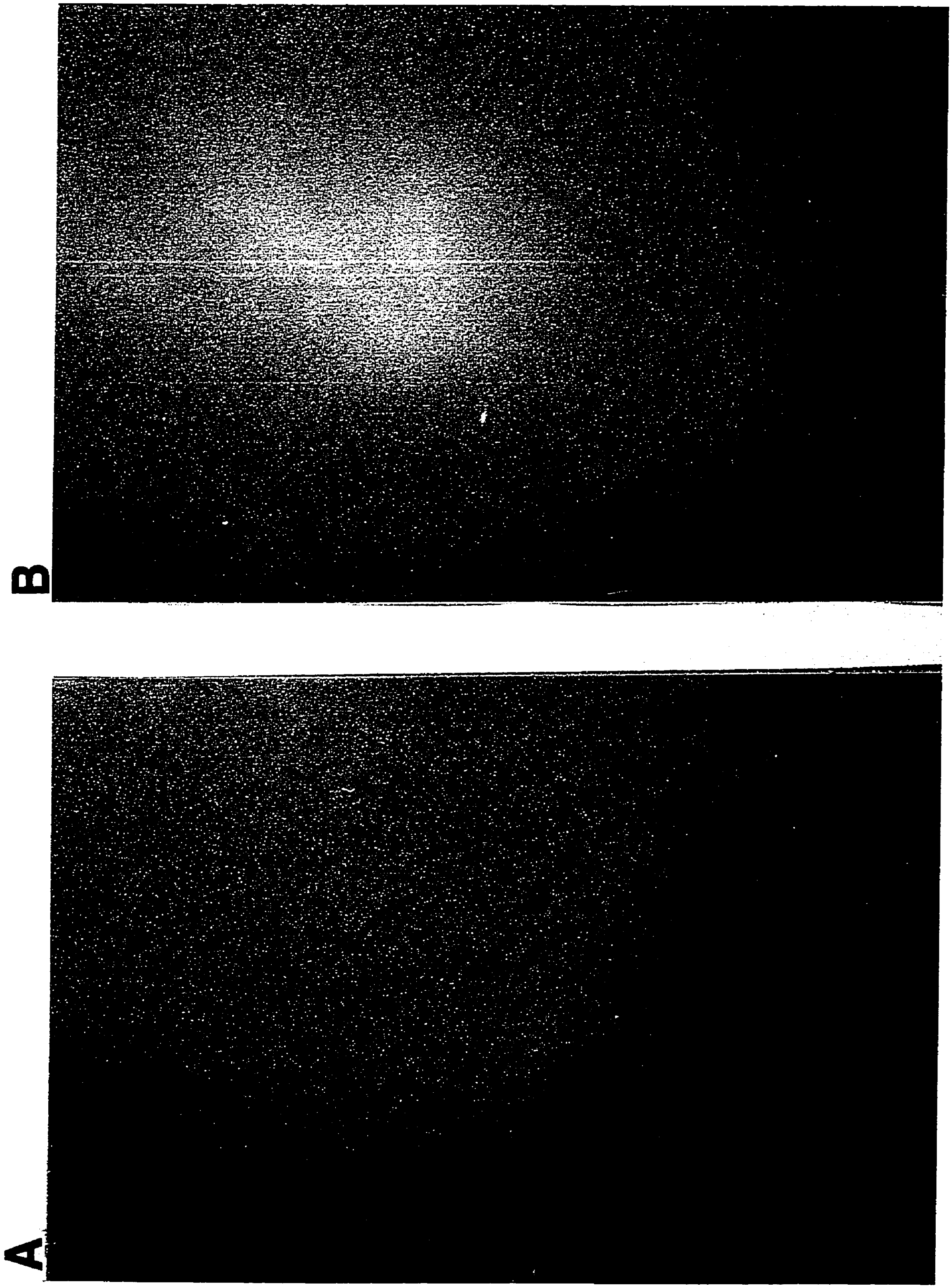
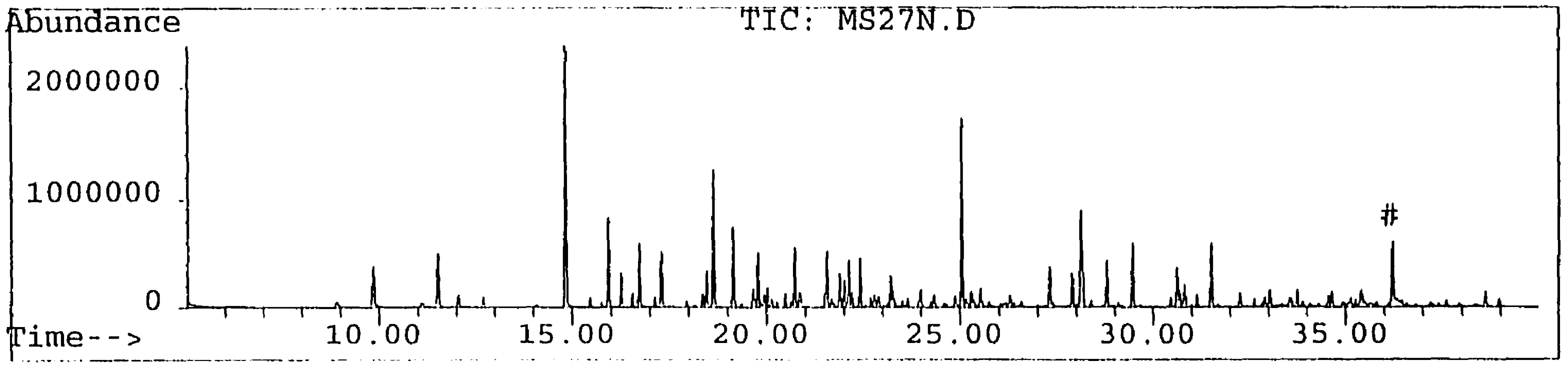
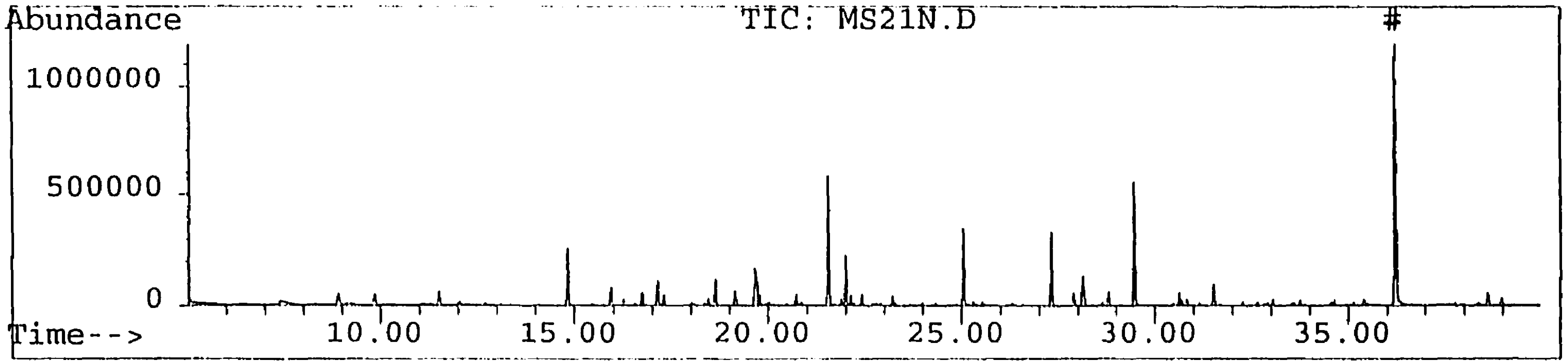

B
A

Figure 42. Chromatograms of air samples obtained at 5, 10 and 15 minutes after the ignition of the gasoline fire shown in Figures 40 and 41. The earliest sample (A) exhibited higher levels of the more volatile and earlier eluting compounds whereas in later samples (B and C), levels of the more volatile substances decreased and compounds with longer retention times increased, e.g. naphthalene as indicated by the pound sign (#).

A.


Abundance
TIC: MS27N.D
2000000
1000000
0
#
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

B.


Abundance
TIC: MS21N.D
#
1000000
500000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

C.

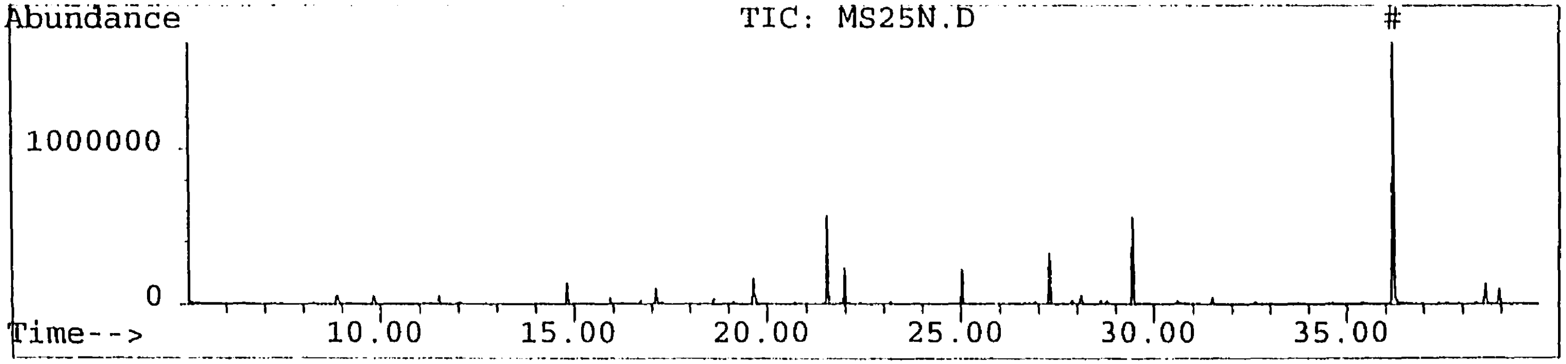
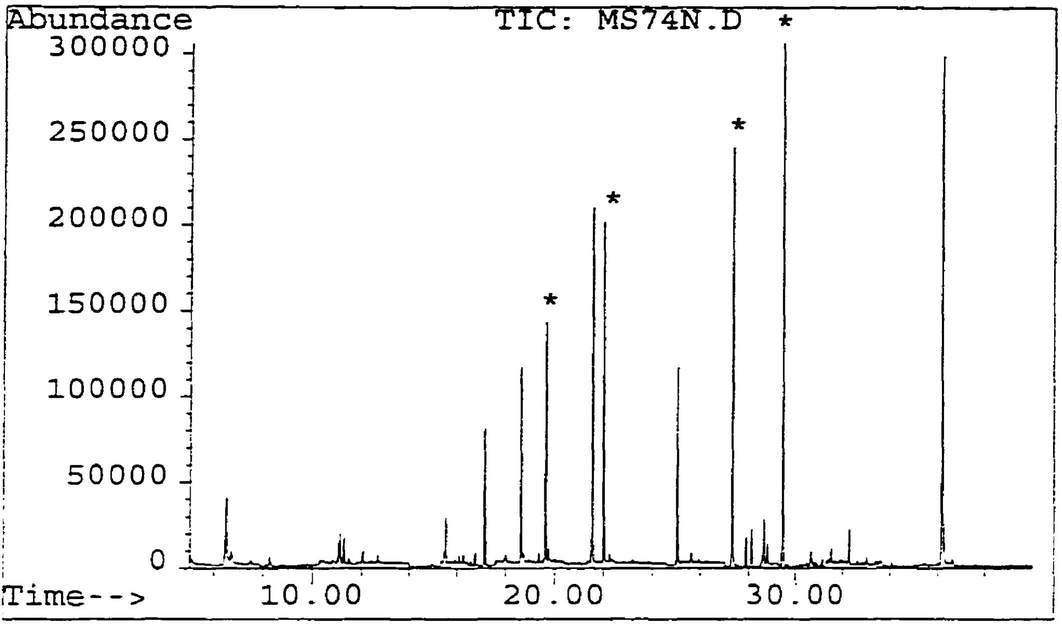

Abundance
TIC: MS25N.D
#
1000000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00

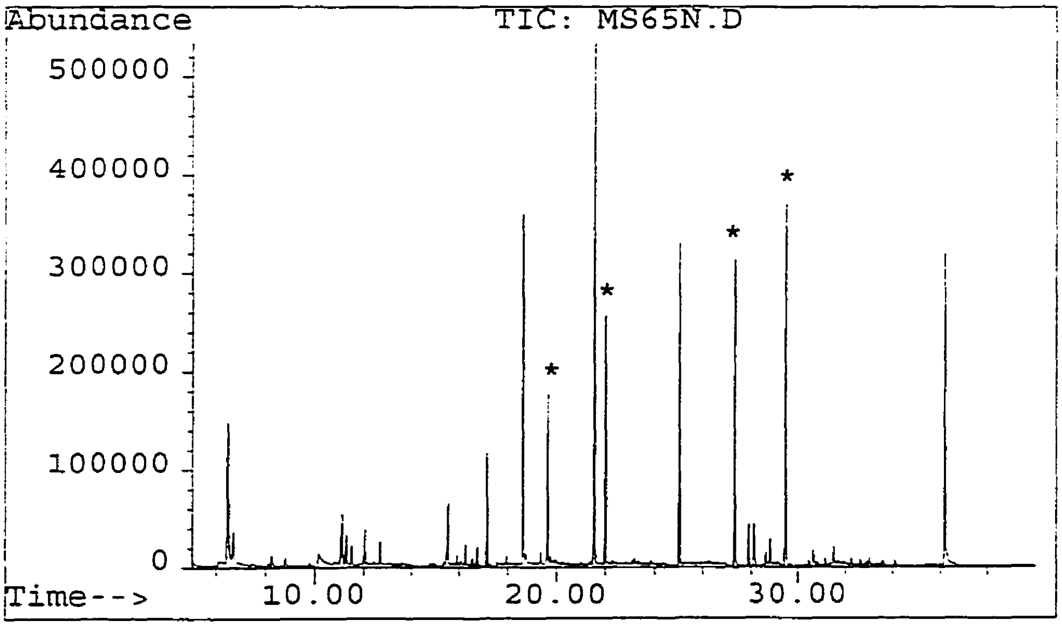
Figure 43. Chromatograms obtained at 10 minutes after the ignition of fires composed of: (A) spruce wood, (B) a mattress, (C) gasoline, (D) varsol; and (E) white foam insulation. Several common peaks were observed or all of these combustible materials. Asterisks indicate the internal standards normally added to samples prior to analysis.

43a

A.

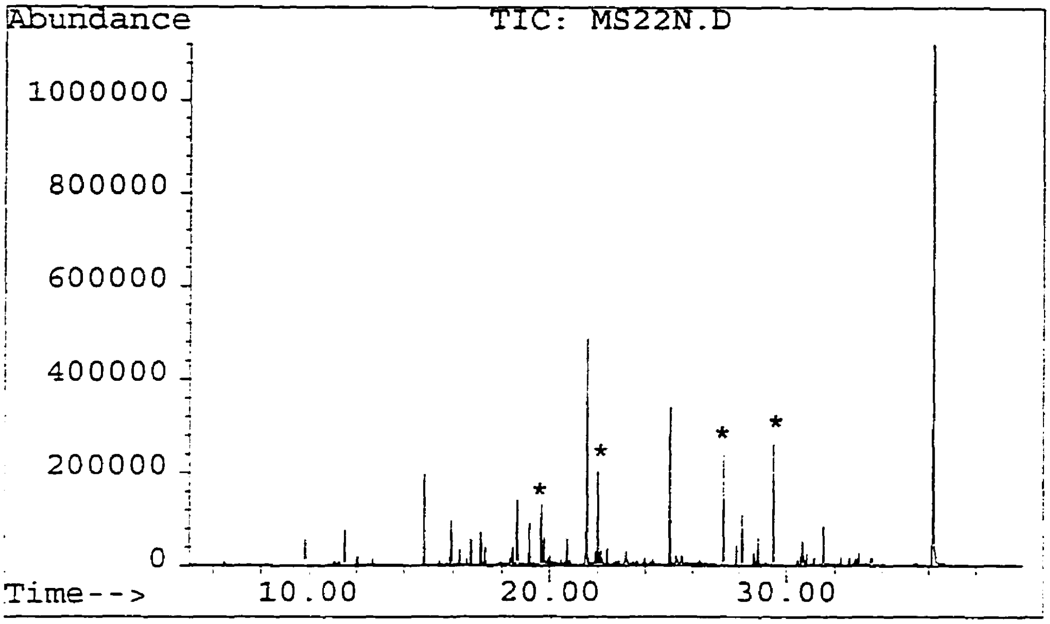

Abundance
TIC: MS74N.D
300000
250000
200000
150000
100000
50000
0
Time-->
10.00
20.00
30.00
*
*
*
*
*

B.

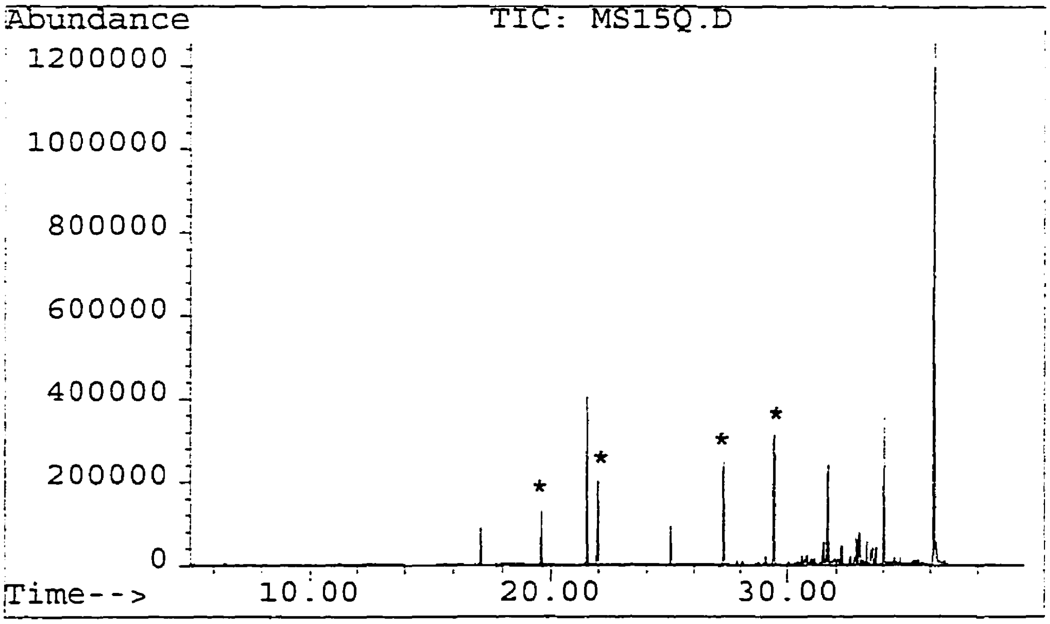

Abundance
TIC: MS65N.D
500000
400000
300000
200000
100000
0
Time-->
10.00
20.00
30.00
*
*
*
*
*

43b

C.


Abundance
TIC: MS22N.D
1000000
800000
600000
400000
200000
0
*
*
*
*
Time-->
10.00
20.00
30.00

D.


Abundance
TIC: MS15Q.D
1200000
1000000
800000
600000
400000
200000
0
*
*
*
*
Time-->
10.00
20.00
30.00

43C

E.

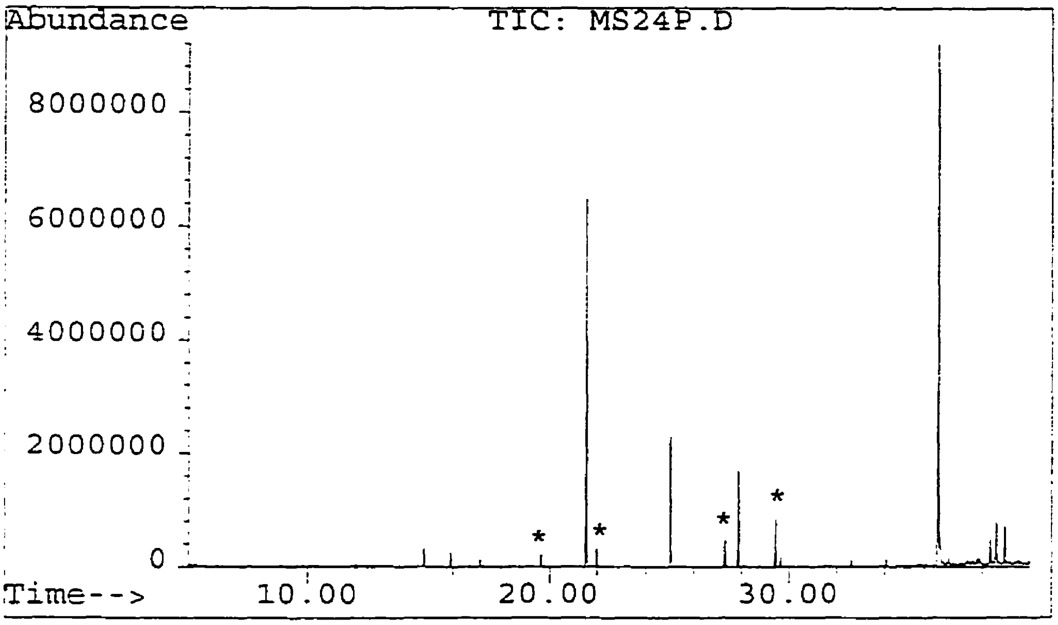
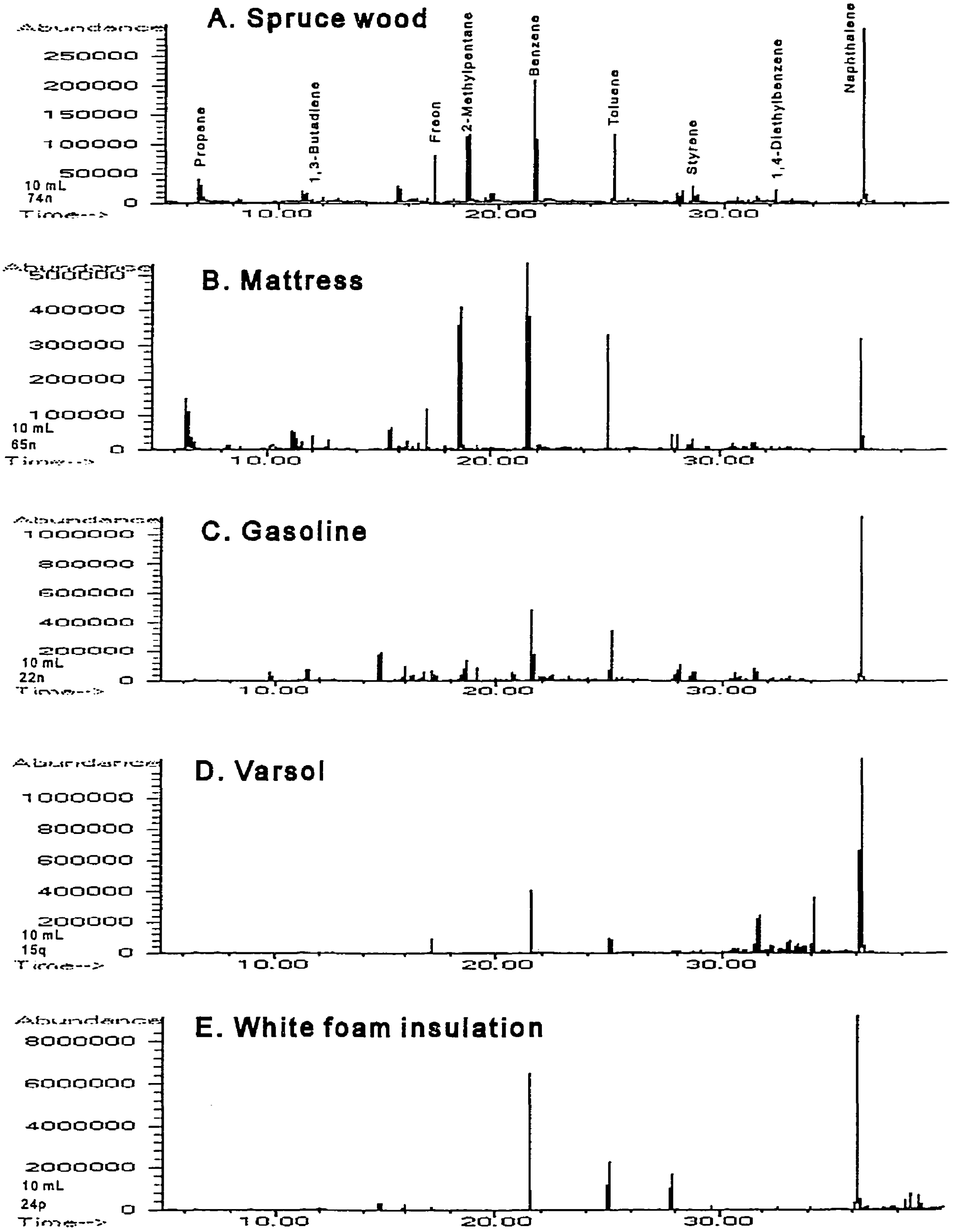

Abundance
TIC: MS24P.D
8000000
6000000
4000000
2000000
0
Time-->
10.00
20.00
30.00
*
*
*
*

Figure 44. Derived chromatograms (CorelDraw™ v4.0) of the major components of the 10-minute samples taken at the experimental fires of different combustible materials (Figure 43). The internal standards have been deleted to simplify comparisons. Propene, 1,3-butadiene, 2-methylpentane, benzene, toluene, styrene, 1,4-diethylbenzene and naphthalene were common to all of these fire samples.

10-MINUTE TIME MARK



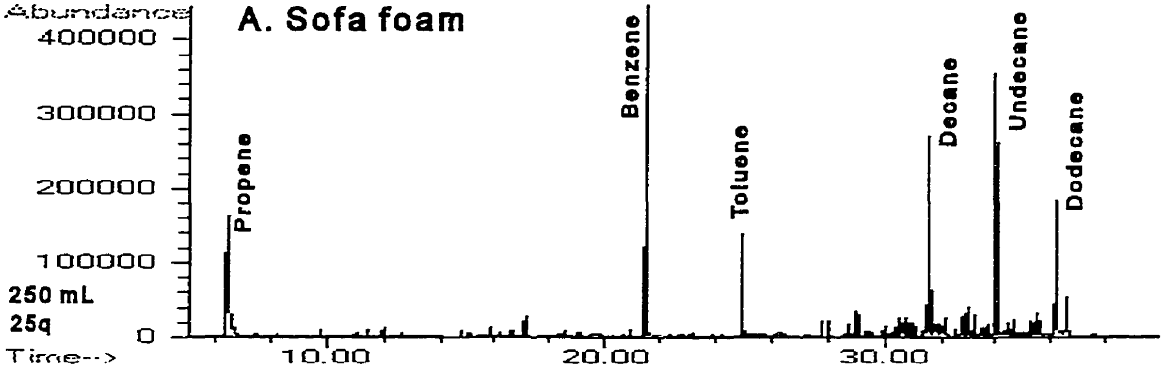
characteristic prevalence of the 2-methylpentane, benzene, toluene, and naphthalene peaks. Not surprisingly, isoprene (2-methyl-1,3-butadiene) was an important component found in samples obtained from burning spruce wood. Isoprene, which has been isolated from the pyrolysis of natural rubber, can also be prepared from turpentine found in the gum of pine trees (Merk, 1983). The derived chromatograms for plywood, cardboard and sofa foam are shown in Figure 45 for analysis of samples taken at the 15-minute mark. While these materials were observed to burn more slowly than other combustible materials, the combustion products were primarily 2-methylpentane, benzene and toluene. Naphthalene, was essentially absent, being replaced by decane, undecane and dodecane.

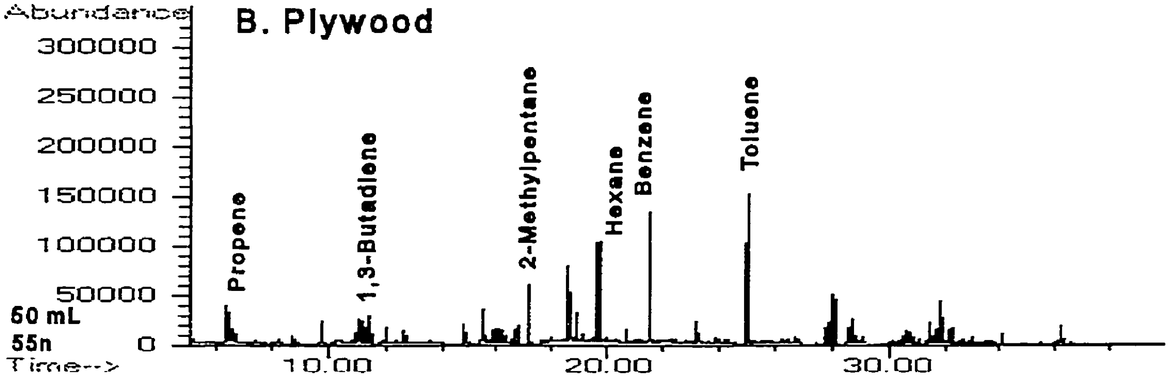
Analysis of chromatograms obtained from experimental fire samples suggests that: (1) it is possible to identify certain types of combustible materials by the distinctive "fingerprints" of their combustion products; (2) the components of the mixture of combustion products originating from any one material remain essentially constant, although their concentrations vary with the material burned and the duration of the burn; and, (3) regardless of the material being burned, the chromatograms of combustion products exhibit certain peaks, characteristic of decomposition in general (benzene and toluene) and of combustion in particular (naphthalene). This chromatographic "fingerprint" may be used to distinguish fire sample chromatograms from those deriving from other sources.

Derived chromatograms from, an outdoor ambient air sample, an LFG sample and a wood fire sample are shown in Figure 46. As has been noted previously, chromatograms originating from fire samples exhibited broad similarities to those obtained from outdoor ambient air and from landfill gas. A marked prevalent peak for toluene was observed with the three samples. Ambient air was characterized by a broad spectrum of peaks, including the butanes, pentanes, benzene, toluene, methyl- and ethyl- substituted benzenes and xylenes (Figure 46A). The LFG sample was characterized by a cluster of approximately 10 major peaks eluting after toluene, including octane, ethylbenzene, xylenes, nonane,

Figure 45. Derived chromatograms (CorelDraw™ v4.0) for fires from sofa foam, plywood and cardboard, the samples being taken 15 minutes after ignition. The combustion products were primarily 2-methylpentane, benzene and toluene. Naphthalene was absent, being replaced by decane, undecane and dodecane.

15-MINUTE MARK





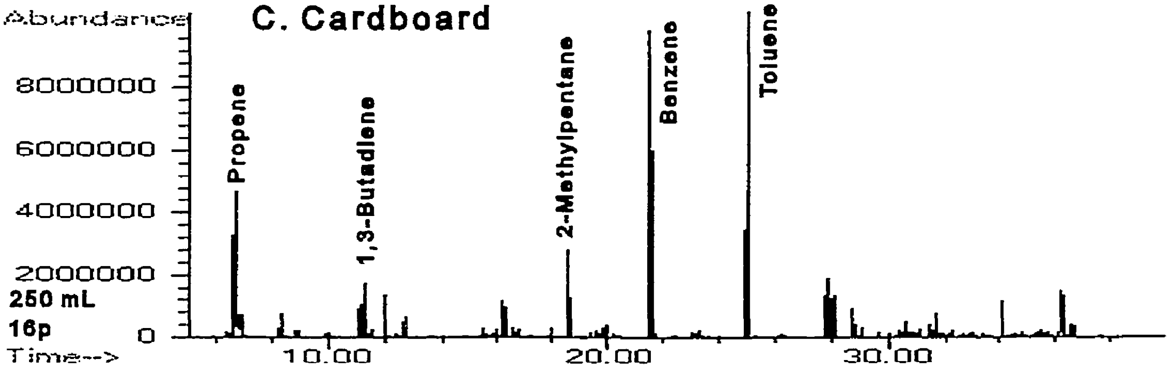
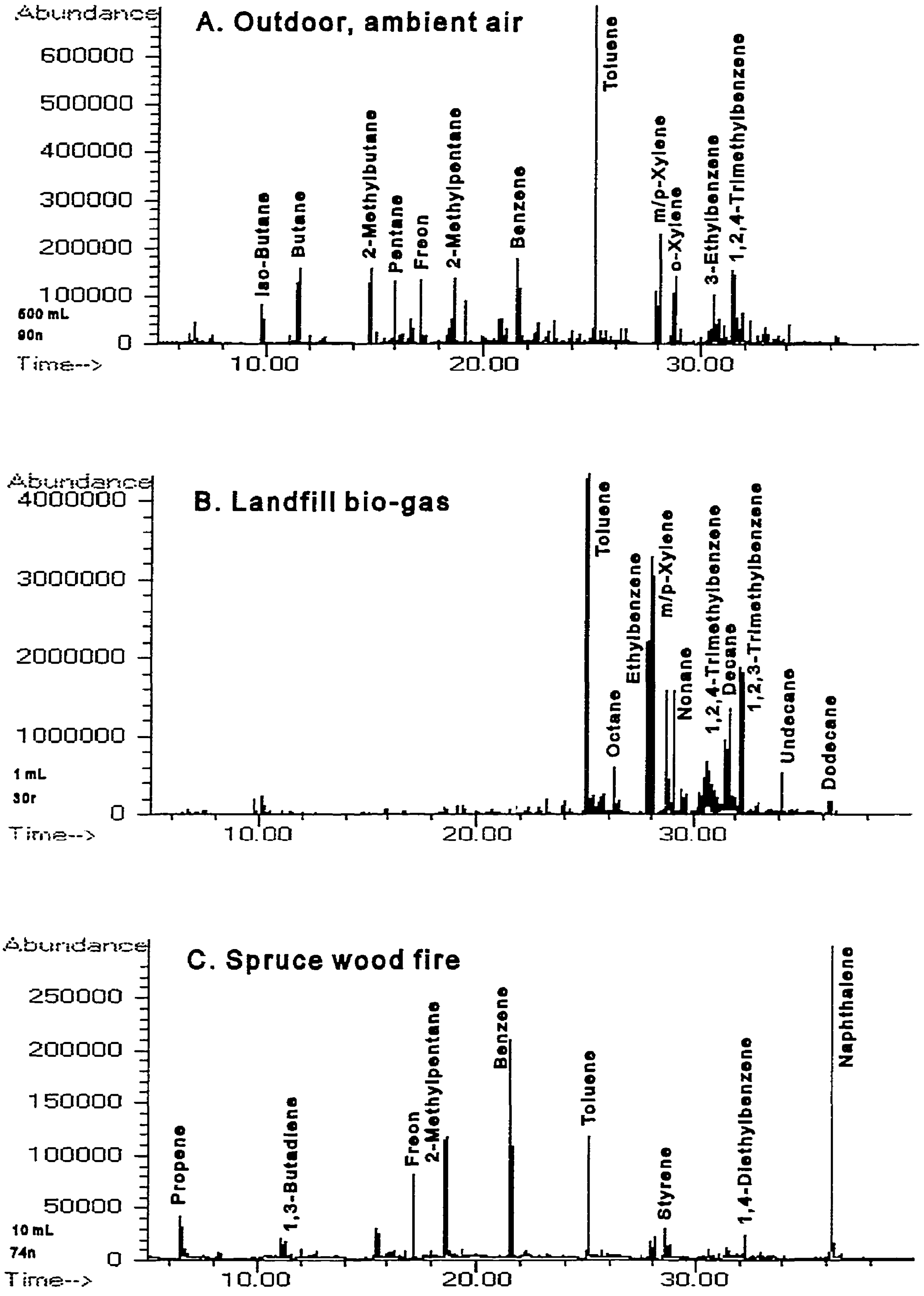


Figure 46. Derived chromatograms (CorelDraw™ v4.0) of: (A) outdoor, ambient, urban air; (B) landfill gas (LFG); and, (C) spruce wood fire, showing distinctive patterns or "fingerprints" of VOC's.


A. Outdoor, ambient air
Abundance
600000
500000
400000
300000
200000
100000
600 mL
90n
0
Time-->
10.00
20.00
30.00
Iso-Butane
Butane
2-Methylbutane
Pentane
Freon
2-Methylpentane
Benzene
Toluene
m/p-Xylene
o-Xylene
3-Ethylbenzene
1,2,4-Trimethylbenzene
B. Landfill bio-gas
Abundance
4000000
3000000
2000000
1000000
1 mL
30r
0
Time-->
10.00
20.00
30.00
Toluene
Octane
Ethylbenzene
m/p-Xylene
Nonane
1,2,4-Trimethylbenzene
Decane
1,2,3-Trimethylbenzene
Undecane
Dodecane
C. Spruce wood fire
Abundance
250000
200000
150000
100000
50000
10 mL
74n
0
Time-->
10.00
20.00
30.00
Propene
1,3-Butadiene
Freon
2-Methylpentane
Benzene
Toluene
Styrene
1,4-Diethylbenzene
Naphthalene

1,2,4-trimethylbenzene, decane, 1,2,3-trimethylbenzene and undecane (Figure 46B). Burning wood produced 108 different VOC's but the chromatograms (Figure 46C) were characterized by a small number of prominent peaks (2-methylpentane, benzene, toluene and naphthalene) and the presence of four peaks not found in the ambient air or landfill samples (propene, 1,3-butadiene, styrene and naphthalene).

2. Quantitative Analysis

Total VOC's found in experimental fires ranged from 0.1-107 ppm depending on the material burned and on the duration of the fire. Of the 144 VOC's measured, 14 substances were found in proportionately higher concentrations in all experimental fires, accounting for 65% (SD=±12%) by mass of total measured VOC's, no statistically significant difference being found between fires burning liquids and fires burning solid combustible materials. The "fingerprints", or relative amounts of these 14 VOC's, were also similar from fire to fire in the case of different solid combustible materials (Figure 47). In the case of liquids such as gasoline, varsol and foam insulation (which melted prior to burning), higher relative levels of benzene and naphthalene were found compared to the VOC's of solid combustible materials (Figure 48). The fingerprints seen for the liquid combustible materials were distinct from each other. This may be explained by different combustion reactions occurring in hotter and more rapidly burning fires and by the contribution of solvent evaporation.

Total levels of the measured VOC's increased with time for all fires burning solid combustible materials (Figure 49). However, total VOC's decreased with time in the case of gasoline (91 ppm at the 5-minute mark to 5 ppm at the 15-minute mark) as did the benzene and naphthalene levels for the other two liquids, varsol and foam insulation. Fires burning liquid combustibles such as gasoline and foam insulation produced much higher levels of smoke particulates (obscuration) than those burning solid combustible materials. Decreasing levels of VOC's with time in combination with increasing levels of smoke in the case of burning liquids, suggest

Figure 47. Characteristic "fingerprints" of the dominant VOC's from fires of single combustible solid materials showing the similarity in composition of the VOC's produced at the 5- and 10-minutes sampling time.

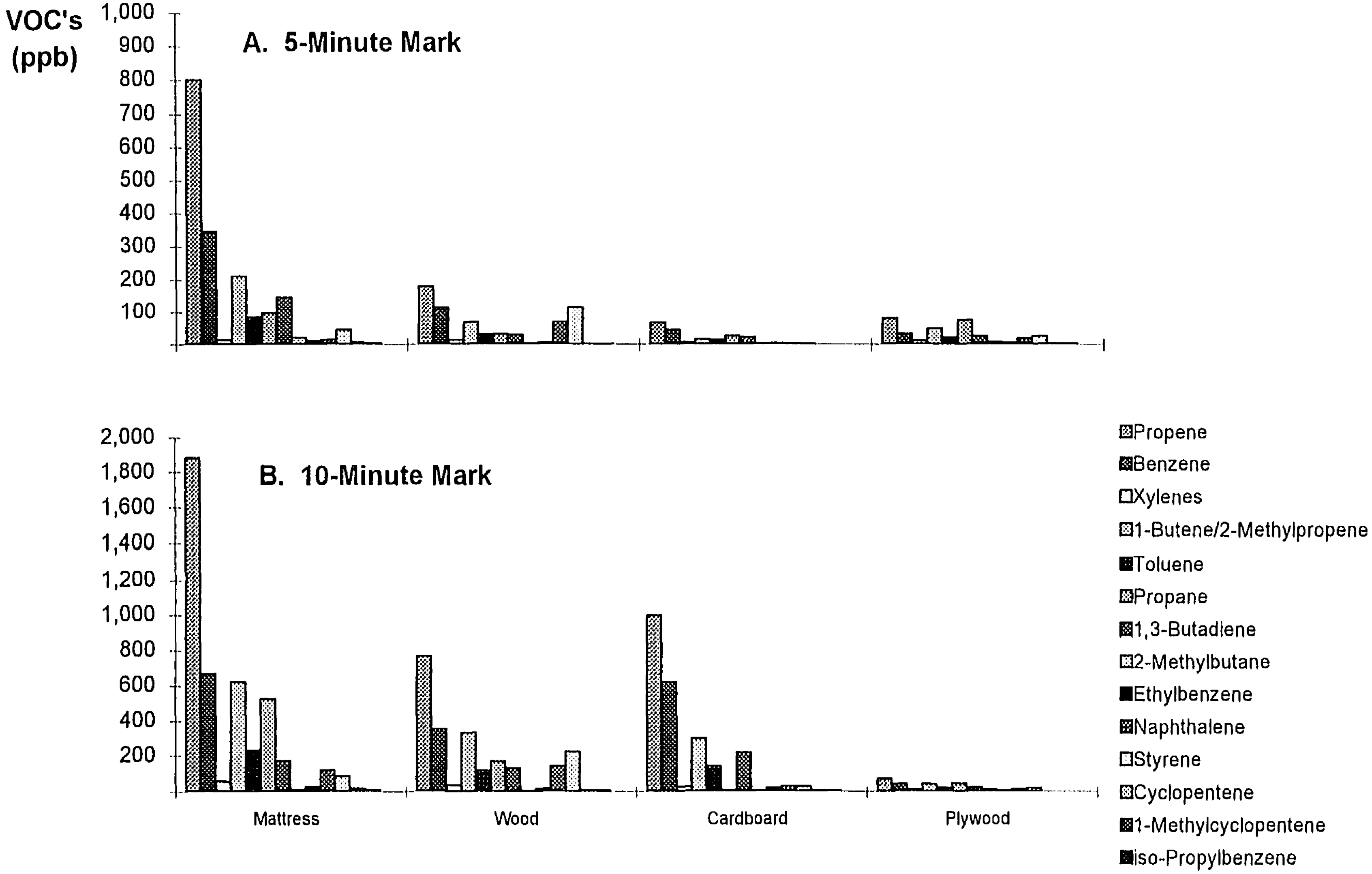
VOC's (ppb)
A. 5-Minute Mark
1,000
900
800
700
600
500
400
300
200
100
B. 10-Minute Mark
2,000
1,800
1,600
1,400
1,200
1,000
800
600
400
200
Mattress
Wood
Cardboard
Plywood
Propene
Benzene
Xylenes
1-Butene/2-Methylpropene
Toluene
Propane
1,3-Butadiene
2-Methylbutane
Ethylbenzene
Naphthalene
Styrene
Cyclopentene
1-Methylcyclopentene
iso-Propylbenzene

Figure 48. Characteristic "fingerprints" of the dominant VOC's from fires of combustible liquids (the foam melted before burning), showing the similarity in composition of the VOC's produced at the 5- and 10-minutes sampling time.

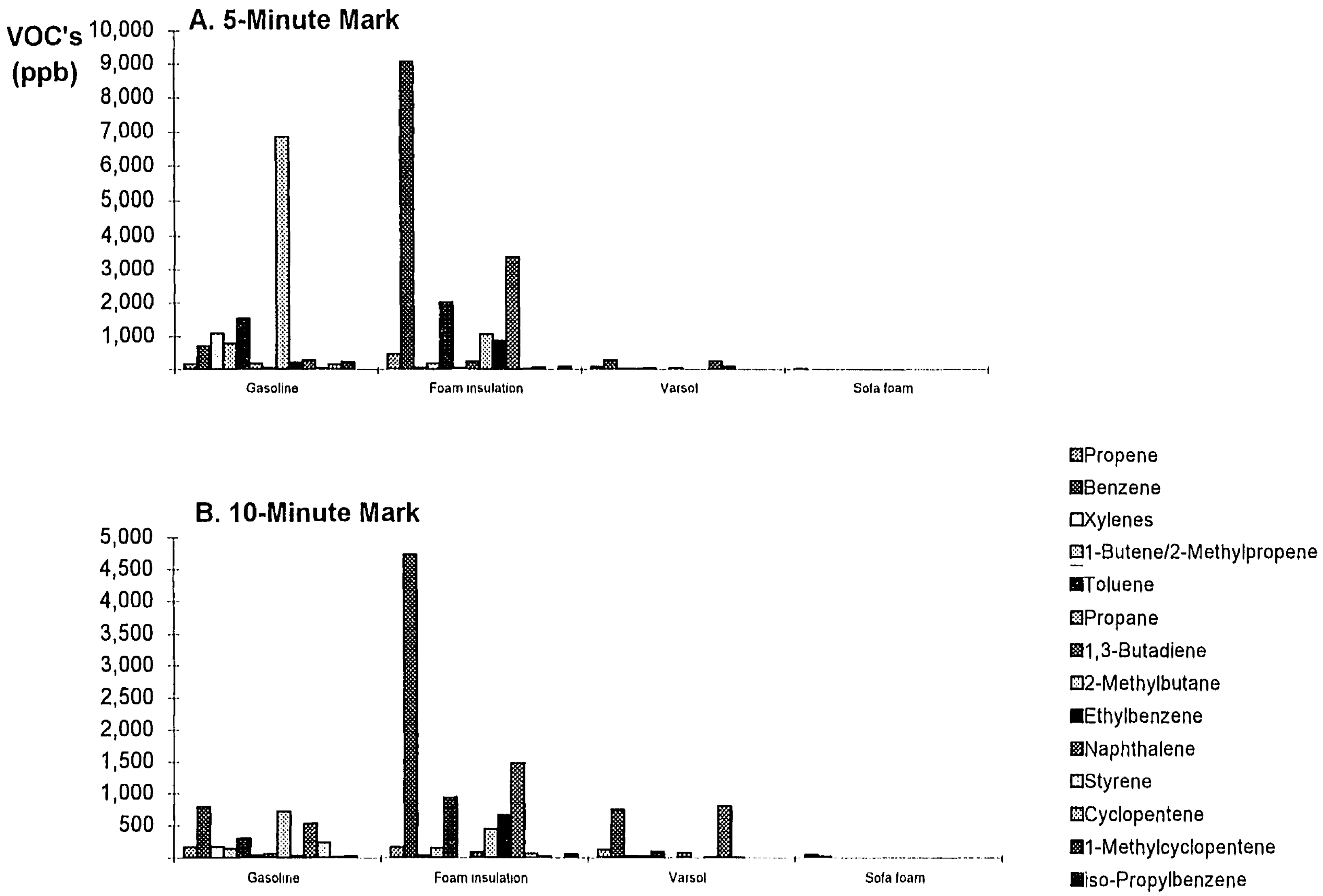
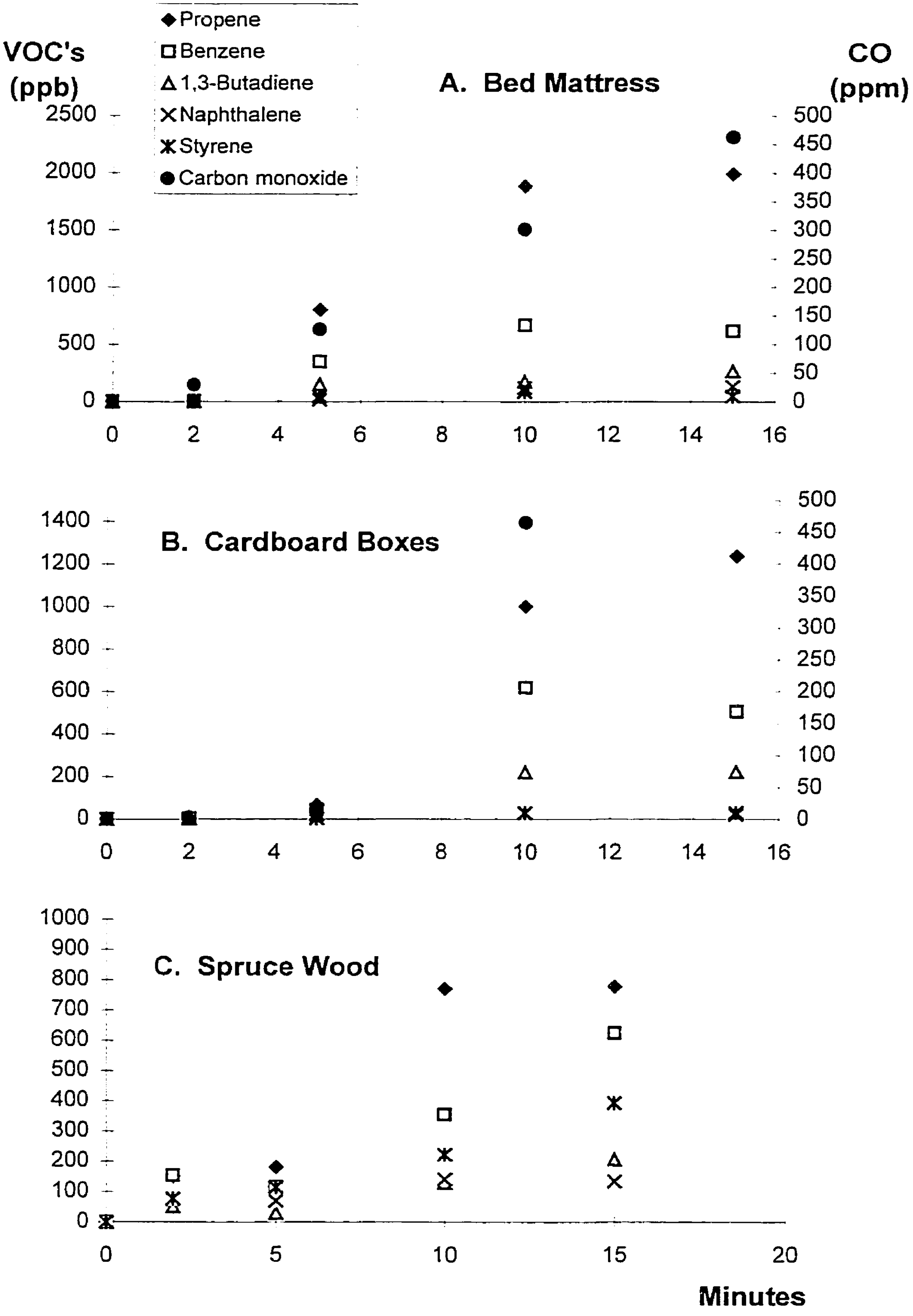

VOC's (ppb)
A. 5-Minute Mark
10,000
9,000
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
Gasoline
Foam insulation
Varsol
Sofa foam
B. 10-Minute Mark
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
Gasoline
Foam insulation
Varsol
Sofa foam
Propene
Benzene
Xylenes
1-Butene/2-Methylpropene
Toluene
Propane
1,3-Butadiene
2-Methylbutane
Ethylbenzene
Naphthalene
Styrene
Cyclopentene
1-Methylcyclopentene
iso-Propylbenzene

Figure 49. Benzene, 1,3-butadiene, naphthalene and styrene produced at fires burning solid combustible materials ((A) bed mattress, (B) cardboard boxes and (C) spruce wood) were found at higher levels than most other VOC's and their concentrations were observed to increase with time together with increasing levels of carbon monoxide.


◆ Propene
□ Benzene
△ 1,3-Butadiene
× Naphthalene
✱ Styrene
● Carbon monoxide
VOC's (ppb)
CO (ppm)
A. Bed Mattress
2500
2000
1500
1000
500
0
500
450
400
350
300
250
200
150
100
50
0
0
2
4
6
8
10
12
14
16
B. Cardboard Boxes
1400
1200
1000
800
600
400
200
0
500
450
400
350
300
250
200
150
100
50
0
0
2
4
6
8
10
12
14
16
C. Spruce Wood
1000
900
800
700
600
500
400
300
200
100
0
0
5
10
15
20
Minutes

that a significant fraction of VOC's are adsorbed onto smoke particles and that these escape detection when only the vapour phase is measured. Benzene, toluene, 1,3-butadiene, naphthalene and styrene were found at higher concentrations than most other measured VOC's and they were found to increase with time in all experimental fires together with increasing levels of CO (Figures 49 and 50). Benzene was found in the highest concentrations, peak levels ranging from 0.6 ppm to 65 ppm, while the levels of 1,3-butadiene, styrene and naphthalene peaked at 0.1, 0.4 and 3.0 ppm, respectively. Carbon monoxide and carbon dioxide levels ranged from 25-465 ppm and from 830-14,549 ppm, respectively, increasing steadily with time during the course of 15 minute experimental fires (n=15).

Statistically significant positive correlations were found between increasing levels of benzene and levels of propene, co-eluants 1-butene/2-methylpropene, 1,3-butadiene, toluene, naphthalene, ethylbenzene and isopropylbenzene in a number of experimental fires burning solid and liquid combustible materials (Table 20). The paired Student's *t*-test revealed significantly different ratios of benzene to selected VOC's between fires burning liquids and fires burning solids (Table 21). These ratios however, remained relatively constant during the course of fires which burned for 15 minutes, varying by 15% on average. The mean ratios of benzene to propene, 1,3-butadiene and to toluene were 18-, 8- and 1.6-fold higher for fires burning liquids than for fires burning solids (Table 21).

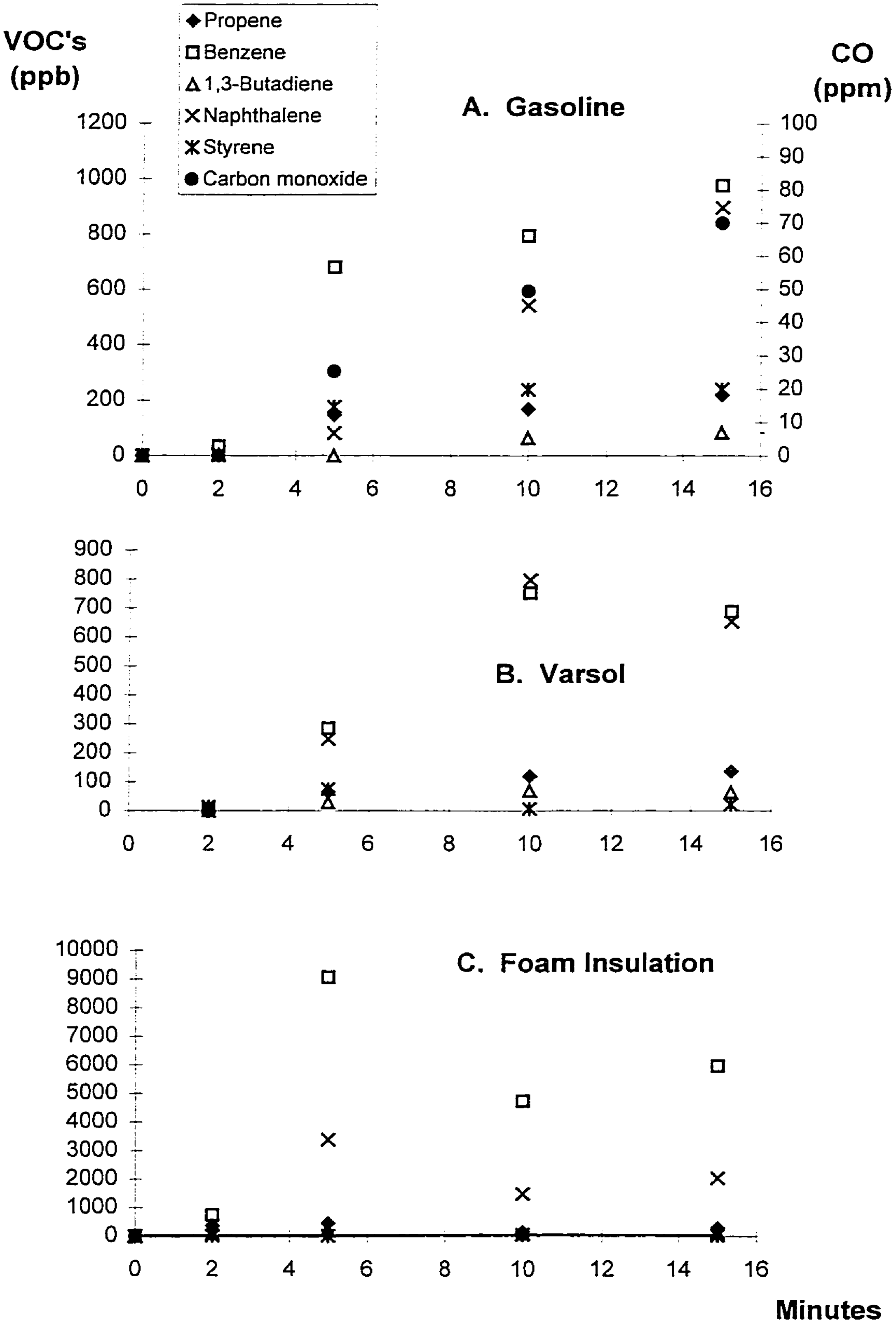
C. MUNICIPAL STRUCTURAL FIRES

1. Qualitative Analysis

The similarity in the nature of the combustion products from a variety of sources, demonstrated by the characteristic prevalence of benzene, toluene and naphthalene, suggests that similar patterns might be found in municipal, structural fires. That this was indeed the case is demonstrated by chromatograms obtained from municipal, structural fires, two typical examples being shown in Figure 51. As

Figure 50. Benzene, 1,3-butadiene, naphthalene and styrene produced at fires burning combustible liquids ((A) gasoline, (B) varsol and (C) foam insulation which melted prior to burning) were found at higher levels than most other VOC's. Their concentrations were observed to initially increase with time, together with increasing levels of carbon monoxide, and then to decrease, possibly as a result of adsorption onto particulates produced in large quantities at these fires.

5 2



VOC's (ppb)
CO (ppm)
◆ Propene
□ Benzene
△ 1,3-Butadiene
× Naphthalene
✱ Styrene
● Carbon monoxide
A. Gasoline
1200
1000
800
600
400
200
0
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
900
800
700
600
500
400
300
200
100
0
B. Varsol
0
2
4
6
8
10
12
14
16
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
C. Foam Insulation
0
2
4
6
8
10
12
14
16
Minutes

Table 20. Linear correlation coefficients for the ratios of selected VOC's with benzene at experimental fires.

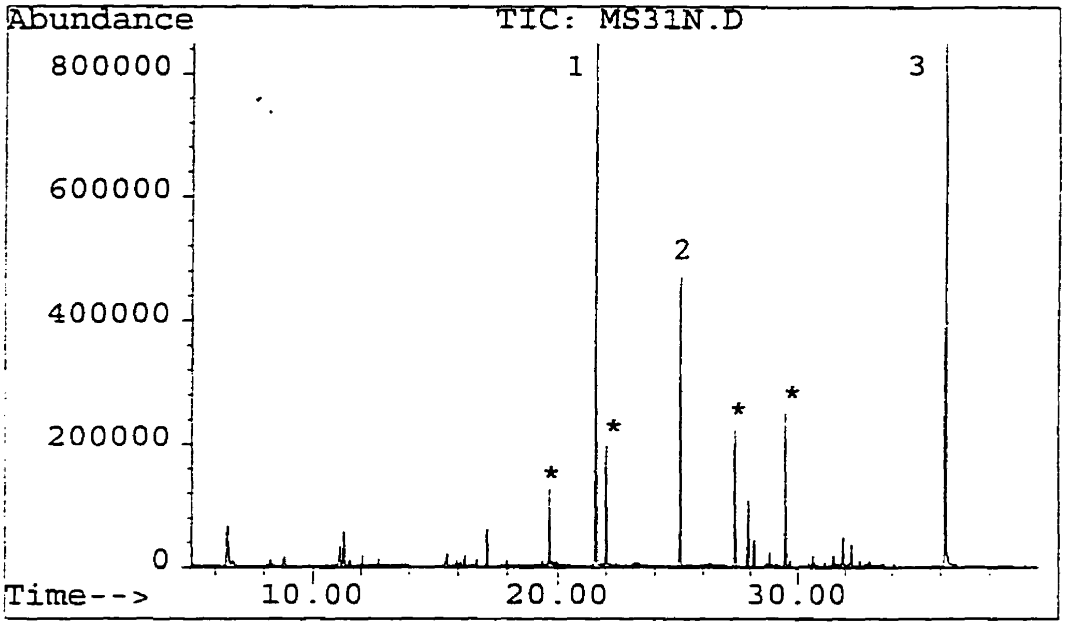
	Solids (n=4)			Liquids (n=4)		
	5 min.	10 min.	15 min.	5 min.	10 min.	15 min.
Benzene / Propene	0.99	0.91	0.98	0.97	0.58	0.81
Benzene / (1-Butene + 2-Methylpropene)	0.98	0.85	0.87	-0.07	0.70	0.31
Benzene / 1,3-Butadiene	0.98	0.95	1.00	0.99	0.71	0.78
Benzene / Xylenes	0.55	0.79	0.77	-0.23	-0.09	0.09
Benzene / Toluene	0.99	0.93	0.94	0.76	0.98	1.00
Benzene / Naphthalene	-0.03	0.38	0.70	1.00	0.92	0.95
Benzene / Ethylbenzene	1.00	0.97	0.98	0.98	0.99	0.99
Benzene / iso-Propylbenzene	0.22	0.96	0.90	1.00	0.99	0.99

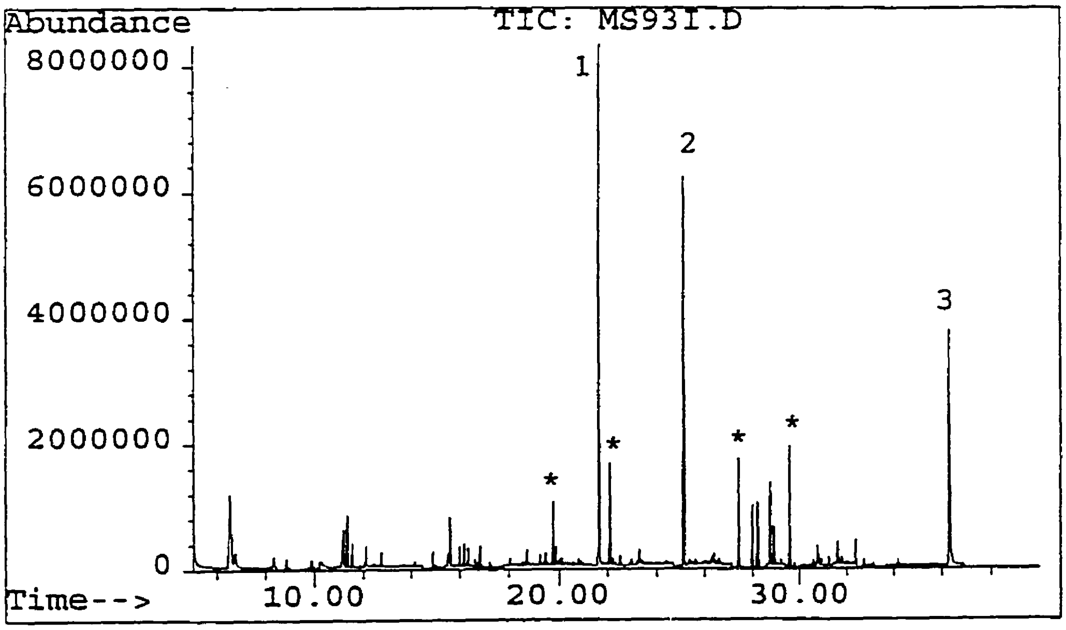
Table 21. Ratio of benzene to selected VOC's in experimental fires

VOC ratios	Fire Duration (Min.)	Mean (ppm)		Liquid / Solid
		Solids (n=4)	Liquids (n=4)	
Benzene / Propene	5	0.5	7.3	13.9
	10	0.5	10.2	20.2
	15	0.4	7.6	19.5
Average		**0.5**	**8.4**	**17.7**
St. Dev.		0.1	1.6	3.5
%rsd		15.7	18.8	19.7
Benzene / (1-Butene + 2-Methylpropene)	5	1.8		
	10	1.3		
	15	1.2		
Average		**1.4**	n.s.[a]	n.s.
St. Dev.		0.3		
%rsd		19.8		
Benzene / 1,3-Butadiene	5	2.4	22.6	9.4
	10	2.8	25.3	8.9
	15	2.0	11.2	5.6
Average		**2.4**	**19.7**	**8.1**
St. Dev.		0.4	7.5	2.1
%rsd		17.2	38.0	25.3
Benzene / Xylenes	5	12.9		
	10	12.6		
	15	14.4		
Average		**13.3**	n.s.	n.s.
St. Dev.		1.0		
%rsd		7.3		
Benzene / Toluene	5	3.3	4.7	1.4
	10	3.2	5.1	1.6
	15	3.0	5.1	1.7
Average		**3.2**	**4.9**	**1.6**
St. Dev.		0.2	0.2	0.2
%rsd		5.7	4.9	10.0
Benzene / Naphthalene	5		5.2	
	10		5.6	
	15		5.1	
Average		n.s.	**5.3**	n.s.
St. Dev.			0.3	
%rsd			5.3	

[a] Not significant

Figure 51. Typical chromatograms from two municipal structural fires exhibiting three major peaks: benzene (#1), toluene (#2) and naphthalene (#3). Asterisks indicate the internal standards normally added to samples prior to analysis.


Abundance
TIC: MS31N.D
800000
600000
400000
200000
0
Time-->
10.00
20.00
30.00
1
2
3
*
*
*
*


Abundance
TIC: MS93I.D
8000000
6000000
4000000
2000000
0
Time-->
10.00
20.00
30.00
1
2
3
*
*
*
*

before, the chromatograms of seven municipal fires were derived using Coreldraw™ v4.0 software to facilitate visual comparison (Figure 52). The spectra were remarkable for their simplicity, this being largely due to the dominating presence of the benzene peak along with toluene and naphthalene. Propene and 1,3-butadiene were also found in all of the municipal fires. Styrene (which had not been found in the experimental fires) and other alkyl-substituted benzene compounds were also frequently identified. One fire which had been smouldering for nine days was sampled and found to contain the same VOC combustion products as had been seen previously: benzene, toluene, naphthalene, propene, 1,3-butadiene and styrene (Figure 53A). One industrial fire involving an electronics manufacturing facility was sampled where, in addition to the usual combustion products, relatively high levels of ethyl benzene and isopropyl benzene were found (Figure 53B).

Fire samples were also analyzed in SCAN mode and examined for the appearance of substances which were not present in the instrument standard calibration mixture. The SCAN chromatogram obtained from the 9-day smouldering structural fire is shown in Figure 54A. Six unknown compounds, not present in the calibration standard mixture, were tentatively identified: furan, benzaldehyde, benzofuran, benzonitrile, 2,3-dihydrofuran and 2-methylfuran (Figures 54B-54E). The probability that a correct match was found with spectra in the NIST (1992) mass spectral library was 90% to 96%. These substances were detected in municipal fire samples but they were not found in the experimental fires where gasoline, wood, foam, plywood and cardboard were burned.

2. Quantitative Analysis

The mean level of 123 VOC's found at nine municipal structural fires was 23.4 ppm (SD=±23.2 ppm). The substances found at municipal fires which were not seen at the experimental wood fires were methyl substituted butanes, pentanes, propanes and hexanes and cyclopentane, all measured at ppb levels. Similar "fingerprints" (relative amounts) of the same 14 substances were found at the

Figure 52. Derived chromatograms (CorelDraw™ v4.0) for samples collected at seven different municipal structural fires. The predominant combustion products were propene, 1,3-butadiene, benzene, toluene, styrene and naphthalene.

Municipal Structural Fires

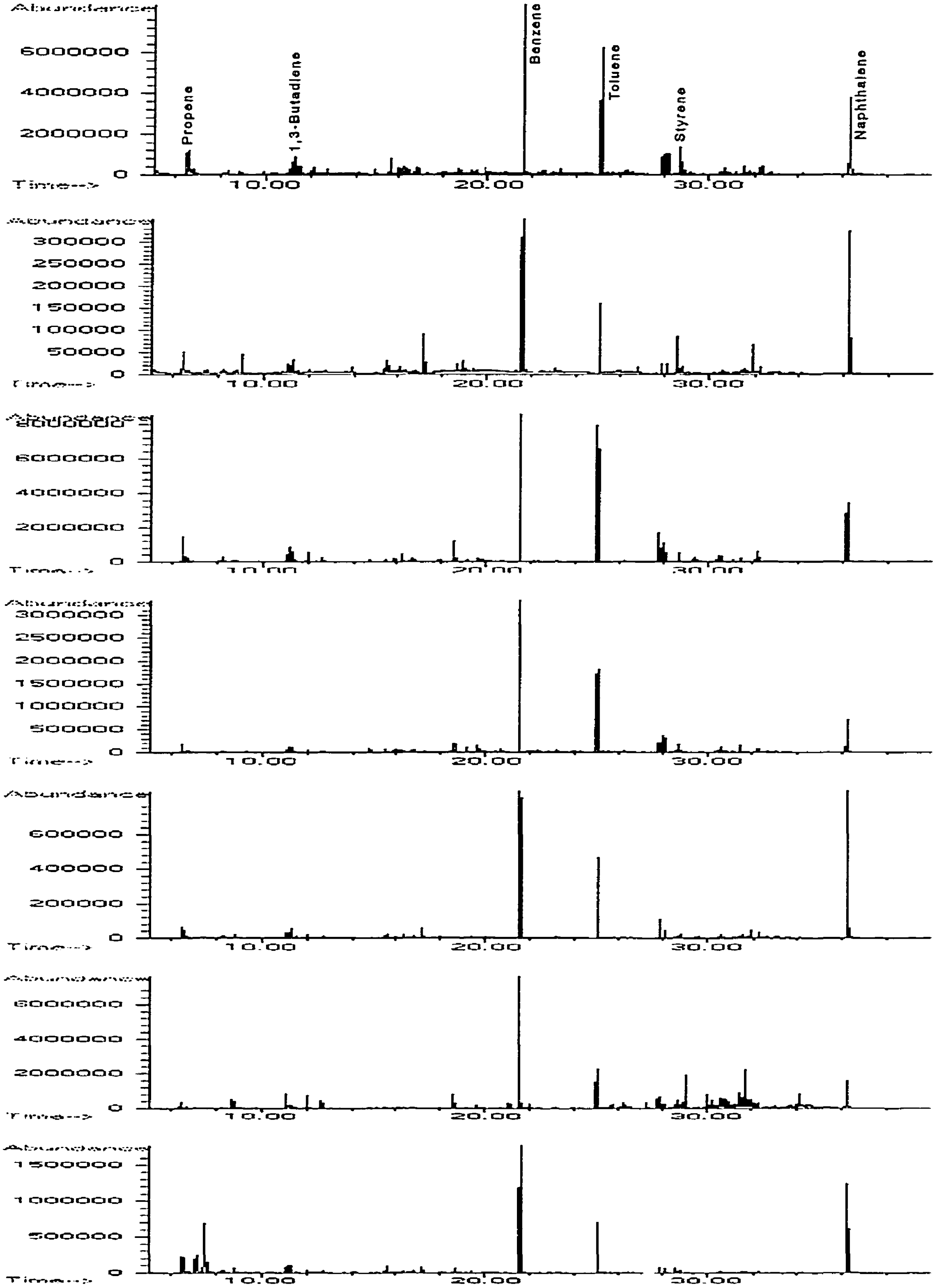
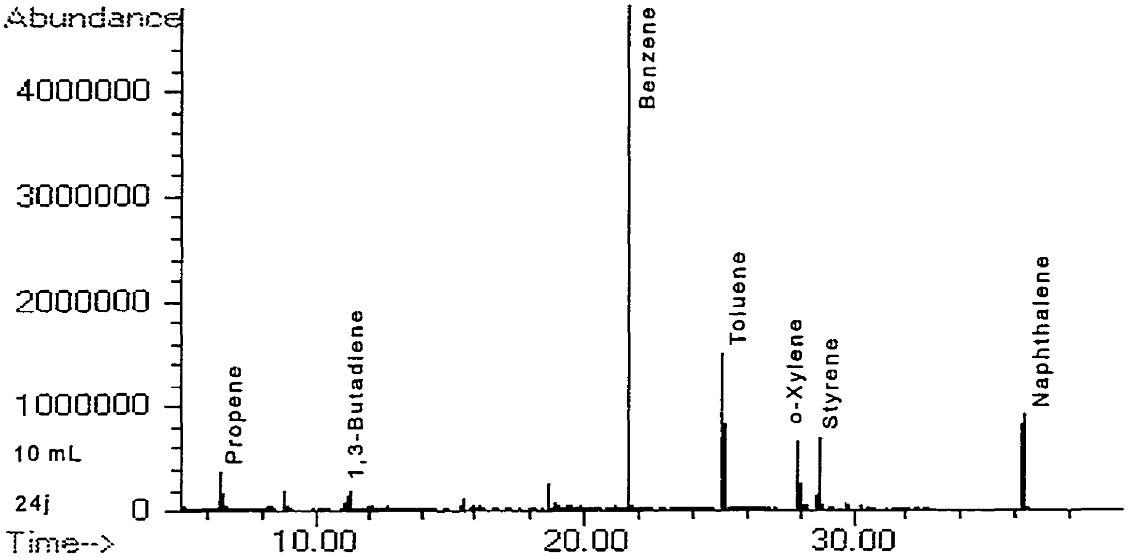
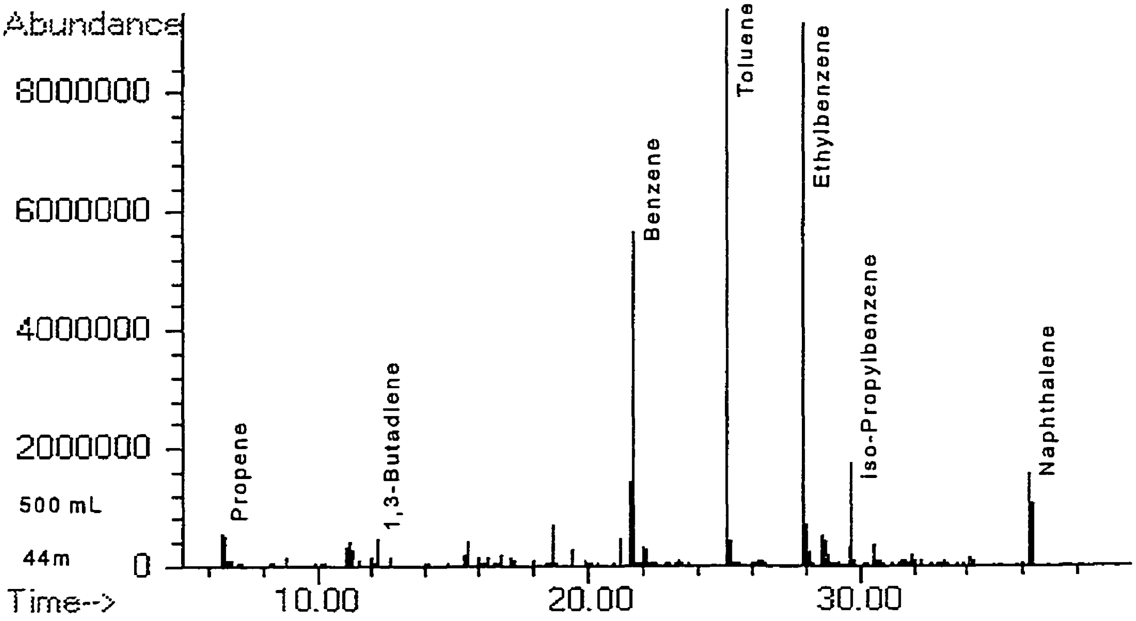


Figure 53. Derived chromatograms (CorelDraw™ v4.0) for samples collected at: (A) a nine-day, smouldering, municipal structural fire, and (B) an electronics industry structural fire. The usual combustion products seen at municipal structural fires were observed to be present (primarily propene, 1,3-butadiene, benzene, toluene, styrene and naphthalene) in both cases. In addition, unusually high levels of ethylbenzene and isopropylbenzene were observed at the electronics industry fire (B).

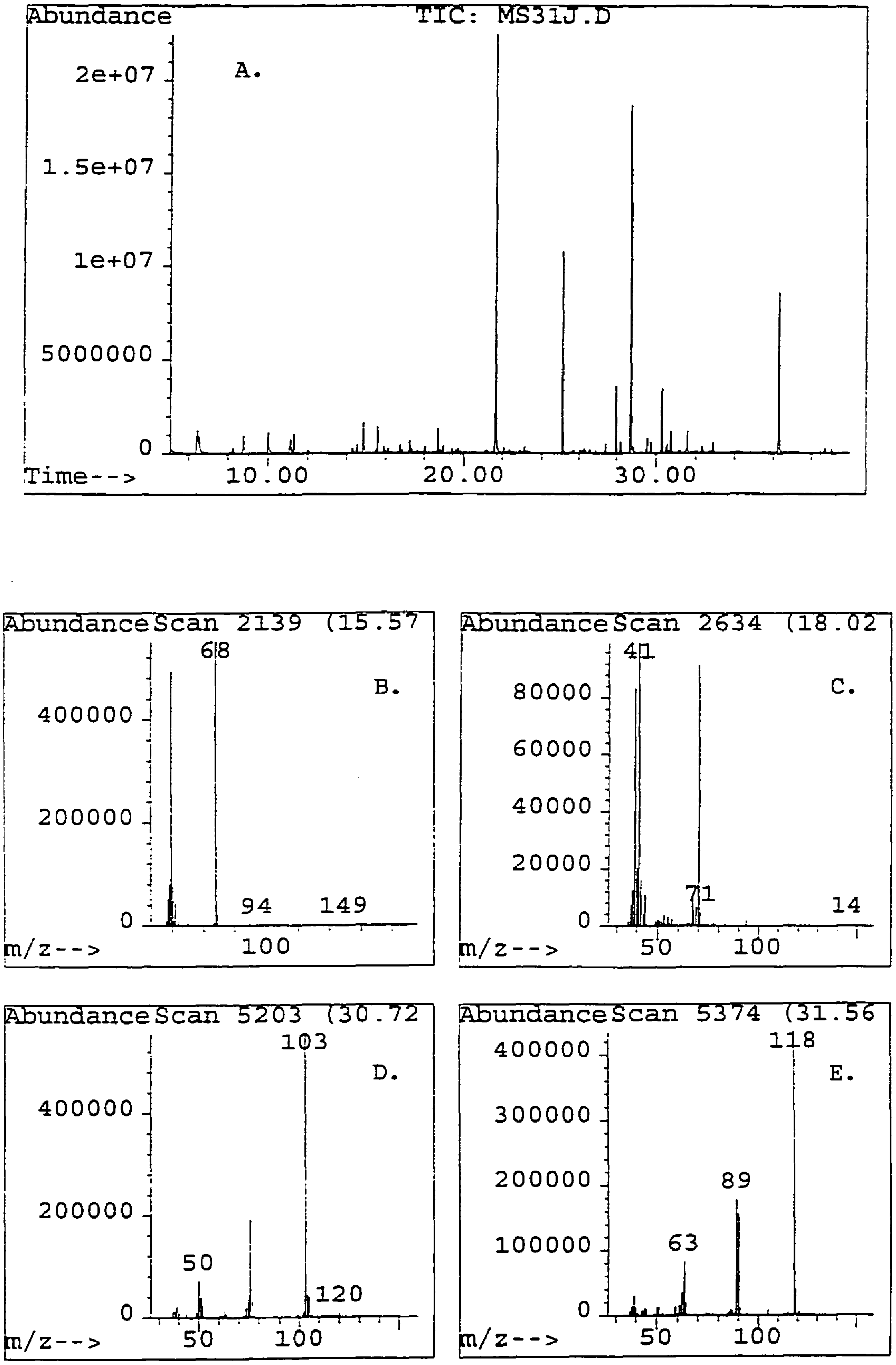


A. Nine-day Smouldering Structural Fire



B. Electronics Industry Fire

Figure 54. GC/MSD analysis in SCAN mode of a sample collected at a nine-day, smouldering, municipal structural fire showing the total ion chromatogram (A) and the mass spectra of tentatively identified unknowns: furan (B), 2,3-dihydrofuran (C), benzonitrile (D) and benzofuran (E). Mass spectra matched NIST (1992) reference library spectra with 90-96% probability.


Abundance
TIC: MS31J.D
A.
2e+07
1.5e+07
1e+07
5000000
0
Time-->
10.00
20.00
30.00
Abundance
Scan 2139 (15.57
68
B.
400000
200000
0
94
149
m/z-->
100
Abundance
Scan 2634 (18.02
41
C.
80000
60000
40000
20000
0
71
14
m/z-->
50
100
Abundance
Scan 5203 (30.72
103
D.
400000
200000
50
120
0
m/z-->
50
100
Abundance
Scan 5374 (31.56
118
E.
400000
300000
200000
89
100000
63
0
m/z-->
50
100

municipal fires as had been seen for experimental fires burning various solid combustible materials (Figure 55). These 14 substances accounted for 85% (SD=±5%) by mass of the total VOC's measured. The highest levels of VOC's found were propene (0.3-22 ppm) and benzene (0.1-11 ppm). Unusually high levels of ethylbenzene (6 ppm) and of isopropylbenzene (0.6 ppm) were found at fire No. 2 (Figure 55), the only industrial fire sampled (electronics factory). These substances had been found to correlate strongly with levels of benzene found in experimental fires burning various liquid and solid combustible materials (Table 20). In samples collected simultaneously at one fire, the concentration of benzene was found to be 100-fold higher on the 2nd floor than on the 1st floor of a burning building.

The same predominant substances (benzene, toluene, 1,3-butadiene, naphthalene and styrene) found at experimental fires were prevalent also at municipal structural fires, levels ranging from 0.035-5 ppm, 0.5-6.0 ppm, 0.01-2.0 ppm and 0-2.0 ppm, respectively (Table 22). These substances accounted for 32% (SD=±16%) of the total VOC's found at municipal structural fires (n=9). Carbon monoxide and carbon dioxide levels ranged from 134-199 ppm and 2,085-5,621 ppm, respectively.

Statistically significant positive correlations were found between increasing levels of benzene and levels of propene, the xylenes, toluene, co-eluants 1-butene/2-methylpropene, 1,3-butadiene and naphthalene (Figures 56 and 57). Their ratios, found by linear regression, were 0.60, 1.6, 2.0, 2.5, 2.9 and 5.5, respectively (Table 23). The ratios of benzene to propene, toluene, (1-butene + 2-methylpropene) and 1,3-butadiene, being 0.6, 2.0, 2.5, and 2.9, respectively, were similar to those found in experimental fires burning solid combustible materials.

The internal standard method was used to estimate the concentrations of tentatively identified unknowns found in fire samples. Area counts from the total ion chromatograms were used for the compound to be measured and for the internal standard. It was assumed that, for the same number of nanograms of unknown compound, the response factor of the unknown would approximately equal that of

Figure 55. Characteristic "fingerprints" of the predominant VOC's from nine municipal structural fires showing the similarity in composition of the VOC's produced as well as the variability found between fires.

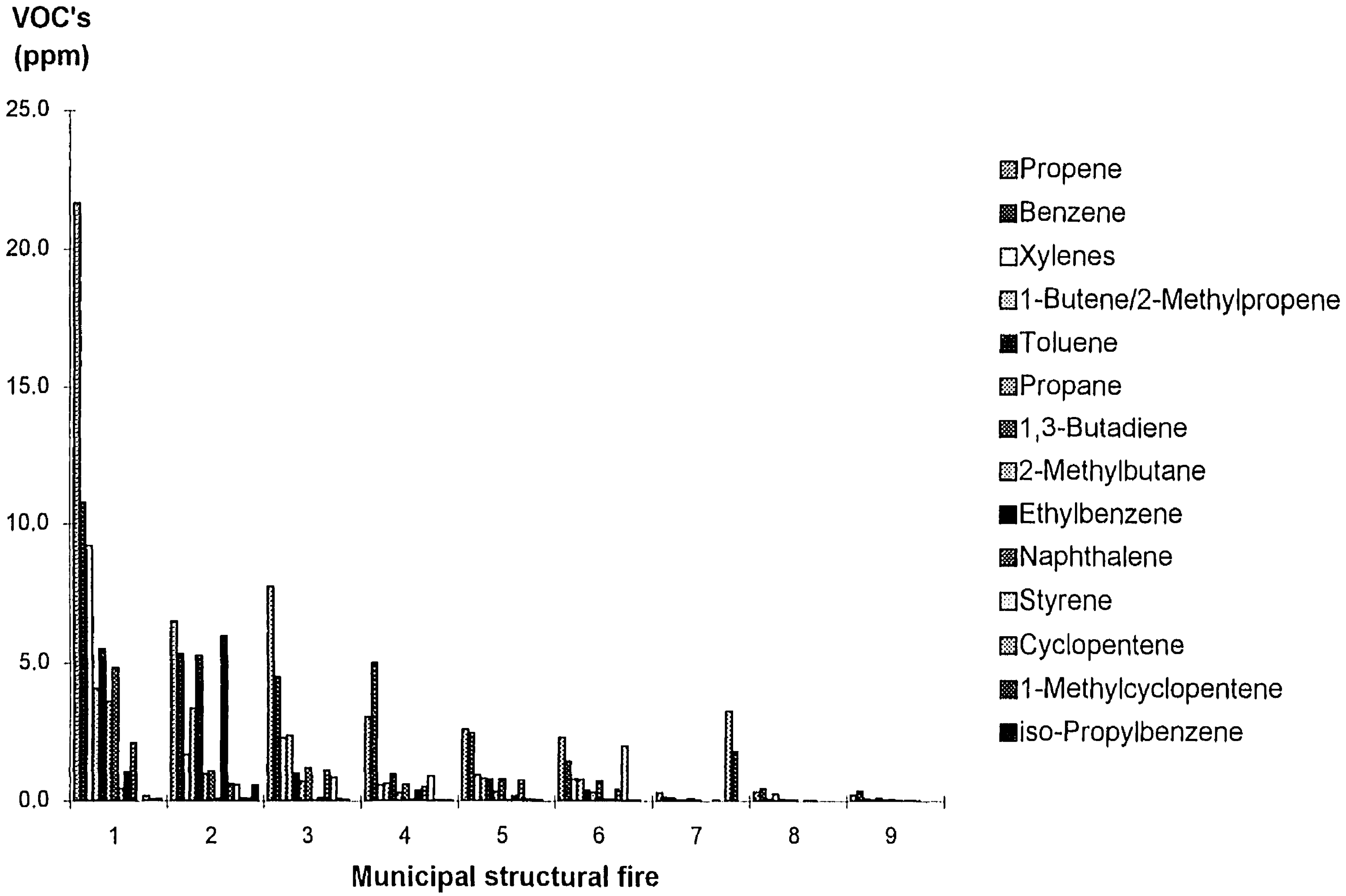

VOC's
(ppm)
25.0
20.0
15.0
10.0
5.0
0.0
1
2
3
4
5
6
7
8
9
Municipal structural fire
▨Propene
▨Benzene
☐Xylenes
▨1-Butene/2-Methylpropene
▨Toluene
▨Propane
▨1,3-Butadiene
▨2-Methylbutane
■Ethylbenzene
▨Naphthalene
▨Styrene
▨Cyclopentene
▨1-Methylcyclopentene
■iso-Propylbenzene

Table 22. Selected toxic substances found in municipal structural fires

	n	Mean ppm	S.D. ppm	Range Min.	 Max.
Total target VOC's	**9**	**25**	**22**	**1**	**72**
Selected VOC's					
Benzene	9	2.80	3.35	0.12	11
Toluene	9	1.30	2.00	0.50	6
1,3-Butadiene	9	0.93	1.37	0.03	5
Naphthalene	9	0.52	0.65	0.01	2
Styrene	9	0.51	0.66	0.00	2
Total selected VOC's	**9**	**6.1**	**-**	**0.7**	**25.2**
Percent of total target VOC's	**9**	**24**	**-**	**53**	**35**
Carbon dioxide	4	3 376	1 593	2 085	5 621
Carbon monoxide	4	160	28	134	199

Figure 56. Graphs showing linear correlations observed for the levels of propene (A), xylenes (B) and toluene (C) vs. the levels of benzene found at nine municipal structural fires.

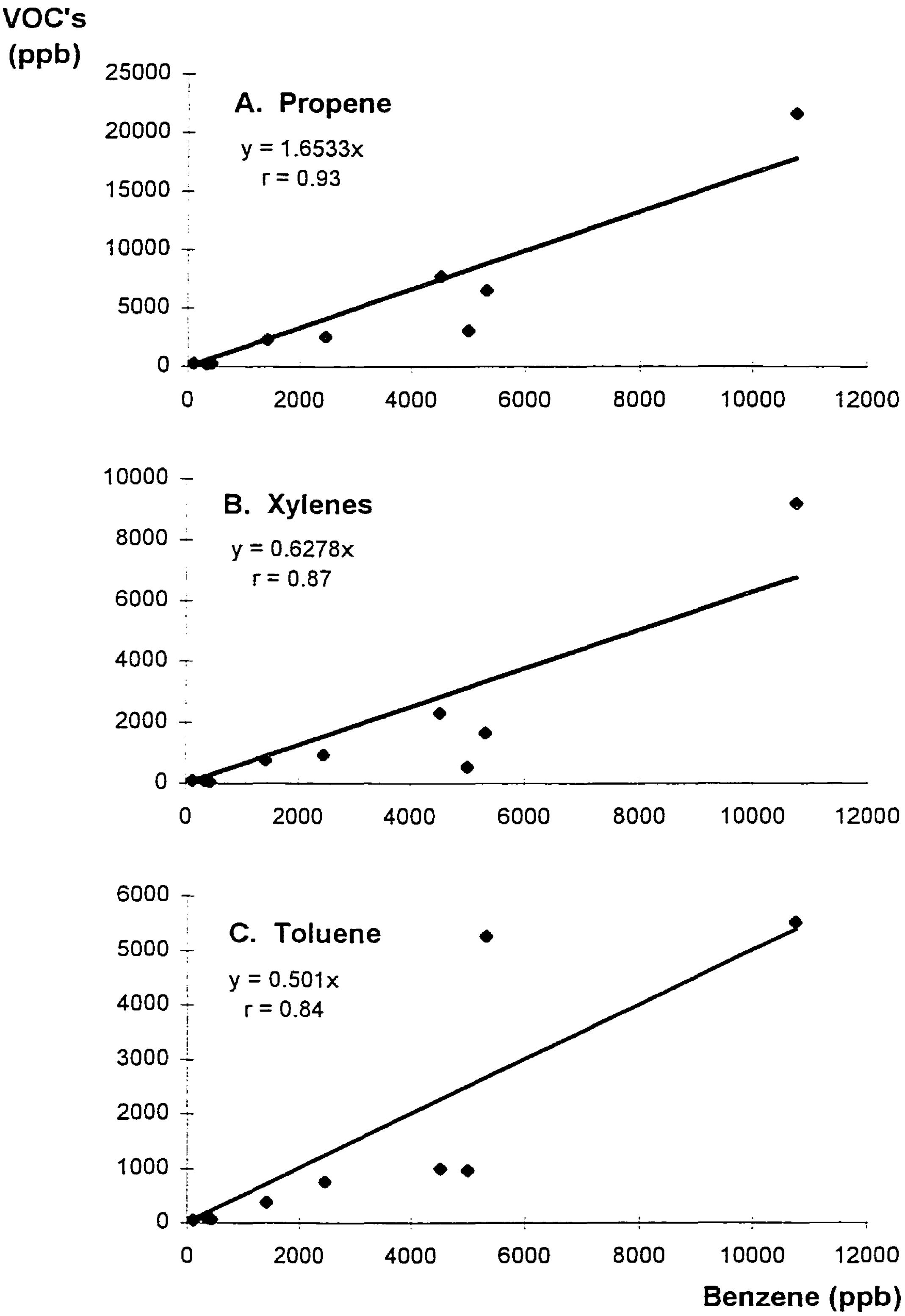

VOC's (ppb)
A. Propene
y = 1.6533x
r = 0.93
25000
20000
15000
10000
5000
0
0
2000
4000
6000
8000
10000
12000
B. Xylenes
y = 0.6278x
r = 0.87
10000
8000
6000
4000
2000
0
0
2000
4000
6000
8000
10000
12000
C. Toluene
y = 0.501x
r = 0.84
6000
5000
4000
3000
2000
1000
0
0
2000
4000
6000
8000
10000
12000
Benzene (ppb)

Figure 57. Graphs showing linear correlations observed for the levels of 1-butene + 2-methylpropene (A), 1,3-butadiene (B) and naphthalene (C), vs. the levels of benzene found at nine municipal structural fires.

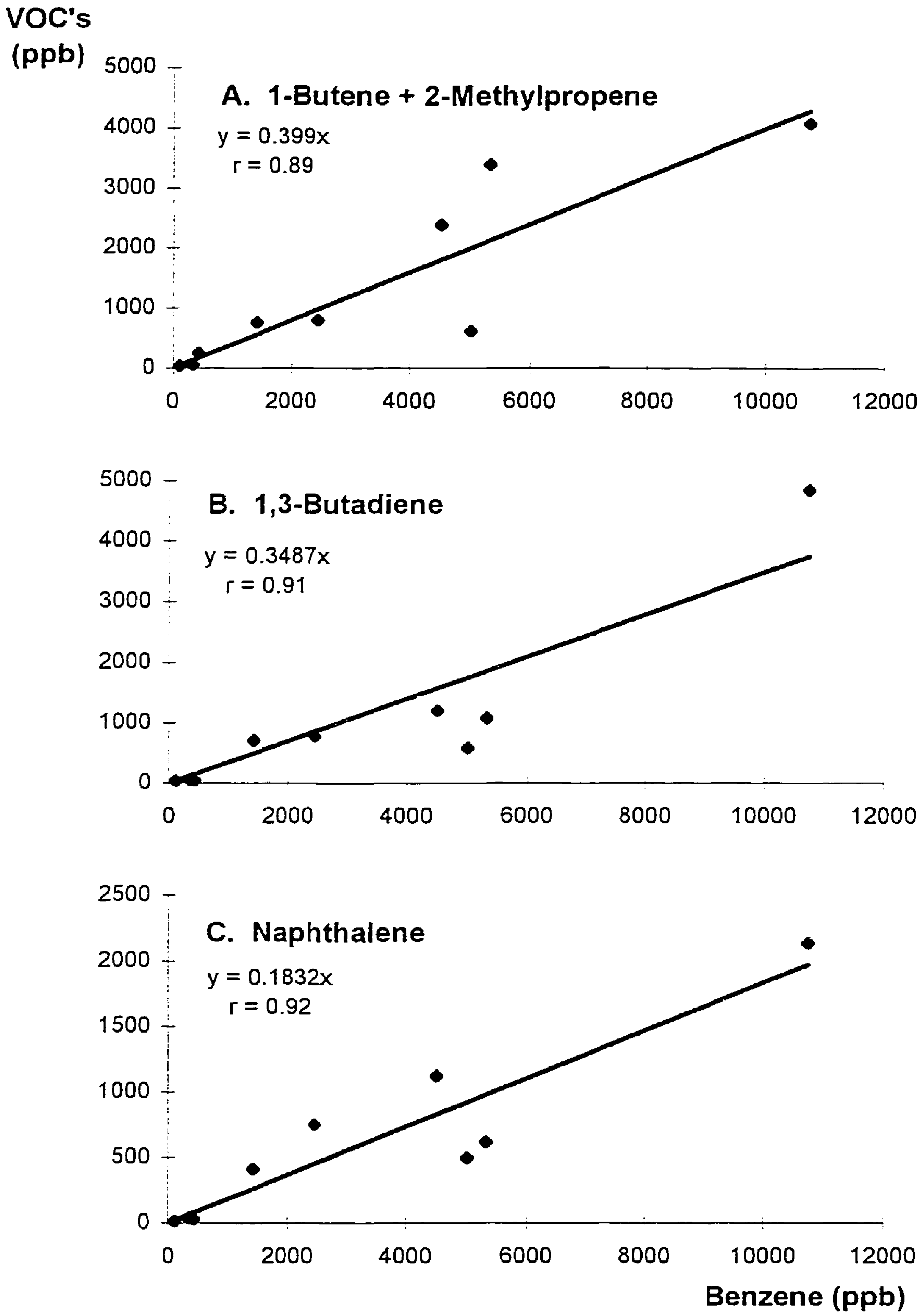

VOC's (ppb)
A. 1-Butene + 2-Methylpropene
y = 0.399x
r = 0.89
5000
4000
3000
2000
1000
0
0
2000
4000
6000
8000
10000
12000
B. 1,3-Butadiene
y = 0.3487x
r = 0.91
5000
4000
3000
2000
1000
0
0
2000
4000
6000
8000
10000
12000
C. Naphthalene
y = 0.1832x
r = 0.92
2500
2000
1500
1000
500
0
0
2000
4000
6000
8000
10000
12000
Benzene (ppb)

Table 23. Ratio of benzene to selected VOC's in nine municipal structural fires.

VOC's	Ratio	95% Confidence Interval		Correlation Coefficient
		Min.	Max.	*r*
Benzene / Propene	0.6	0.5	0.8	0.94
Benzene / Xylenes	1.6	1.2	2.5	0.89
Benzene / Toluene	2.0	1.4	3.2	0.85
Benzene / (1-Butene + 2-Methylpropene)	2.5	1.9	3.5	0.89
Benzene / 1,3-Butadiene	2.9	2.2	4.1	0.91
Benzene / Naphthalene	5.5	4.4	7.1	0.92

the closest eluting internal standard. Estimates for the tentatively identified substances ranged from 0.2 ppm to 2 ppm, furan and benzaldehyde being present in the greatest concentration.

IV. FIREFIGHTER EXPOSURE TIME AT FIRES

There was no direct measure of the time that individual firefighters spent at fires. The difficulty in estimating exposure times, given the currently available databases, is complicated by a number of factors:

(1) firefighters do not work standard 8-hour shifts, schedules allowing for 10-, 14- or 24-hour shifts only;

(2) unlike many other fire departments, there was a fair degree of flexibility allowing for movement of firefighters from one crew to another or from one firehall to another within the City of Montréal Fire Department;

(3) although accurate information was available concerning the activities of individual crews associated with specific vehicles, it was very difficult to know which firefighters were assigned to them at any point in time;

(4) time spent at a fire is not a measure of exposure time since firefighters may be employed in diverse tasks from a variety of positions;

(5) the size of a fire is not a measure of the degree of exposure since a fire may be fought aggressively from the inside or defensively from the outside;

(6) standard operating procedures allowed for considerable personal judgment as to when SCBA's must be used;

(7) it was impossible to know when firefighters used their personal issue SCBA cylinders or who used spare and reserve cylinders.

Given the new database developed as part of this study, it was possible to accurately determine the volume of compressed breathing air produced by the compressors, the number of SCBA refills and, for each of the SCBA cylinders, the volume of compressed breathing air used in any time period as well as the dates of all refills and the source of the air. It was also possible to compile and analyze fire department statistics, accurately relating the number, types and severity of fires, types and movement of vehicles, distribution and assignment of firefighters by job title, firefighter injuries and fatalities. Information was extracted from these databases and combined to provide indirect measures of firefighter total time (broken down by job title) spent at the scene of fires and the total volume of respiratory breathing air used by different categories of firefighters as a percentage of the time spent at the firescene.

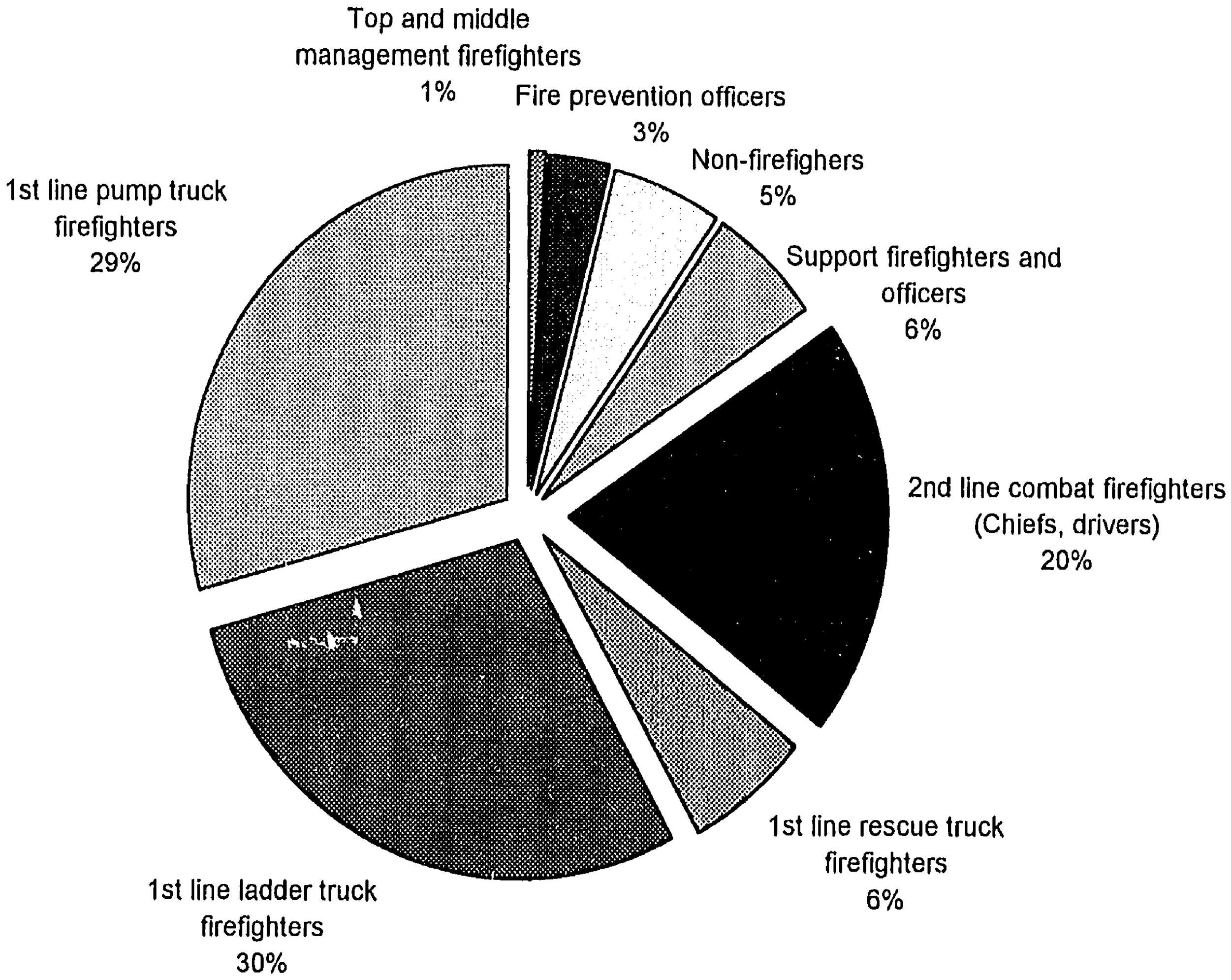
In 1994, the City of Montréal Fire Department comprised 1,883 men and women serving a population of one million people living on a territory covering 175 km^2 which was divided into nine sectors (Table 24). The department was organized under one Director assisted by nine Division Chiefs (one per sector) and 36 Operations Chiefs (four per sector) who attended fires, sometimes entering buildings. Figure 58 shows the breakdown of fire department personnel according to job title and potential exposure time at fires. Some 9% of personnel holding the title "firefighter" never attended fires. They may or may not have been exposed to fires earlier in their careers. This group included top and middle management, fire prevention officers and support firefighters or officers. Only 64% of Fire Department personnel (n=1,211) were 1st-line combat firefighters potentially exposed to smoke (Table 24). Second-line combat firefighters (those who attended fires but who did not necessarily enter buildings) included Chiefs and vehicle drivers, accounting for 20% of Fire Department personnel. Analysis (below) of firefighter functions and firehall assignments shows that there was a wide variation in exposure time between individual, 1st-line combat teams.

There were 85 combat crews (3-year average) assigned to 36 firehalls: four teams per crew and 4-6 firefighters (including one driver and one Lieutenant or Captain) per team. Firefighters worked 192 days per year for a total of 2,184 hours in 10-hour shifts during the day, 14-hour shifts during the night and, on occasion,

Table 24. Fire department personnel (City of Montréal)

Top and middle management	
Director and assistant directors	7
Division chiefs	8
Fire prevention officers	60
Non-firefighters	
Management	11
Professionals	12
White collar workers	73
Blue collar workers	5
Support firefighters and officers	110
1st-Line combat firefighters	
Assigned to rescue trucks	120
Assigned to ladder trucks	539
Assigned to pump trucks	552
2nd-Line combat firefighters	
Division chiefs	9
Operations chiefs	36
Drivers	341
TOTAL	**1883**

Figure 58. A chart showing the allocation of Montréal Fire Department personnel according to job description in 1994. Only 65% of fire department personnel were 1st-line combat firefighters.


Top and middle management firefighters 1%
Fire prevention officers 3%
Non-firefighers 5%
Support firefighters and officers 6%
2nd line combat firefighters (Chiefs, drivers) 20%
1st line rescue truck firefighters 6%
1st line ladder truck firefighters 30%
1st line pump truck firefighters 29%

24-hour shifts. First-line combat firefighters and officers were assigned to rescue, pump and ladder trucks and were potentially exposed at most fires. Based on discussion with fire department personnel, the potential exposure of 2nd-line combat firefighters was estimated to be less than 50% that of 1st-line combat firefighters.

Table 25 summarizes some of the non-firefighting activities occupying firefighters during most of the time spent on the job. Firefighting activities, summarized in Table 26 for the years 1987-1994, accounted for a small percentage of a firefighter's time on the job. In 1994, a total of 20,612 emergency calls were received of which 4,115 (20%) were for actual fires. Only 41% (1,684) of all fires were structural fires. The vast majority of fires were small, one-alarm fires (97%). There were 67 two-alarm fires (1.6%) and 58 three-, four- or five-alarm fires (1.4%). This explains why it was so difficult to obtain Summa™ canister fire samples, these samples being collected only at 3-alarm fires or larger. In 1994, there were a total of 59,303 vehicle responses by combat crews to all types of alarms, the average response time being 4.34 minutes. In one 12 month period, 80 combat crews responded 11,421 times to actual fires and spent a total of 597,557 minutes on the firescene. It was not possible to determine what proportion of this time was spent at structural fires where potential exposure to smoke was estimated to be the greatest. There was a wide variation between crews in the time spent at fires depending on the task and the geographical location of the firehall to which they were assigned (Figure 59). The ten teams in Montréal spending the most time at fires were on the fire scene for a total of 3,244 minutes, on average, during one year (62 fires) while the ten crews spending the least time at fires were on the fire scene for a total of 906 minutes, on average, during the year (19 fires). On average, each combat team responded to 37 fires per year and spent 52 minutes at the scene of each fire (1,924 min/yr). The average total time spent at fires for firefighters assigned to the least busy firehalls was 28% of the time spent by those assigned to the busiest firehalls. Since only 41% of all fires were structural fires, it can be assumed that combat teams responded to 8-25 structural fires per year or 15

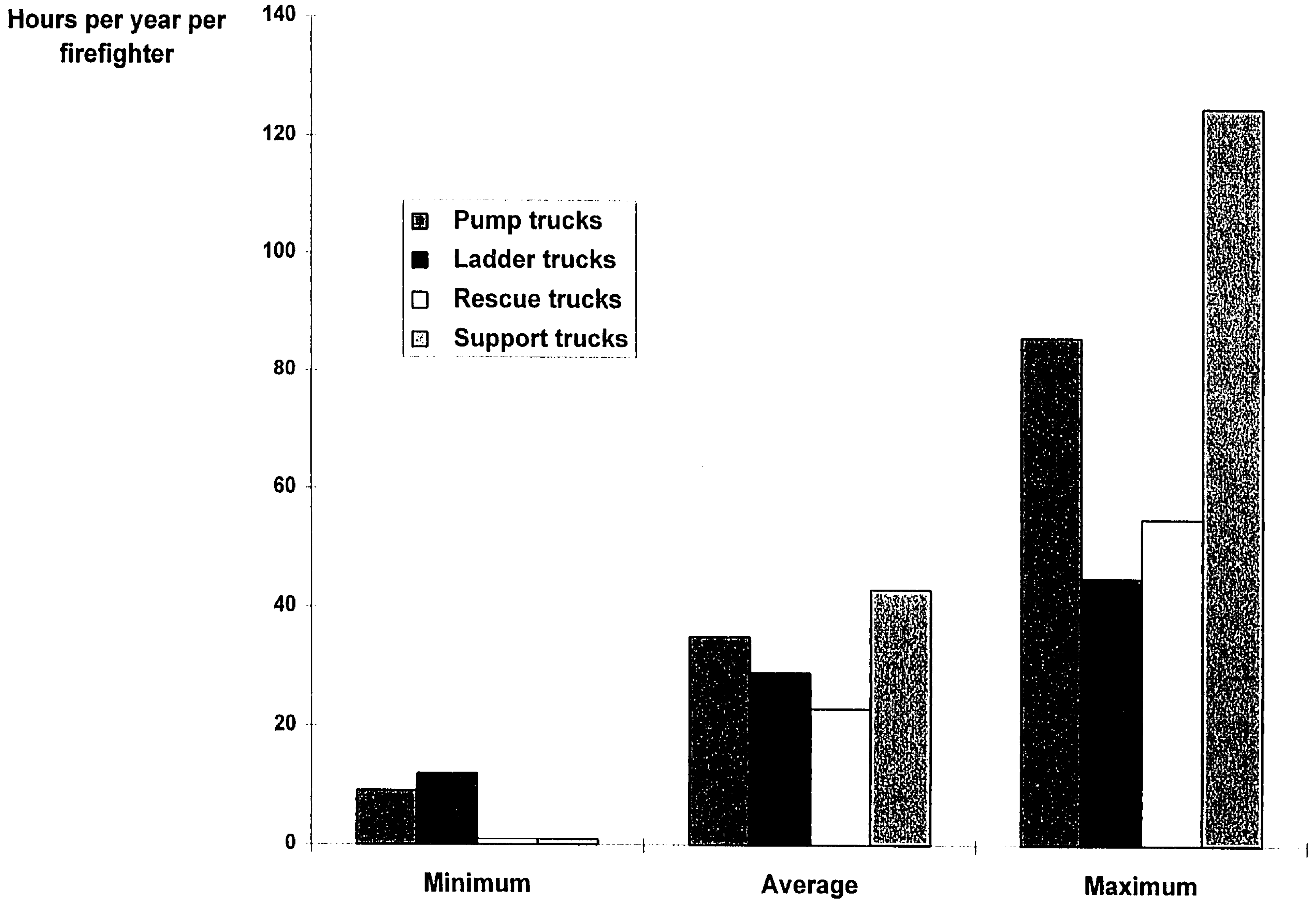
Table 25. Non-firefighting activites (City of Montréal)

Activity	Mean	SD	1990	1991	1992	1993	1994
Investigations (numbers):							
Arson investigations	**567**	**25**		572	589	539	
Identification of criminal fires	**262**	**30**	256	293	275	222	
Dangerous buildings	**64**	**46**			112	21	60
Vacant buildings	**443**	**163**			256	516	556
Public safety (no. participants):							
Home visits	**14 384**	**9 731**	22000	24655	14156	11000	110
Fire prevention inspections	**41 814**	**8 389**	33057	51419	42630	33550	48416
Complains	**8 991**	**1 287**	7775	11037	9405	8277	8462
Infractions	**22 542**	**8 046**	35813	24390	16380	17251	18876
Fire drills	**746**	**233**	374	822	678	970	884
Court cases	**925**	**310**	1268	596	644	910	1206
Approval of permits	**3 630**	**387**			3451	3365	4074
Safety courses	**1 464**	**403**	1916	1617	897	1667	1221
Respiratory protection courses	**133**	**118**	218	287	6	42	111
Fire brigade courses	**1 636**	**679**	2179	1296	2542	1074	1089
Safety courses for immigrants	**2 188**	**329**	1637	2308	2189	2510	2297
Educational visits to firehalls	**3 206**	**1 210**	4467	3440	1189	3517	3417
Educational visits to schools	**2 923**	**1 108**	4304	3729	1851	2905	1824
Special events	**2 899**	**1 633**	4870	3995	845	1742	3045
Information booths	**15 499**	**4 577**	12337	15905	18195	9770	21290
Day camp safety classes	**2 567**	**2 237**		3600	0	4100	
Fire prevention week	**20 580**	**820**				21159	20000
Repairs (numbers):							
Vehicle repairs	**6 400**	**532**		6916	6801	5958	5925
Hose repairs	**2 689**	**331**		2479	2558	2534	3183
Commun. & electrical repairs	**3 891**	**482**		3645	3641	3663	4613
Hydraulic system repairs	**667**	**132**		551	555	800	761
Shop repairs	**1 764**	**166**		1590	1792	1693	1979
SCBA repairs	**4 538**	**833**		4718	4762	3356	5315
Other repairs	**3 808**	**622**		3508	3316	4712	3695
Firefighter training (numbers):							
Production of training videos	**13**	**1**		12	12	14	
Practice (participants)	**11 924**			11924			
Practice (hours)	**6 982**	**4 259**		9993	3970		
Courses (participants)	**2 354**			2354			
Courses (hours)	**1 376**	**66**		1329	1422		

Table 26. Emergency calls to the Fire Department (City of Montréal)

	Average	St. Dev.	%rsd	1987	1988	1989	1990	1991	1992	1993	1994
No. of emergency calls	**18369**	**1488**	**8**	16094	16812	18119	17685	19029	19007	19591	20612
Total fires	**4187**	**250**	**6**	4156	4359	4226	4109	4452	4414	3664	4115
Non-fire emergencies	**13500**	**1584**	**12**	11276	11774	13245	12833	13765	13932	15299	15875
False alarms	**681**	**62**	**9**	662	679	648	743	803	661	628	622
Structural fires	**1920**	**201**	**10**	2041	2185	1975	1988	1919	2001	1563	1684
Vehicle fires	**753**	**57**	**8**	775	701	848	807	774	685	722	709
Miscellaneous fires	**1515**	**190**	**13**	1340	1473	1403	1314	1759	1728	1379	1722
All fires:											
1-alarm fires	**4063**	**244**	**6**	4057	4200	4101	3959	4332	4291	3556	4004
2-alarm fires	**67**	**15**	**23**	42	85	66	89	71	59	55	66
3-alarm fires	**24**	**5**	**23**	28	36	19	22	21	21	25	22
4-alarm fires	**8**	**4**	**51**	7	7	13	11	3	11	7	2
5-alarm fires	**26**	**4**	**17**	22	31	27	28	25	32	21	21
Structural fires:											
1 hose	**1107**	**574**	**52**					446	1488	1386	
2 hoses	**141**	**16**	**11**					154	146	124	
3 hoses	**42**	**3**	**6**					43	44	39	
4 hoses	**26**	**3**	**12**					25	29	23	
5 hoses	**12**	**3**	**22**					14	13	9	
6 - 10 hoses	**32**	**3**	**8**					32	30	35	
11 - 15 hoses	**20**	**5**	**26**					18	26	16	
16 - 20 hoses	**8**	**3**	**30**					6	11	8	
21 - 30 hoses	**8**	**4**	**45**					10	4	11	
More than 30 hoses	**1**							1	1	1	

Figure 59. Bar-graph showing minimum, average and maximum times, as an annual average determined over a three-year period (1991-1993), that firefighters assigned to pump, ladder, rescue and support trucks spent at fires.


Hours per year per firefighter
140
120
100
80
60
40
20
0
Pump trucks
Ladder trucks
Rescue trucks
Support trucks
Minimum
Average
Maximum

structural fires per year, on average.

It was difficult to estimate the proportion of the time spent at fires that firefighters were close enough to the fire to be exposed to smoke. Part of their time was occupied with fighting the fire at a distance from the outside, with rolling and unrolling hoses, changing air tanks, resting, etc. Since firefighters were required to use SCBA's when exposed to smoke, their actual respiratory exposure was, theoretically, zero. In practice, this was not the case, smoke inhalation accounting for up to 10.7% of firescene accidents (Table 27). Firefighters tend to use their SCBA's when they "see lots of smoke."

Log book data detailing the purging and filling of SCBA cylinders was analyzed to provide an estimate of the time during which firefighters used their SCBA's at the firescene. Approximately 530,000 ft^3 (15 x 10^6 L) of air were processed by the Fire Department compressors in a 12-month period. As expected, crews spending more time at fires used more compressed breathing air, pump truck crews using the most air and spending the most time at fires (Figure 60). In a year, a total of 10,911 SCBA cylinders were used at fires. Two air supply trucks refilled 5,041 cylinders per year at firehalls and attended 474 fires (probably structural fires) where they refilled 5,870 cylinders, between two and 112 cylinders being filled at any one fire (Figure 61). Each firefighter was issued one personal SCBA cylinder and one spare cylinder while reserve cylinders were stored in the air supply truck. Approximately 15% of SCBA cylinders used were reserve cylinders, the remainder being equally divided between personal and spare cylinders (Figure 62). This suggests that firefighters generally used two SCBA cylinders (occasionally three) at fires where respiratory protection was employed. Table 28 shows the use of compressed breathing air at fires. On average, respiratory protection was used by pump truck crews and by ladder truck crews for only 6% of the time spent at fires (Figure 63). A similar result is arrived at by performing the calculation somewhat differently: 1,382 exposed firefighters (1,211 combat firefighters + ½•341 drivers) spent 2,658,968 man minutes (1,382 exposed firefighters x 1,924 min/yr) at fires

Table 27. Firefighter accidents (City of Montréal)

	Average	St. Dev.	%rsd	1990	1991	1992	1993	1994
Firescene accidents:								
Smoke inhalation	**5**	**3**	**50**		4	5	3	9
Burns	**12**	**5**	**40**		10	18	7	12
Injury	**64**	**17**	**26**		58	88	48	63
Other	**38**	**29**	**77**		58	17		
Non-firescene accidents:								
Non-fire emergencies	**11**	**4**	**36**	16	9	9		
Training	**27**	**8**	**30**	35	26	19		
Travelling	**39**	**9**	**22**	39	30	47		
Fire hall	**110**	**21**	**19**	134	98	98		
Sick leave due to accidents (hrs.)	**62728**	**23925**	**38**	81470	90947	63089	42414	35722
Accident rates:								
Firescene per 100 fires	**3**	**1**	**20**	4	3	3		
Firescene per 100 firefighters	**9**	**1**	**15**	10	8	8		
Non-fire emergency per 100 incidents	**0.08**	**0.03**	**41**	0.12	0.07	0.06		
Line-of-duty deaths per 100,000 fires	**4**	**1**	**16**	0		4	4	5

Figure 60. Graph showing the man-minutes of compressed breathing air used from SCBA's as a function of the total man-minutes which firefighters assigned to rescue, ladder and pump trucks spent at the scene of all types of fires.

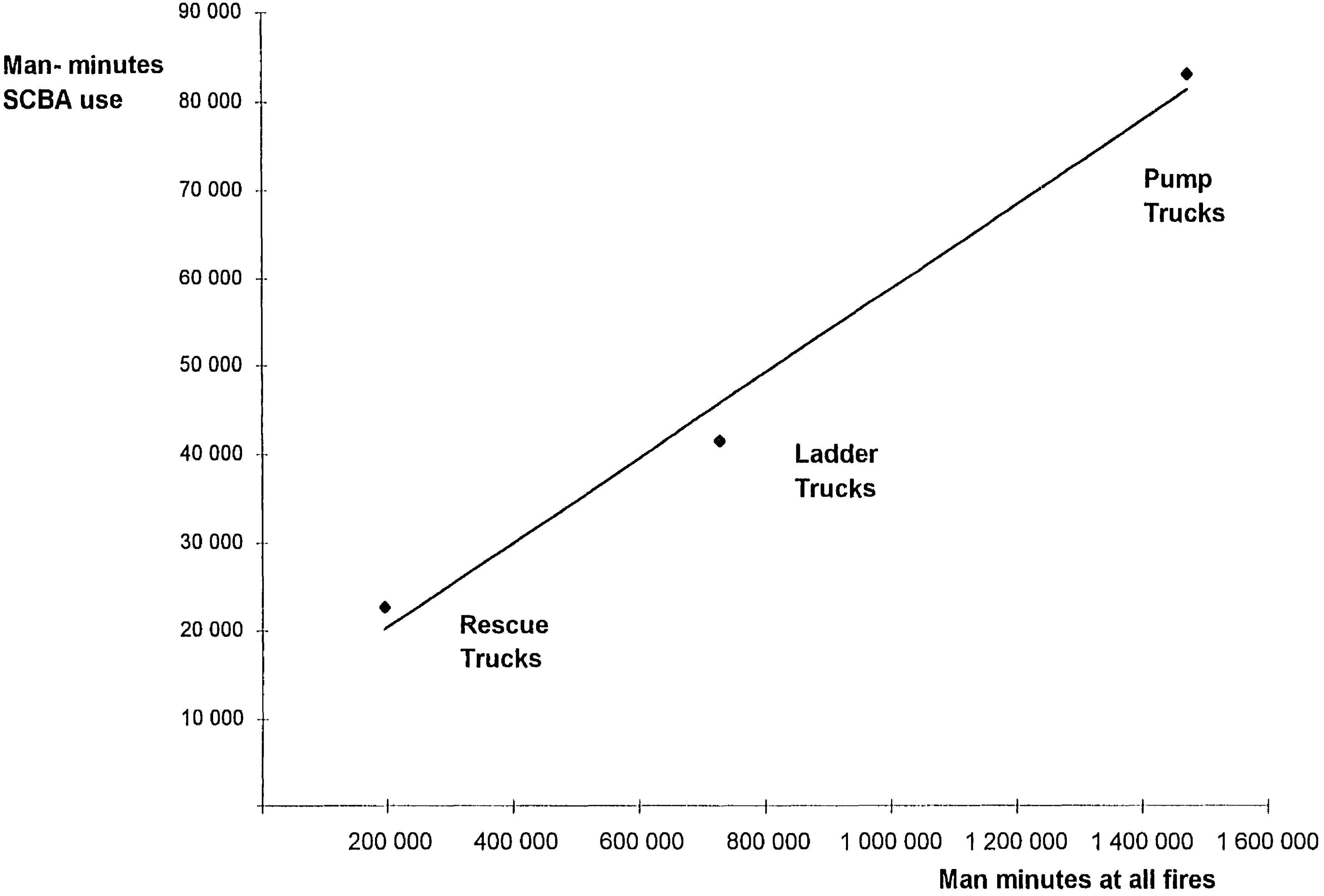

Man- minutes SCBA use
90 000
80 000
70 000
60 000
50 000
40 000
30 000
20 000
10 000
Pump Trucks
Ladder Trucks
Rescue Trucks
200 000
400 000
600 000
800 000
1 000 000
1 200 000
1 400 000
1 600 000
Man minutes at all fires

Figure 61. Histogram showing the number of SCBA cylinders filled by the air supply truck at the scene of fires.

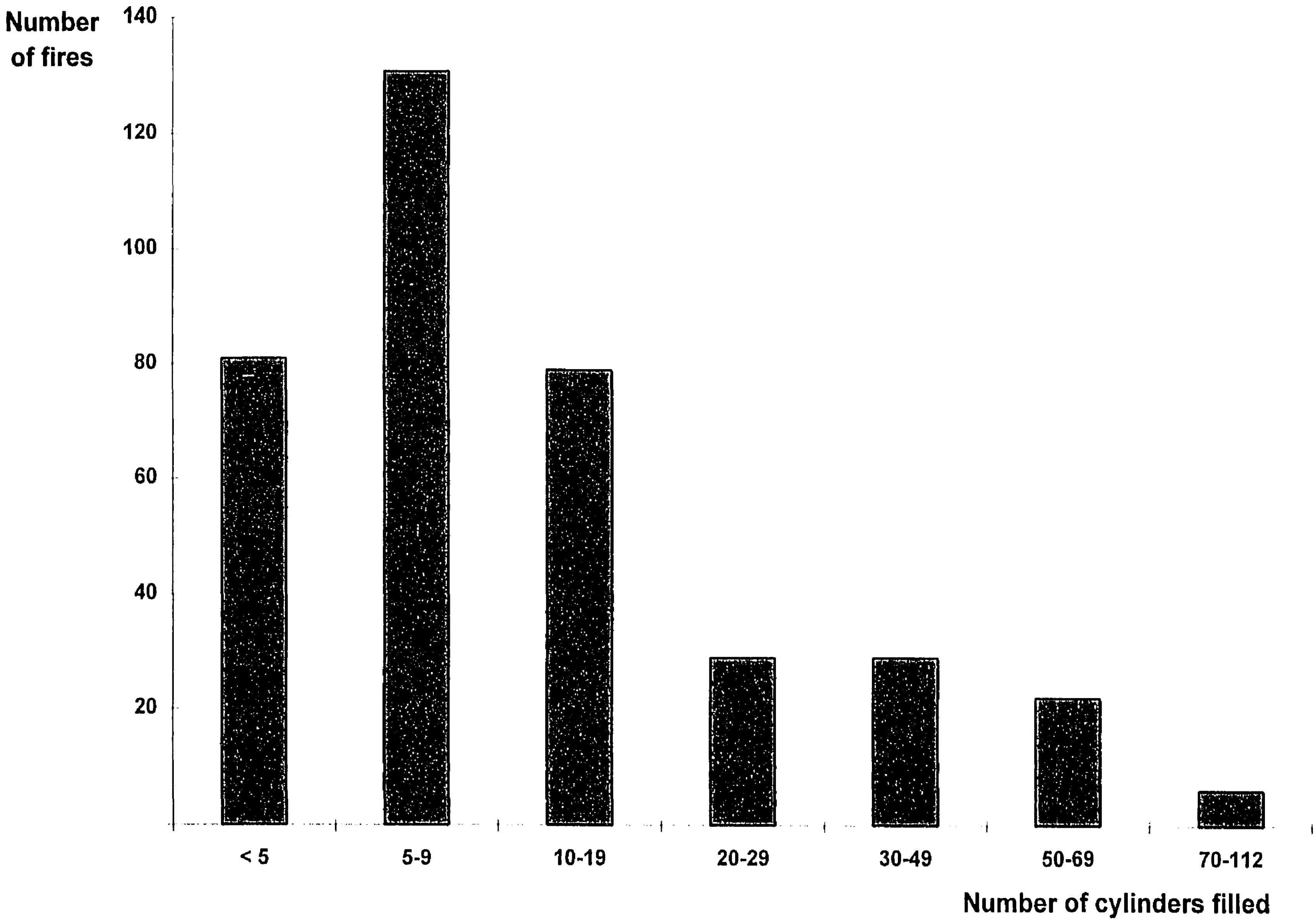

Number of fires
140
120
100
80
60
40
20
< 5
5-9
10-19
20-29
30-49
50-69
70-112
Number of cylinders filled

Figure 62. Bar graph showing the use of SCBA cylinders assigned to firefighters as well as spare cylinders assigned to rescue, ladder and pump trucks. Firefighters who had emptied their own and the spare SCBA cylinders then used reserve cylinders allocated to the air supply truck.

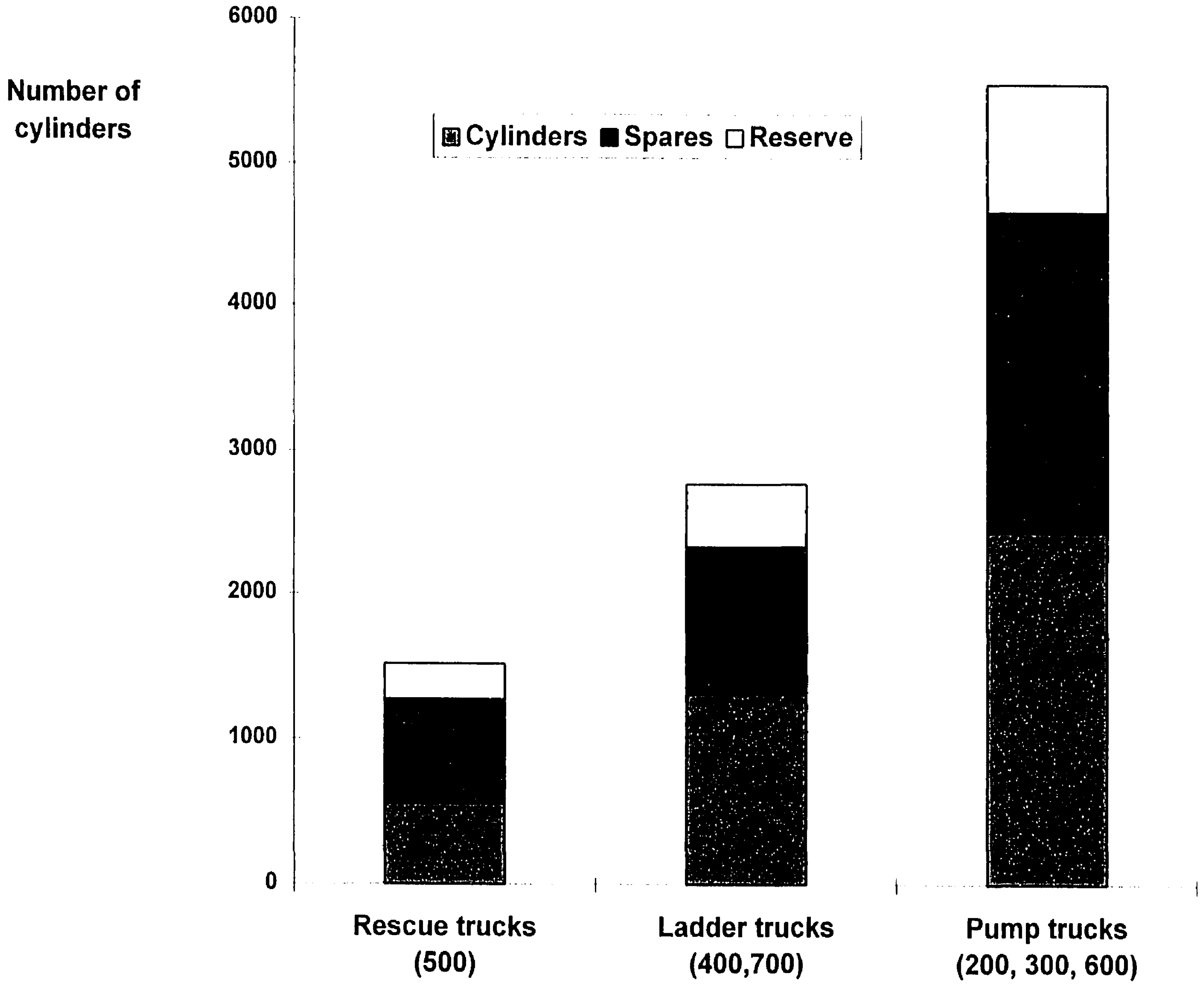
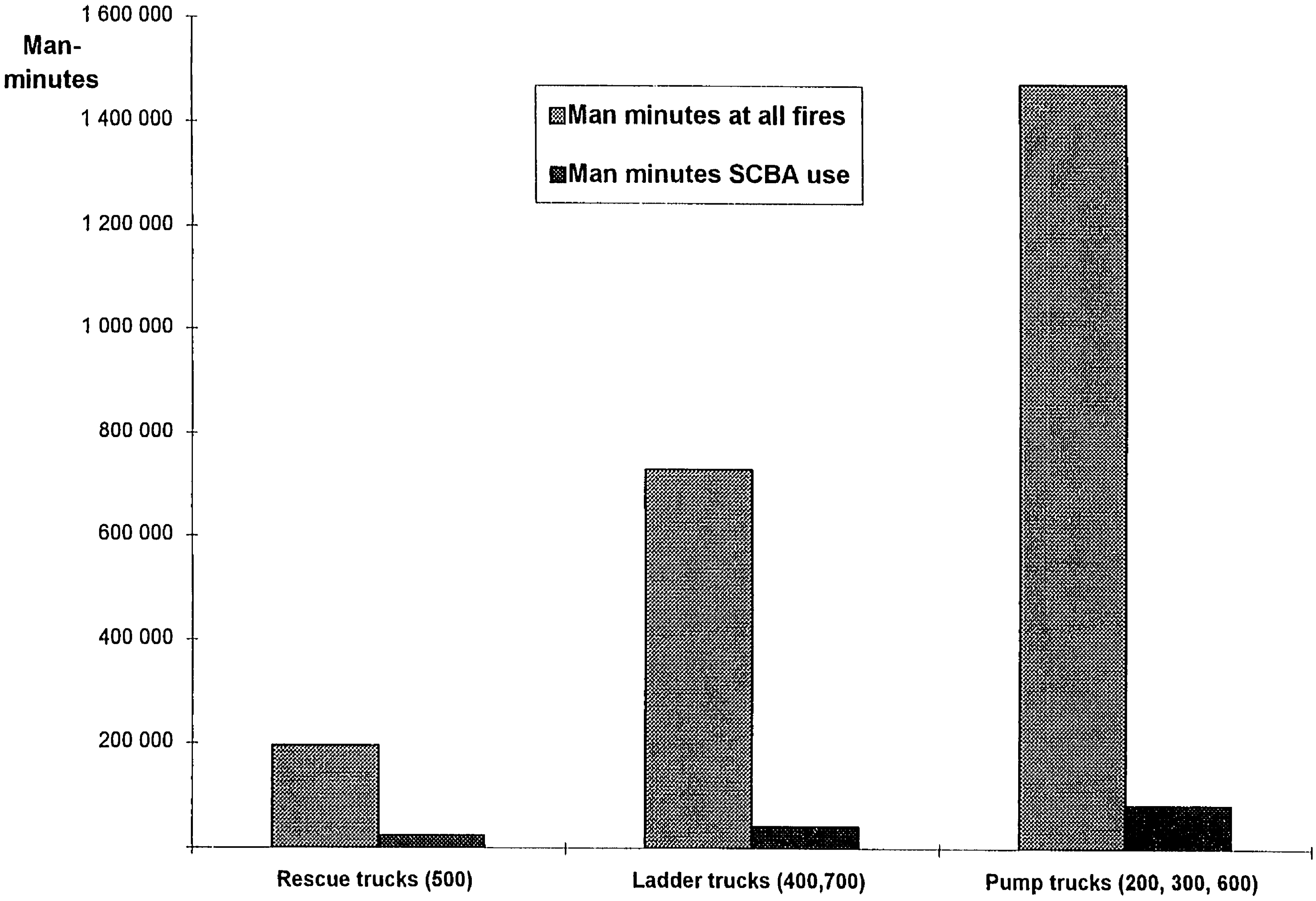

Number of cylinders
6000
5000
4000
3000
2000
1000
0
▨ Cylinders ■ Spares ☐ Reserve
Rescue trucks (500)
Ladder trucks (400,700)
Pump trucks (200, 300, 600)

Table 28. Use of compressed breathing air (SCBA's) at fires

	Man minutes at all fires	Man minutes SCBA use	Truck minutes at all fires	% SCBA usage at fires
Rescue trucks (500)	195 624	22 665	48 906	12
Ladder trucks (400,700)	728 329	41 550	208 094	6
Pump trucks (200, 300, 600)	1 472 460	83 220	368 115	6
Total	**2 396 413**	**147 435**	**625 115**	**6**

Figure 63. Bar graph comparing the total man-minutes of SCBA use to the total man-minutes spent at the scene of fires for rescue, ladder and pump trucks.


Man-minutes
1 600 000
1 400 000
1 200 000
1 000 000
800 000
600 000
400 000
200 000
▨ Man minutes at all fires
▨ Man minutes SCBA use
Rescue trucks (500)
Ladder trucks (400,700)
Pump trucks (200, 300, 600)

where 10,911 SCBA cylinders (or a maximum of 163,665 man minutes of compressed breathing air) were used i.e. SCBA's were used for 6% (163,665 man minutes ÷ 2,658,968 man minutes) of the time spent at fires, on average.

Since it is not known how much time firefighters spent at structural fires, nor how much time was spent exposed to smoke without respiratory protection, it is not possible to accurately calculate firefighters' respiratory exposure to smoke. However, it is known that individual firefighters spent a total of 1,924 min/yr at fires, on average, and that there was a wide range of exposure times between firefighters (906-3,244 min/yr) depending on firehall assignment. It is also known that exposed firefighters each used an average of 118 min/yr (163,665 man minutes ÷ 1,382 firefighters) of compressed breathing air.

The standard work load for a City of Montréal firefighter was 192 days per year for a total of 2,184 hr/yr. If all sick leave due to accidents (Table 27) is assigned to exposed firefighters (62,728 hrs ÷ 12 hrs/workday ÷ 1,382 firefighters = 4 days), then exposed firefighters worked 188 days per year, on average. If SCBA's were never used, the maximum time of respiratory exposure to smoke and fire gases, for a firefighter working at one of the 10 busiest firehalls in Montréal, would be 17 min/day (3,244 min/yr ÷ 188 days/yr), on average. On the other hand, it has been noted that firefighters spent an average of 54 minutes at the firescene when responding to fires. Clearly, firefighters spend much more time at some fires than at others and the reliance on time weighted averages to describe the exposure patterns of this occupational group can be highly misleading. It was also noted that firefighters appear to have used two SCBA cylinders (2x15=30 minutes of compressed breathing air) at fires where respiratory protection was worn. This would suggest that, when respiratory protection was used, firefighters wore their SCBA's for 27 minutes of the 54 minutes that they were on the firescene. The discrepancy between this speculative estimate and the 94% of the total time spent at fires that firefighters are known not to have used their SCBA's may be explained by the large number of fires where firefighters used no respiratory protection at all and by the fact that it was never used during mop-up operations. It could be that firefighters used their SCBA's at 12% of fires and that at these fires they used them for 50% of the time spent on the firescene, on average. This would be consistent with the finding that, on average, firefighters responded to 15 structural fires per year while using eight SCBA cylinders per year (10,911 cylinders/yr ÷ 1,382 exposed firefighters) and two to three cylinders at fires where respiratory protection was used. The question remains as to whether or not firefighters should be using their SCBA's more often than they do.

CHAPTER 4

DISCUSSION

This study has focused on three potential sources of firefighter chemical exposures to toxic gases and vapours: (1) diesel emissions in firehalls; (2) contaminated compressed breathing air; and, (3) VOC's at fires. While each aspect will be discussed in detail, a summary of the findings have demonstrated that:

A. the seriousness of the problem of chemical contamination in firehall garages was much less dramatic than was implied by Froines et al. (1987), who suggested that the levels of diesel emissions were sufficient to require the installation of mechanical ventilation in firehall garages. There was no evidence that such protection was necessary, the degree of firefighter exposure to diesel emissions in Montréal firehalls having been found to be insignificant. However, a potentially useful finding of this investigation was the strong evidence for linear correlations between the gaseous components of diesel exhaust, permitting the use of carbon monoxide, for example, as a surrogate for the rapid estimation of the concentrations of the other components.

B. contamination of compressed breathing air was an unexpected source of exposure of firefighters to toxic gases. Recognition and solution of this problem has improved the quality of respiratory protection for Montréal firefighters and it is hoped that dissemination of this information will improve the situation for other users of compressed breathing air (SCUBA divers, for example).

C. approximately 123 VOC's were identified at municipal structural fires. Only 14 of these substances were found at high levels relative to the others, accounting for 85% of the total VOC concentrations measured. Eight of these substance have established ACGIH (1996) TLV's and five of them have Biological Exposure Indices (BEI's). Five of them (benzene, toluene, 1,3-butadiene, naphthalene and styrene) account for 40% of the total VOC concentrations. The maximum levels of benzene (IARC Group 1, a proven human carcinogen), 1,3-butadiene (IARC Group 2A, a probable human carcinogen), styrene (IARC Group 2B, a possible human carcinogen) found were 11 ppm, 5 ppm and 2 ppm, respectively (IARC 1987, 1992, 1994). Given that firefighters function at maximum work levels, comparison with TLV's necessitates calculation of absorbed doses rather than simple comparison with ambient exposure level (discussed below, pages 247-248).

D. this study provided the first real data permitting accurate estimation of the time that firefighters spend at the scene of municipal fires. The average City of Montréal firefighter spent some 906-3,244 minutes per year at all types of fires in 1994, depending on the firehall assignment. Firefighters were not exposed to smoke and fire gases for extended periods of time, a Montréal firefighter attending between 19 and 62 fires per year, 46% of which were structural fires, and spending an average of 54 minutes at the scene of each fire. Although firefighters appear to have useed their SCBA's for approximately 50% of the time at fires where respiratory protection was required (probably structural fires, Figure 62), they were protected for only 6% of the total time spent at fires when this is calculated as a percentage of the time spent at all fires (Figure 63). This still seems to be an inadequate rate of respiratory protection given the results of experimental fires which show that considerable amounts of thick smoke are produced within a few minutes even in the case of small fires which can be rapidly extinguished.

I. DIESEL EMISSIONS IN FIREHALL GARAGES

The measurement of one of the components of diesel emissions as a surrogate for the estimation of the concentrations of the other components is a simple, rapid and convenient method for the evaluation of occupational exposures to diesel emissions. However, preliminary data must first be obtained for each of the contaminants of interest in order to establish the slope of the linear regression lines characteristic of the situation and location being monitored. The continuing validity of these relationships should be checked periodically in order to adjust for changing conditions.

Any of the components of diesel emissions could be used as a surrogate for the measurement of the other contaminants. Carbon dioxide was preferred by many authors because it was useful when making calculations for mechanical ventilation. Carbon dioxide is the only stable, nonreactive pollutant in the exhaust that is unaffected by emission control devices or engine wear (Daniel, 1988). While NO_2 is a specific marker for diesel emissions, it is not a product of gasoline combustion , also of concern in firehalls since automobiles also operated from some of the garages. There was no smoking permitted during monitoring of firehall garages and the only sources of CO were the operation of diesel and gasoline powered vehicles responding to alarms and the use of gasoline powered tools and generators during weekly maintenance checks. Carbon monoxide was, therefore, a convenient marker for the operation of contaminant-producing tools and vehicles in firehall garages. Other advantages in the use of CO as a marker are: (1) data-logging, personal monitors are easily available; (2) it is not necessary to subtract baseline levels, as is the case for CO_2; (3) measurements are not affected by human respiration, as is the case for CO_2; (4) the use of CO gives a direct measurement of at least one of the more toxic components emitted from combustion processes, which is not the case for CO_2.

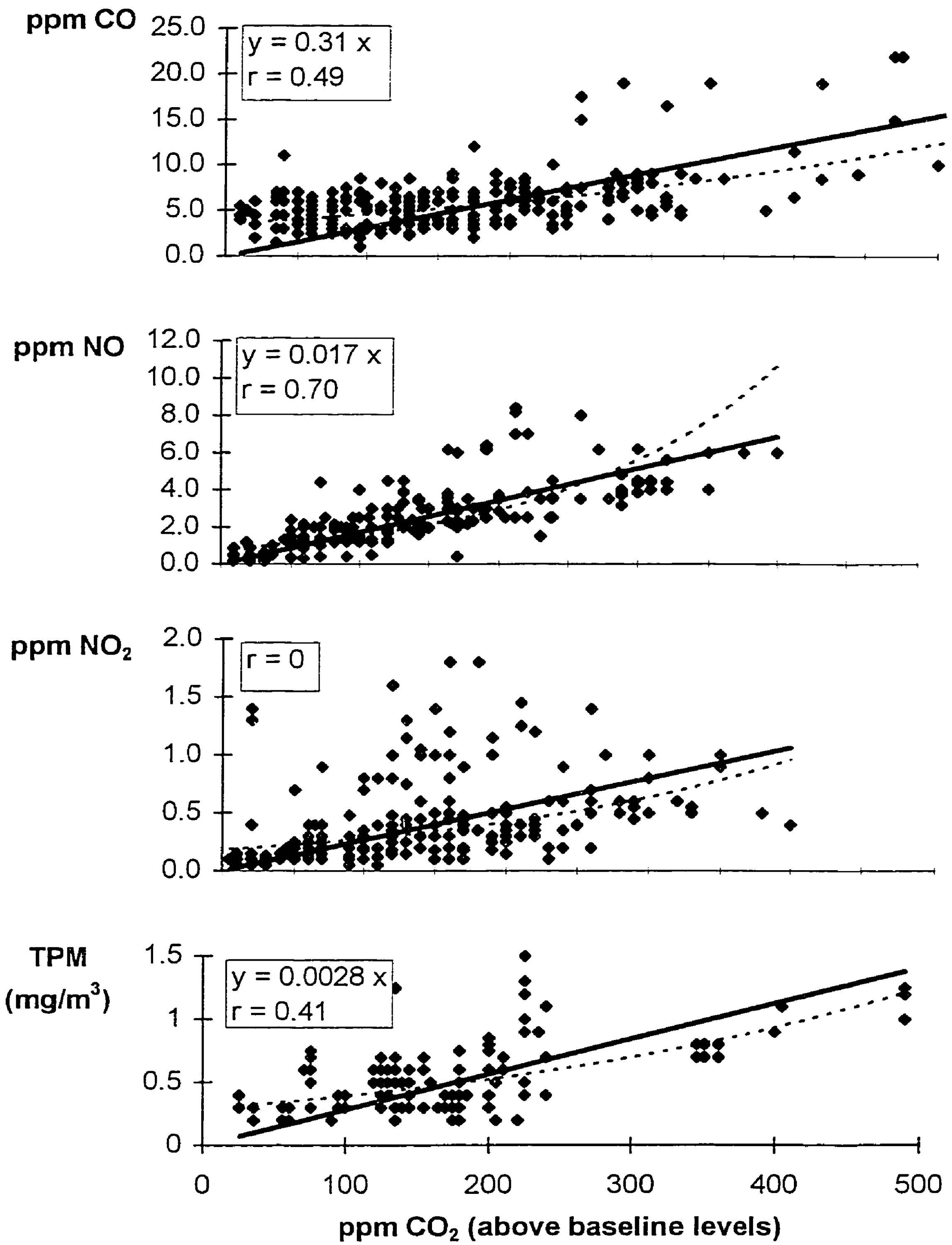
The peak CO concentration of 4.1 ppm (Table 16) found in firehall garages due to diesel emissions from two trucks during alarms was less than the ACGIH TLV of 25 ppm and, calculated as a TWA, would be insignificant over an 8-hour shift. The peak levels of CO found were similar in magnitude to TWA's found in other studies of diesel emissions in mines and tunnel construction where equipment was operated more or less continuously in ventilated areas (Sutter, 1975; Little, 1977; Holland, 1978). The results from a number of studies suggested that when the concentration of CO was less than 10-20 ppm, the concentrations of the other toxic components of diesel emissions were also below their respective TLV's (Stewart et al., 1978; Sutton et al., 1978; Johnson, 1980; Westaway et al., 1983; Mogan et al., 1983; French and Mildon, 1979, 1984; Sampara, 1986). The peak concentration of NO_2 (2.2 ppm) found in firehall garages was roughly the same order of magnitude as the measured CO and below the STEL of 5 ppm (ACGIH, 1996). However, other studies found the concentration of NO_2 to be approximately an order of magnitude lower than that of CO (Sutter, 1975; Little, 1977; Holland, 1978). Possible explanations for this discrepancy include: (1) measurements were obtained during the idling of engines and it is known that more NO_2 is produced during low loads; (2) diesel producing engines in other studies may have been fitted with anti-pollution devices which removed NO_2.

Lavoie and Roberge (1991) obtained area samples of components of diesel emissions (CO, NO, NO_2 and TPM) in municipal bus garages. Samples were obtained on Monday mornings during winter months when buses were exiting the garages. Mechanical ventilation provided three to four air changes per hour. The research report showed plots of the concentration of measured pollutants against CO_2. However, mean values and standard deviations were not included in the results. An exponential equation was derived from regression analysis of the data to show a mathematical relationship between the various components. It was proposed that these equations would allow the use of CO_2 as a surrogate measure of CO, NO, NO_2, and TPM.

Recalculation of the Lavoie and Roberge (1991) results revealed two sets of

CO_2 data having ambient concentrations (mean ±95% CI) in municipal bus garages of 178±17 ppm and 152±14 ppm above baseline levels (Figure 64). The ambient concentrations (mean ±95% CI) of other components of diesel emissions were: CO=13±9 ppm, NO=2.7±0.3 ppm, NO_2=0.5±0.1 ppm, TPM=0.6±0.1mg/m^3. Linear and exponential regression curves were fitted to the data (Figure 64). In the case of CO vs. CO_2, the correlation coefficients for linear and exponential regression were 0.49 and 0.39, respectively (n=257). There is no theoretical reason to prefer exponential to linear regression and there is, in this case, a better correlation for linear regression. The use of the exponential equation to predict pollutant levels from measured CO_2 levels results in an underestimation of the pollutant of interest in the mid-range of CO_2 or an overestimation at either extremity of the curve. A similar argument holds also for the case of NO vs. CO_2 where a difference of 0.02 in the respective correlation coefficients does not justify, on that basis alone, the rejection of linear regression. Similarly, there is no obvious reason to reject linear regression in the case of TPM vs. CO_2. In the case of NO_2 vs. CO_2, the linear regression coefficient is equal to zero and fitting an exponential curve to this data (r=0.43) does not improve its quality. The ratios for ppm CO/ppm CO_2, ppm NO/ppm CO_2, and mg/m^3 TPM/ppm CO_2 were 0.031±0.3, 0.017±0.001 and 0.0028±0.0003, respectively. Other authors have found linear relationships of diesel-emitted pollutants with CO_2 in ventilated underground mines (Schnakenberg 1986; Dainty, 1989; Gangal et al., 1991a, b; Dainty and Gangal, 1993; Gangal and Dainty, 1993). Schnakenberg (1986), for example, found that the concentration (ppm) of CO, NO, NO_2 and mg/m^3 TPM plotted against levels ppm CO_2 yielded slopes of 0.01000, 0.00712, 0.00108 and 0.00096, respectively. The data found in the literature, however, frequently exhibit considerable scatter about the regression line. This was the difficulty encountered in the measurements in bus garages and may be attributed to a number of possible factors: (1) the operation of a number of different vehicles; (2) some vehicles were in movement while others were stationary; (3) simultaneous occurrence of a number of different situations.

Figure 64. Graphs of CO vs. CO_2, NO_2 vs. CO_2, NO_2 vs. CO_2, and total particulate matter (TPM) vs. CO_2 resulting from diesel emissions in municipal bus garages. The solid lines show the results of linear regression and the dotted lines show the results of exponential regression analysis. Data was taken from the Lavoie and Roberge (1986) study, "*Détermination d'un indice du maintien de la qualité de l'air lors de l'utilisation de moteurs diesels.*"


ppm CO
25.0
20.0
15.0
10.0
5.0
0.0
y = 0.31 x
r = 0.49
ppm NO
12.0
10.0
8.0
6.0
4.0
2.0
0.0
y = 0.017 x
r = 0.70
ppm NO_2
2.0
1.5
1.0
0.5
0.0
r = 0
TPM (mg/m^3)
1.5
1
0.5
0
y = 0.0028 x
r = 0.41
0
100
200
300
400
500
ppm CO_2 (above baseline levels)

Rigorous controls in firehall garage experiments and the inclusion of worst-case scenarios resulted in very strong correlation for linear regression. This confirms the choice of a linear, rather than an exponential, model when using CO_2 as a surrogate for the estimation of the levels of other diesel-emitted pollutants. The greater precision obtained for the linear models, as evidenced by the higher correlation coefficients, may be explained by the following: (1) better controlled experimental conditions; (2) ventilation between experiments; (3) emissions only - does not include decay; (4) doors closed - no mixing with outside air during the experiment; (5) no ventilation during the experiment; (6) no other combustion sources such as smoking or the operation of other machinery; (7) smaller garage, therefore more homogeneous dispersion of emissions.

Given the concentration of 4.1 ppm CO measured for 2-truck response to alarms in firehall garages, the Lavoie and Roberge (1991) linear regression model would predict a corresponding level of 132 ppm of CO_2 while the regression model based on Schnakenberg's (1986) data would predict a concentration of 410 ppm CO_2. The 195-257 ppm CO_2 predicted by regression of the firehall garage data lies between these two models. The TWA concentration of particulates (0.17-0.48 mg/m^3) found by Froines et al. (1987) in firehall garages was similar to levels found in mine and bus garage studies. Use of the TPM/CO_2 linear model derived from the Lavoie and Roberge (1991) data for bus garages would predict a peak concentration of 0.28 mg/m^3 of TPM when applied to the Montréal firehall garages. This is comparable to the levels of TPM found in the firehall, bus garage and mine studies mentioned previously. Particulate matter remains suspended in ambient air for extended periods of time and its concentration may not follow the same rapid decay patterns as was seen for the gaseous components of diesel exhaust. This may explain why the measured particulate levels in the Froines' et al. study, and the estimated peak levels in the present study, were not lower than has been found in the mine and bus garage studies where vehicles operated more or less continuously (Sutter, 1975; Little, 1977; Holland, 1978). Nonetheless, results suggest that the exposure of firefighters in firehalls is well below the ACGIH TLV of 3 mg/m^3 for respirable particulate matter as well as the proposed MSHA maximum limit of 1 mg/m^3 for diesel soot (Grenier, 1992). Furthermore, it is unlikely that the TWA's would exceed the exposure limit of 0.2 mg/m^3 for PAH's, which constitute a fraction of the TPM produced by diesel engines.

II. COMPRESSED BREATHING AIR CONTAMINATION

Normally functioning and well maintained compressors still produce toxic contaminants which must be removed by air purifying systems. The presence of odours or of contaminants such as carbon monoxide, water vapour, or oil are indicators of possible compressor malfunction, maintenance deficiencies and/or air purifier inefficiency. Since CO is converted to CO_2 by the catalytic purifying system, higher than expected levels of CO_2 (> 450 ppm) may be an early indicator of other potential problems. Since the catalyst life is reduced in the presence of water vapour, water vapour in the compressed breathing air should alert the user to the possibility of other contaminants. The high levels of water vapour (70 ppm) detected early in 1995 were found together with 500-600 ppm of CO_2 (above the 500 ppm allowed) although there was no evidence of other contaminants (Figure 10). This was followed shortly thereafter by higher than normal levels of CO (3 ppm) and NO_2 (0.25 ppm). While Figure 10 illustrates how easily the system can get out of control even when adhering to current standards, regulations and manufacturers' instructions, the data, summarized in Table 18, demonstrate that it is possible to maintain levels of contaminants far below the maximum allowed in the Canadian Standard. The fact that water and CO are only two components of a complex toxic mixture is clearly illustrated by their positive correlation with each other and with the presence of NO_2 (Figure 10). The limits set forth in the Canadian Standard (Table 2) are maximum allowable ceiling levels not to be exceeded at any time and they should not be used as a guide for normal levels of contaminants in compressed breathing air (CSA, 1985).

Water vapour in compressed air will condense and freeze in a regulator causing it to malfunction when the ambient temperature is lower than the pressure dew-point. For example, compressed breathing air used by a SCUBA diver at 3,000 psig containing 5,918 ppm (mL/m^3) of water vapour, is equivalent to 29 ppm of water vapour measured at atmospheric pressure (CSA, 1985). At this concentration, water could condense and freeze at an ambient temperature of 0°C (pressure dew-point) as it passed through air regulators of the type found on a SCUBA or SCBA (Figures 13 and 37). The absolute maximum concentration of water vapour allowed in systems at or above 1,800 psig is 27 ppm measured at atmospheric pressure (CSA, 1985). Figure 10 shows that, even with rigorous controls in place and frequent monitoring of the air quality, water vapour levels safe for winter diving are difficult to achieve, a possible factor in SCUBA diving deaths in recent years (Boudrias, 1991, 1995, 1996). A firefighter's 2,216 psig SCBA regulator might freeze when used at an ambient temperature of -31°C if it contained 2.3 ppm of water vapour measured at atmospheric pressure (Figure 13). A low pressure system used by firefighters in confined space entry at 100 psig containing 305 ppm of water vapour is equivalent to 45 ppm measured at atmospheric pressure and could cause the air regulator to freeze when used at an ambient temperature of -31°C. The Standard for medical air is less stringent and must not be applied to compressed breathing air. The pressure dew-point of medical air at 100 psig may be as high as +10°C corresponding to 10,590 ppm of water at 100 psig or 1,557 ppm of water measured at atmospheric pressure (CSA, 1992). In addition, twice as much nitrous oxide is allowed in Medical Air as in compressed breathing air, and the maximum concentration of non-methane organic compounds or other unspecified contaminants in Medical Air is five times higher than that which is allowed in compressed breathing air (CSA, 1992).

Exposure limits to chemical contaminants in ambient workplace air are the same for firefighters as for other workers and are expressed as an 8-hour time-weighted average. The limits may vary slightly from province to province in Canada but they are similar to the TLV's documented by the *American Conference of Government Industrial Hygienists* (ACGIH, 1996) The current 25 ppm TLV for carbon monoxide is intended to prevent adverse neurobehavioral changes and maintain cardiovascular exercise capacity (ACGIH, 1991a). This is calculated for people at rest and is based on the BEI of 3.5 %COHb which was adopted by the ACGIH in 1992 (Figure 14). Most of the published guidelines are based on humans at rest and do not take into account the unusual working conditions in occupations where SCBA's would be used. The *International Fire Service Training Association* (IFSTA) makes this error in its manual on SCBA's as do some of the compressor operating manuals (IFSTA, 1982). End-users who consult these tables are therefore misled as to the health risk to which they expose themselves when using compressed breathing air contaminated with CO.

The heart and the central nervous system have a higher oxygen demand than other tissues and will be more susceptible to the effects of CO exposure (Adams, 1988). Decrements in visual task performance and in hand-eye coordination have been observed at 5% COHb (Putz et. al. 1976 and 1979; Putz, 1979). Diminution of visual perception, manual dexterity, mental confusion, ability to learn or performance in complex sensorimotor tasks such as driving have been observed at COHb levels of 4-17% (Halperin et. al., 1959; Ray and Rockwell, 1970; Bender et. al., 1971; McFarland, 1973; Putz et. al., 1976; NRC, 1985). Headache, nausea and vomiting have been associated with 16%, 20% and 30% COHb respectively (Stewart, 1975a, b). It appears that mental confusion or disorientation may have been a factor in some SCUBA diving deaths (Boudrias, 1991, 1995, 1996). Active subjects are affected much earlier and much more seriously than resting subjects exposed to the same concentration of CO (Figure 14). Decreases in time to exhaustion have been associated with 3.3-5.5% COHb in humans (Aronow, 1975; Horvath et. al., 1975; Klein et al., 1980). Subjects at 7% and 20% COHb levels experienced 29% and 48% decreases in time to exhaustion, respectively, during maximal exercise (Ekblom 1972). Firefighters work under maximum physiological, psychological and heat stress, thereby increasing the uptake of contaminants within a given time period. Firefighters and others working at maximum exercise levels utilize oxygen at a more rapid rate so that they are more susceptible to the effects of COHb in the blood.

While the regulation of the manufacture and use of the breathing apparatus itself is closely controlled, there are alarming deficiencies in the production and quality control of the air which is put into these units. This occurs in spite of a recommendation by the *National Fire Prevention Association* (NFPA) that compressed breathing air be tested at least monthly and of a requirement by the *Bureau de normalisation du Québec* and the *Canadian Standards Association* that stored compressed breathing air be replaced every three months (CSA, 1982; NFPA, 1986; BNQ 1989). Investigations have suggested that many breathing air supply systems in use in the province of Alberta are not properly designed and that a number of operators do not have a firm grasp of the engineering principles associated with the systems in their care (Manecon, 1987). People need to appreciate the reasons why rigorous maintenance and quality control procedures are necessary before they will be willing to implement them.

The seriousness of the situation is all the more urgent given the widespread, naive trust which is placed in the safety of the air stored in the tanks that are an integral part of these units. This lackadaisical attitude appears to stem, in part, from the idea that "It's just breathing air." The fallacy arises from ignorance of the sources and nature of contamination of the stored breathing air itself and of the potential morbid and lethal outcomes resulting from the use of this air. There is little demand for publication of detailed operating procedures due to ignorance that there is anything wrong with the prevailing way of doing things. The NAUI Pro Manual for SCUBA divers (NAUI, 1977), for example, states, "Carbon monoxide poisoning is rare in diving and should be emphasized only if local conditions utilize "portable" compressors. ... Reputable dive stores have spent thousands of dollars to install an air station which should insure safe, high quality compressed air." In a Technical Report to the U.S. Department of Health and Human Services, McClure (1987) also stated that, "If the compressor operates at excessive temperatures, it may actually form deadly CO within the machine, although such CO formation is rare." Based on a single study of compressor failure, which did not show that high temperatures would lead to increased CO, the requirement for continuous CO monitoring of compressors has been dropped from the *ANSI Z88.2-1992 Standard for Respiratory Protection* (Nelson et al., 1994). In opposition to this, the results of the present study suggest that continuous CO and H_2O monitoring of compressed breathing air compressors should be made mandatory.

There is little or no regulation of the manufacture, installation, operation and maintenance of compressors which are used to produce the compressed breathing air (OPPBTP, 1966). The Standards merely limit the allowable degree of contamination without specifying how this is to be achieved. Standards do not have force of law in all jurisdictions. Other than the relevant Standards and the operating manuals available from the manufacturers, there is little information available on the subject. Consequently, producers and users are left largely on their own in this matter with fragmentary knowledge and little or no regulatory controls. In light of the above facts, it is surprising that coroners' investigations of SCUBA related deaths have not focused more attention on CO and H_2O contamination when the toxicological effects and safety hazards of these are known.

The Montréal experience points to two serious flaws in the Standard: (1) testing of the air purity every six months is insufficient; and (2) it is not adequate to test the air purity following compressor maintenance procedures or replacement of air purification cartridges. Such a strategy may be doing little more than concealing serious underlying problems occurring during the previous 6-month period and during the months following analysis. Processing of a high volume of air such as in a large fire department or SCUBA equipment supply store may necessitate changing the air purification cartridges more frequently than once every six months thereby necessitating more frequent testing.

Based on the results of the Montréal Fire Department QA/QC program, it is recommended that testing of compressed breathing air production systems at least once every three months, ideally once every month, be made mandatory. It should be required that the air be tested prior to as well as following compressor or air purifier maintenance procedures. Samples should be taken from a hot compressor that has been running for at least as many hours as might occur on any one occasion during the year. Action levels are proposed, taking into account the maximum levels of contaminants allowed by the *Canadian CAN3 180.1-M85 Standard on Compressed Breathing Air and Systems* (CSA, 1985) and the mean concentrations and standard deviations found for CO_2, CO and H_2O during the 42 months of quality control sampling. To prevent potential deterioration in the quality of the compressed breathing air being produced, corrective measures should be taken when CO_2 is found at levels greater than or equal to the proposed action levels: 450 ppm for CO_2, 0.5 ppm for CO and 1.9 ppm for H_2O. Finally, sampling should not be limited to compressor air but should be broadened to include periodic sampling of cascade storage systems and randomized sampling of SCBA's. Implementation of these operating procedures and QA/QC program has resulted in a significant improvement in the quality of the compressed breathing air supply available to the City of Montréal firefighters.

III - SUMMA™ CANISTER METHOD FOR VOC's AT FIRES

The objectives of this study are timely in that they address the recent calls for research to develop new analytical methods for the measurement of combustion gases in smoke and to identify and quantify the components of fire gases, vapours and smoke having chronic and carcinogenic toxicity (Chaturvedi et al., 1996; Hartzell, 1996; Levin, 1996; Tewarson, 1996). The U.S. EPA TO-14 method for the analysis of organics involves the collection of air samples in Summa™ canisters followed by quantification of VOC vapours by capillary GC coupled to a choice of detectors (EPA, 1988). A revised TO-14 method (TO-14A), due to be released in 1997, will require the exclusive use of GC-MS in the analytical method. The present study demonstrated that the collection of VOC's, including a number of PVOC's (such as 1,3-butadiene, isoprene and styrene) and SVOC's (such as naphthalene), into Summa™ canisters was a simple sampling method, able to withstand the rigours of the firescene environment. Canisters were reusable, total VOC's remaining after thorough cleaning being less than or equal to 2 ppb (Figure 27). It was demonstrated that, when the smoke particulates were filtered out of the air stream during collection, adsorption/desorption of analytes onto the inner walls of the Summa™ canisters did not occur (Figure 29). Accuracy, precision and other technical acceptance criteria of the modified TO-14 GC/MSD analytical method, met or exceeded U.S. EPA (1991) and TO-15 (1997) method requirements. The average analytical accuracy was ±5.3% (SD=±2.9%) for 10 NIST-traceable standards present in concentrations ranging from 0.2 ppb to 10 ppb and ±5.0% for four other NIST-traceable standards present at a nominal concentration of 10 ppm. The average analytical accuracy for the quantification of the 144 target compounds was ±15%. The overall sampling/analytical precision was ±23% for the target VOC's and ±12% for the 14 VOC's which were ultimately of interest in the fire study (Figure 34). This can be said to be a reliable and sensitive method for the analysis of complex mixtures of non-polar VOC's present in an extremely wide range of concentrations in such diverse samples as ambient air, landfill gas and fire samples (Figure 45). Although the database of municipal fire samples is small, the validation of the analytical method and the rigorous quality control measures used throughout this study have ensured that the results that were obtained were highly reliable.

The U.S. EPA TO-14 method for the determination of VOC's in air was developed during the 1980's and has been validated for the analysis of low-level (ppb), "clean" air samples (McClenny et al., 1984; Pellizzari et al., 1986a, b; EPA, 1988; McCallister et al., 1991; McClenny et al., 1991). The present study demonstrates that this technique can be applied also to high-level, "dirty" air samples without degradation of precision, accuracy or selectivity of the method. It was expected that interferences would arise due to the presence of unknown reactive gases and other degradation products but these did not materialize. Fire samples were stable in Summa™ canisters for six months (see Figure 31) and the potential difficulty in the GC/MS analysis of these samples, due to high levels of CO_2 known to be present, was avoided by the use of small 1 mL and 10 mL aliquots withdrawn from diluted samples. In addition, the present study demonstrates that it was possible to obtain "grab" samples and 15-minute time-integrated samples using sub-atmospheric sampling of air into small, 1-Litre Summa™ canisters without the use of a pump and without significant degradation of precision or sensitivity. This was shown to be a highly rugged sampler, easily operated by workers and requiring no field calibration or other special equipment.

Benzaldehyde (C_6H_5CHO) was tentatively identified in appreciable quantities (approximately 1 ppm) in fire samples. Although this substance is of no significant toxicological importance, benzaldehyde is a known product of the reaction of styrene (also a major combustion product) with ozone (O_3) and with the free radicals, $OH^\bullet$ and $NO_3^\bullet$, being produced with yields of 40%, 63% and 11%, respectively (Tuazon et al., 1993). Free radicals are formed in all combustion reactions (see page 4), including $OH^\bullet$ and, probably, $NO_3^\bullet$ and also when alkenes (present in the fire samples) react with O_3 in the dark (Meyer, 1989; Tuazon et al., 1993). These dark reactions are not thought to occur in Summa™ canisters however, O_3 being destroyed by contact with the stainless steel interior of the canister and dilution air fill lines. The presence of benzaldehyde is therefore attributed to its source as a combustion product.

While Purdue (1991) found that PVOC's had limited storage stability in Summa™ canisters, a study by Pate et al. (1992) revealed that humidified canisters greatly enhanced the stability of both non-polar and polar VOC's. As has been explained previously, it is necessary to remove this water vapour prior to GC-MSD analysis. In so doing, the polar, reactive and water soluble compounds are also removed from the sample, precluding their analysis. Kelly and Callahan (1993) reported that PVOC's were successfully measured in Summa™ canister samples using a two-stage sorbent trap (in lieu of a Nafion™ dryer and cryogenic trap) prior to GC analysis. The GC was coupled to a quadrupole ion trap mass spectrometer (GC-ITD) which was largely unaffected by water vapour in the sample.

The TO-15 method (EPA 1997) is an extension of the TO-14 method and differs from it in that: (1) it includes 70 new target compounds, including PVOC's (see Appendix 3); (2) it uses GC/MS techniques as the only means to identify and quantitate target compounds; (3) it establishes method performance criteria for acceptance of data; and, (4) it includes enhanced provisions for inherent quality control (EPA, 1994). The TO-15 method uses alternative water management approaches to the Nafion™ dryer, enabling the analysis of non-polar compounds, including many aldehydes. One of these techniques involves trapping the air sample on a hydrophobic, multiadsorbent packing at or above ambient temperature with subsequent thermal desorption. Water-related problems can also be alleviated by reducing sample volume if reduced sensitivity is acceptable. Brymer et al. (1996) reported that 168 of 194 compounds studied, including alkenes, aldehydes, ketones, alcohols and sulphur-containing compounds, were stable in Summa™ canisters, samples being analyzed by GC and a multi-detector system consisting of FID, PID and ECD detectors. It is known that firefighters are exposed to a number of toxic aldehydes, including acrolein and formaldehyde (see Table 10). Given that many PVOC's (including acrolein and formaldehyde), reactive compounds and water soluble substances are now known to be stable in Summa™ canisters, and with the recent publication the U.S. EPA TO-15 method, investigation of firefighter exposures can now be extended to include these classes of compounds employing the same Summa™ canister collection methods used in the present study.

IV. FIREFIGHTER EXPOSURES TO VOC's AT FIRES

Epidemiological studies have found statistically significant associations between firefighting and certain forms of cancer (see Table 7). The present study has found that, relative to the other 120 VOC's found at municipal fires, three potentially carcinogenic substances (1,3-butadiene, benzene and styrene) were among the substances measured in the highest concentrations (Figure 55 and Table 22).

Benzene (C_6H_6) is a myelotoxicant and a confirmed human carcinogen (IARC Class 1) associated with aplastic anemia and acute myelogenous leukaemia (Rinsky et al., 1987; ACGIH, 1991a). Rinsky et al. (1987) estimated that the odds ratios (OR) of benzene-induced leukaemic death for a worker inhaling 1 ppm and 10 ppm of benzene for 40 years were, respectively, 1.7 and 155, while the OR for a worker exposed to 0.1 ppm of benzene for 40 years approached the OR of a non-exposed worker. The ACGIH (1990) proposed that the TLV be lowered to 0.1 ppm, but, as of 1997, the TLV remains at 10 ppm benzene. The current BEI for benzene is 0.08 ppm in mixed-exhaled air and 0.12 ppm in end-exhaled, or alveolar, breath (ACGIH, 1996).

IARC (1992) has classified 1,3-butadiene as a probable human carcinogen (Group 2A) due to sufficient evidence for cancer in animals and limited evidence of cancer in humans (IISRP, 1981; ACGIH, 1991a). Malignant lymphomas have been observed in mice exposed to 6.25 ppm of 1,3-butadiene for 6 hr/day, 5 days/week for up to two years (Melnick et al., 1990a). Epidemiological studies over the past 20 years of workers exposed to 1,3-butadiene monomer indicate excesses in lymphohaematopoietic cancers, principally lymphosarcomas, while recent studies showed that 1,3-butadiene is also causally associated with the occurrence of leukaemia in humans, increasing leukaemic mortality having been observed with increasing exposure (Delzell et al., 1995, 1996; Macaluso et al., 1995, 1996; Acquavella, 1996; Koppikar, 1996). The TLV was lowered from 10 ppm to 2 ppm 1,3-butadiene in 1994 (ACGIH, 1994).

Isoprene is the 2-methyl structural analogue of 1,3-butadiene (2-methyl-1,3-butadiene) and has been classified by IARC (1994) as a possible human carcinogen (Group 2B), associated with increased tumour risk of the lung, liver, forestomach, heart and Harderian gland among male mice (Cox et al., 1996). Unlike 1,3-butadiene, isoprene is endogenously produced by both plant and mammalian metabolism, its concentration in human breath being 2-3 ppb (Bus, 1996). Cox et al. (1996) have suggested that isoprene exposure may act primarily on cells that have already been made susceptible (eg. initiated) by other sources.

Styrene ($C_6H_5CH{=}CH_2$) is a central and peripheral neurotoxicant and has been classified as a possible human carcinogen by IARC (Group 2B) and as a probable human carcinogen by the U.S. EPA (ACGIH, 1991a; IARC, 1994). The excess cancers most frequently observed in workers exposed to styrene are neoplasms of the lymphatic and haematopoietic tissues (IARC, 1994). However, the studies suffer from poor exposure data and confounding due to concomitant exposures to other substances (ACGIH, 1991a). The ACGIH (1996) proposed that the TLV be lowered from 50 ppm to 20 ppm styrene.

Propene, which was the VOC generally found in the highest concentration at municipal fires (Figure 55), is not considered to be toxic. However, propene metabolises to propylene oxide in rats which is a possible human carcinogen (IARC Group 2B), the latter having been found to be a rodent nasal carcinogen (Renne et al., 1986; Maples and Dahl, 1991; ACGIH, 1991a; IARC, 1994). On the other hand, Egedahl et al. (1989) found no increased risk for respiratory tract cancer, digestive or circulatory disease for workers employed at a propylene oxide production plant.

Acrolein and formaldehyde were not measured in this study but are assumed to have been present, having been identified in previous studies (see Table 10). The carcinogenic potential of acrolein has not been adequately determined, but glycidaldehyde, considered as a metabolite of acrolein, is carcinogenic and up to 10 ppm of formaldehyde has been found at municipal fires (IARC, 1979; Beauchamp et al., 1985; Brandt-Rauf et al., 1988, 1989; Jankovic et al., 1992).

Formaldehyde is a probable human carcinogen, causing cancer of the nasal cavity in rodents but the evidence for cancer in humans is limited and controversial (ACGIH, 1991a).

Total VOC's quantified in the present study were 1-72 ppm (Table 10), lower than the 300-700 ppm and the 500-1200 ppm found by Abeles et al. (1973) and by Lowry et al. (1985b), respectively. However, the analytical method used in the present study precluded the analysis of methane, ethane and ethene, low molecular weight C_1 and C_2 hydrocarbons likely to be produced in large quantities at fires. The results of previous studies measuring levels of combustion products at municipal fires covered a very broad range of values, benzene, for example, ranging from 0.2-1200 ppm (see Table 10). In general, the results of the Jankovic et al. study covered much narrower ranges for various substances than did the other studies, reflecting the fact that this study was the only one to attempt to differentiate between knockdown and overhaul. Carbon monoxide levels measured in the present study varied from 134-199 ppm, levels comparable to those found by Jankovic et al. (1992) during overhaul and lower than was found during knockdown. The 0.12-11 ppm benzene measured in the present study was at the lower end of the range (0.2-1200 ppm) found in a number of the previous studies (see Table 10). However, it agreed favourably with the 1-20 ppm and n.d.-0.3 ppm found by Jankovic et al. (1992) during knockdown and overhaul, respectively. Examination of the distribution of the sampling results of Burgess et al. (1979) and of Treitman et al. (1980) reveals that 95% of the values were less than approximately 25 ppm benzene. In the case of the Jankovic et al. study, 95% of values were less than approximately 20 ppm benzene. All three of these studies used charcoal as a sampling medium. The Treitman et al. study used a glass fibre filter upstream from the charcoal tube but the use of a filter is not specified in the other two studies. If filters were not used, desorption of benzene from the collected particles could occur during analysis and the results would represent both vapour phase and some fraction of the particulate phase of benzene. In the case of the Brandt-Rauf et al.

study (1989), which used colorimetric detector tubes, 80% of values were less than approximately 197 ppm. Again, information concerning the use of filters was not provided. Unfortunately, these data do not allow estimations of the relative levels of VOC's in the vapour and particulate phases. However, in a study of incinerator emissions, Wilshire and Johnson (1994) found a positive bias (i.e. desorption of VOC's from soot into the vapour phase) in the case of benzene sampled through a moderately heavy soot-loading (3.5-70 mg) of the sampling train. The same study found some evidence that higher boiling-point compounds, such as octane and chlorobenzene, were negatively biased (i.e. loss of VOC's by adsorption onto soot particles) by moderately heavy soot-loading. The adsorptive efficiency of soot is thought to be less than that of activated carbon, its surface area being an order of magnitude lower than the latter (Wilshare and Johnson, 1994). In the present study, soot loading was minimized by the collection of only a small volume of air (1.0 or 3.0 L) for each sample.

In the present study, firefighters were instructed to collect samples inside structural fires under conditions where they judged that at least some firefighters would remove their masks. The fact that the mean levels of benzene (2.8 ppm), carbon dioxide (3,376 ppm) and carbon monoxide (160 ppm) were found at the lower end of the range found in previous studies (see Table 10 and Table 22) provides some degree of confidence that these instructions were carried out. If, in fact, firefighters were not wearing their masks, then the results of this study are indeed an indication of the actual levels of firefighter exposure to VOC's present in the vapour phase inside burning municipal buildings. It can then be reasonably inferred that the 6% of the time spent at fires where firefighters use respiratory protection does not constitute protection from the levels of VOC's measured in the present study.

The TLV for polynuclear aromatic hydrocarbons (PAH's) found in coal tar pitch volatiles is 200 μg/m^3 present as benzene solubles (ACGIH, 1995). One might expect, given the voluminous amounts of smoke produced at fires, that firefighters would be exposed to high levels of PAH's. On the other hand, the chemical structure of the two principle components of wood, cellulose and lignin (see pages 9-10), do not suggest that this would be the case, no fused ring structures being present. Although Jankovic et al. (1992) found some PAH's at municipal structural fires, they were not present at high levels, concentrations measured being 0.284 $\mu g/m^3$ and 0.022 $\mu g/m^3$ during knockdown and overhaul, respectively, while levels of total particulates ranged from n.d. to 560 mg/m^3. Kelly et al. (1991) found that forest firefighters, who, typically, do not wear respiratory protection, were exposed to 370 mg/m^3 of respirable particulate matter, far in excess of the TLV of 3 mg/m^3 (ACGIH, 1996). In addition to the health risk posed by the inhalation of respirable particulate matter these particles can be expected to be a vehicle for the transportation of VOC's, free radicals and other potentially toxic substances adsorbed on surfaces, into the bronchioles and alveolar spaces where they can be desorbed, thereby increasing the levels of VOC exposure. The results of the present study do not permit an estimation of the relative contributions of VOC exposures resulting from VOC's present in the vapour phase as well as those adsorbed onto particulates. However, it was found that VOC's levels decreased with time in combination with increasing levels of smoke in the case of burning liquids, suggesting that a significant fraction of VOC's may be adsorbed onto smoke particles and that these escape detection when only the vapour phase is measured. The next logical step would be to determine the amount of VOC's adsorbed onto smoke particles relative to the amount present in the vapour phase and relative to the amount of smoke.

A chemical marker for combustion products should be distinctive and unambiguously determinable and present in sufficiently high concentration to be quantifiable. The most promising candidates for use as surrogates for the estimation of the degree of firefighter exposure to toxic fire atmospheres are benzene, toluene and CO, which were present at considerably higher levels than other VOC combustion products (see Figure 52 and Table 22). Benzene has the interesting and unexpected property of correlating directly with the levels of a number of other VOC's, in particular propene, toluene, 1,3-butadiene and naphthalene (Tables 20 and 21). It was particularly surprising that these ratios were found to be similar for different substances, the variability being ±15% rsd, on average (Table 22). Results from this study (Figures 49A, 49B, 50A and 56-58) suggest that good correlations can be expected to be found between CO and other products of incomplete combustion. This is consistent with the findings of Tewerson (1996) who found positive correlations between the equivalence ratio and the mass of CO, hydrocarbons (methane) and smoke generated in fires. The equivalence ratio, describing the effect of ventilation on combustion, is determined by the ratio of the fuel generation rate to the flow rate of air multiplied by the air-to-fuel ratio, this ratio increasing with reduced ventilation which favours incomplete combustion (Tewerson, 1996). The correlations found between benzene or CO and other organic toxicants could be combined with as yet-to-be-developed models for chronic/carcinogenic effects. This would simplify, considerably, the development of a multi-component exposure model and the ensuing calculations leading to an estimate of the chronic effects toxic potential of fire atmospheres.

The significant difference seen in benzene/VOC ratios between the burning of solid and liquid combustible materials also has a potential usefulness for arson investigators where the use of fire accelerants is suspected. Since the ratios of benzene to propene, toluene and 1,3-butadiene (0.6, 2.0 and 2.9, respectively) found at municipal fires were similar to those found for experimental fires burning solid materials (Table 21 and 23), the discovery of much higher ratios than these at municipal fires would be an unusual finding. A much larger database would be required in order to be able to generalize this statement with certainty. However, these preliminary findings suggest the possibility of the development of a new tool useful to arson investigators who currently rely on headspace analysis of fire debris to identify the remains of such liquid accelerants as gasoline, varsol, etc., a method that is plagued by problems of wide error margins. As a result, it is difficult to obtain positive identification of evaporated accelerants with a degree of certainty acceptable to a court of law. Firefighters have reported cases where they have been able to identify the presence of gasoline by odour but were unable to obtain a conviction because it was not possible to identify significant differences in the chromatograms of normal fire debris and fire debris containing residues from the accelerant (gasoline) known to have been used (Ménard, 1995). If a firefighter can smell the gasoline, it should be possible to quantify it by GC/MSD. A completely different methodology (distillation and head-space analysis or purge-and-trap) has been in use to analyze characteristic VOC "fingerprints" of accelerants in fire debris samples. These techniques have low orders of recovery of the partially evaporated accelerants and suffer from interferences from the normal residue of fires, resulting in large uncertainties when comparing the sample chromatograms with standards. In such an instance, the firefighter could easily obtain a "grab" sample using a Summa™ canister. The present study has found that benzene/1,3-butadiene and benzene/propene ratios were 8- and 18-fold higher, respectively, in fires burning combustible liquids than in fires burning solid material or in municipal structural fires (see Tables 21 and 23). Such a finding at a suspected criminal fire may provide strong evidence for the presence of accelerants. This line of inquiry merits further investigation.

From the standpoint of firefighter epidemiology, the greatest difficulty with almost all of the fire toxicology to date is that it has focused on the acute toxicity of the fire effluent. The objective has largely been the prediction of time to incapacitation, or time to death, of humans in a single fire in order to determine if some materials produce more toxic combustion products than other materials and to keep them out of the market. This line of research does not address the question of long term health effects of repeated exposure to fire effluent. It is easily forgotten that the degree of toxicity referred to by toxicologists in combustion studies is based on acutely toxic effects, which have no bearing on the long term effects studied by epidemiologists. In addition, a number of epidemiologists have voiced the hypothesis that modern fires are more toxic than those in the past due to new composite, synthetic, building materials. This supposition has undoubtedly arisen from some widely held beliefs of the 1970's that such new building materials had the potential of to yield "super toxicants" in modern fires. However, this scenario has been largely dismissed since there have been few documented examples (Bendix, 1978; Levin et al., 1987a; Hartzell, 1996). It is now generally accepted that the acutely toxic effects of smoke can usually be explained both qualitatively and quantitatively on the basis of a small number gases including CO, CO_2, HCN, halogen acids and organic irritants such as formaldehyde and acrolein (Purser and Wooley, 1983; Hartzell, 1996; Levin, 1996). Levin (1996), for example, have developed the N-Gas Model for acute effects of combustion products. More germane to the situation of firefighters would be the potential generation of substances having chronic effects. These would include products of combustion and thermal degradation of plastics and rubbers in modern fires (benzene, toluene and ethylbenzene) as well as the VOC monomers used as initial reactants in the manufacture of the polymeric material (see pages 6-9), for example: propene, isoprene, styrene, and 1,3-butadiene.

Consistent with the result of this study was Burgess et al.'s (1979) finding that benzene was highest at fires involving wood structures. Combustion of wood at experimental fires in the present study yielded 108 different VOC's. However there were only 14 substances, including benzene, present at high levels relative to the other 94 compounds (see Figures 43 and 46). The presence and concentration of contaminants, such as benzene, styrene and 1,3-butadiene, having known long term effects, may not have been less in previous decades (where wood, cotton and wool dominated the fire scene) than in modern fires where there is a prevalence of polymers. This study has demonstrated that there were no new or novel toxicant VOC's resulting from the burning of modern building materials, the analysis of samples obtained at experimental fires and at municipal structural fires finding the same substances (propene, isoprene, benzene, toluene, ethylbenzene, styrene, propene and 1,3-butadiene) at high concentrations relative to other combustion products (see Figures 43, 44 and 52 and Table 22). Along with naphthalene, these degradation products of polymeric material were also the principal combustion products of wood (Figure 46C), the predominant construction material in the past. The absence of new, toxic VOC's was confirmed by GC/MSD analysis of fire samples in SCAN mode. Only six compounds not already present in the standard calibration mixture were identified (Figure 54) and none of these are known to be particulary toxic. Furthermore, the spectra of combustion products were similar at municipal structural fires, an electronics industry fire and a 9-day smouldering fire (Figures 51 and 52). Jankovic et al. (1992) found lower levels of combustion products during overhaul than during knockdown. This, together with the results of the present study showing no new toxicants during a smouldering fire, belie the suggestion that, all other things being equal, the toxic risk is greater to firefighters during overhaul than during knockdown.

Even from the point of view of acutely toxic effects, the toxicological models would have some serious limitations if applied to human exposures in fires since they are largely based on exposure to steady-state concentrations of contaminants. Although a gross misrepresentation of the reality of a structural fire, since the concentrations of the components of fire effluent vary with time (Figure 49), this design allows comparison of various materials and products. None of the fire or toxicological models view the problem from the point of view of the firefighter who approaches the fire from the outside, some time after the onset of the fire, and with an attack strategy which minimizes exposure to smoke. Not only are firefighter exposures fundamentally different from those of occupant victims upon whom attention has been focused until now, but, in the case of firefighters, time to incapacitation or death is not the sole issue. The question which also needs to be addressed is, "What, if any, are the long-term health effects of intermittent exposures to smoke and fire gases?" Unfortunately, the focus of combustion toxicology research thus far has done little to shed light on this important issue.

The next step to be taken in the field of combustion toxicology should include the investigation of the chronic toxicity/carcinogenesis of fire gases and smoke. Experimental protocols should include inhalation exposure to fire gases, vapours and smoke generated by fires, to fire gases and vapours alone (obtained by filtering out the smoke particles) and to selected substances (individually and in various combinations) known to be present at fires. A step-wise approach should be taken, beginning with the carcinogens identified in this study (benzene, 1,3-butadiene, styrene) in addition to acrolein and formaldehyde, and to various combinations of these gases to determine target organ effects and whether the toxicity of the mixtures is additive, synergistic, or antagonistic.

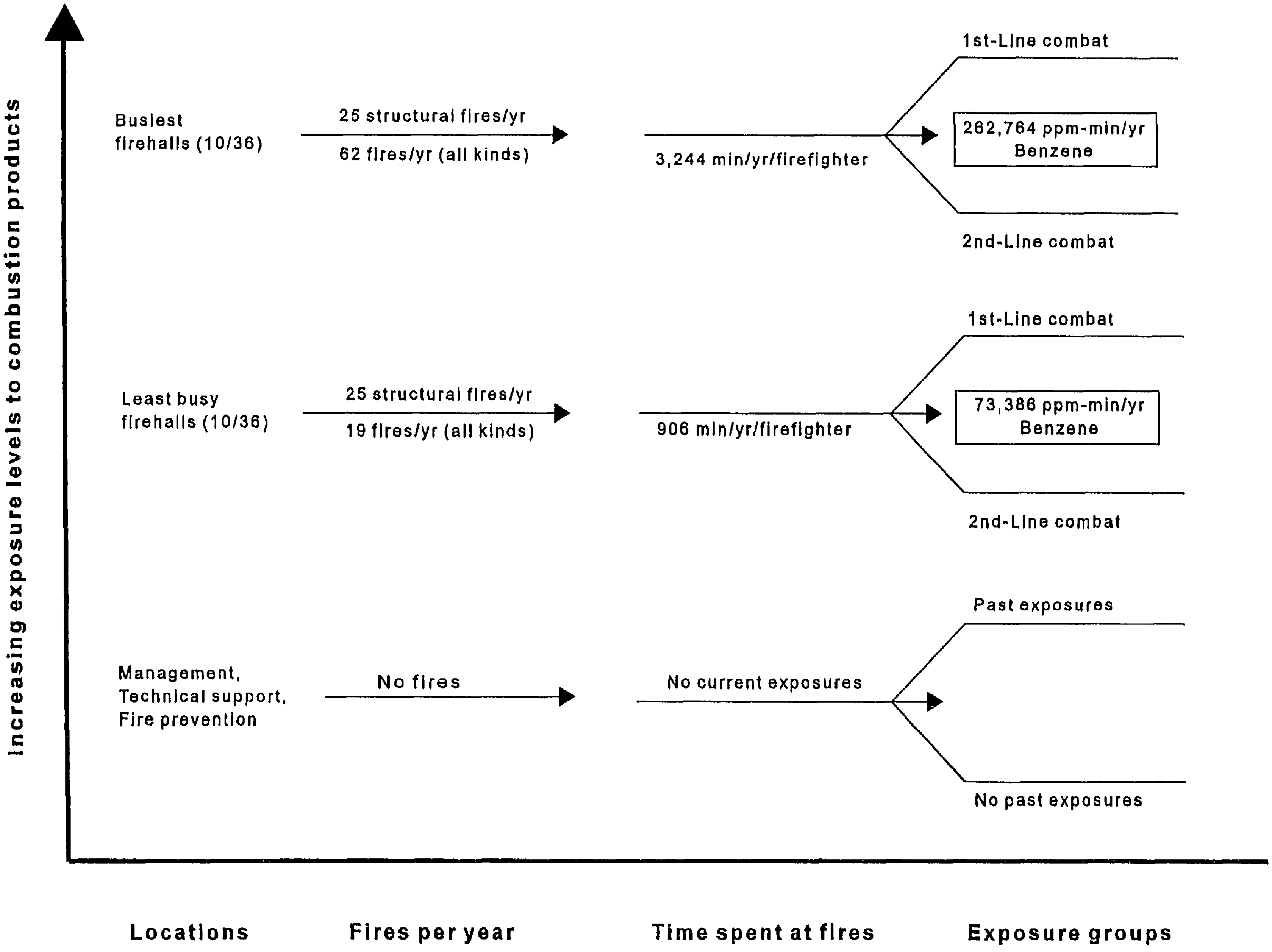
Since the results of epidemiological studies of firefighters suggest an association between exposure to fire atmospheres and cancer and, since the identification of a number of carcinogens in the fire gases in this and in other studies confirms the presence of causative agents at fires, the field is ripe for confirmation of these effects at the molecular level. As discussed by Grossman (1995) and by Levin (1996), little research has been done on the potential damage to human mitochondrial DNA (mtDNA) resulting from exposures to environmental toxicants. Mitochondrial DNA lends itself to this type of investigation because: (1) it has a high copy number; (2) it is maternally inherited so that distant relatives can be used for identification; (3) it has a high mutation rate; and, (4) it is highly polymorphic (Levin, 1996).

Following discussions with firefighters at the Tucson fire department, Burgess and Crutchfield (1995) report that 2-8 firefighters enter structural fires. Assuming that eight firefighters enter all structural fires, they have made a rough upper-bound estimate that Tucson firefighters entered 25 structural fires per year and (correcting rounding off errors made in the calculations) spent 783 minutes per year inside structural fires. Taking away the uncertainty factor of 2.0 which was used in their calculation, this translates to 12.5 structural fires per year per firefighter and 392 minutes per firefighter per year inside structural fires. On-scene time spent at fires not being available, it was assumed that each firefighter entered the fire once for

75% of the fires and twice for 25% of the fires. It was further assumed that firefighters remained inside fires for as long as the air in an SCBA cylinder would last and it was assumed that each cylinder would provide 25 minutes of breathing air. Although it is true that these cylinders are designed to provide 30 minutes of air, when used under conditions of maximum physiological and psychological stress, as is the case for firefighters, the air is used up in half this time (15 minutes). Taking this into account, Burgess' and Crutchfield's (1995) upper-bound estimate is further reduced to 235 minutes per firefighter per year spent inside structural fires and wearing respiratory protection. If the median (5) of 2-8 firefighters per entry is used rather than the upperbound number of eight, then the estimate for the average number of minutes per year that Tucson firefighters spent inside structural fires with respiratory protection would be 147 minutes per firefighter per year. This number compares reasonably well with the 118 min/yr average per firefighter that City of Montréal firefighters were found to have used respiratory protection. The present study has shown that firefighters use only 118 minutes per year per firefighter, on average, of compressed breathing air. However, these numbers provide no indication of the time spent at the scene of a fire nor of the time which firefighters were exposed to smoke without respiratory protection.

This is the first study to provide a good estimate relating the proportion of fire department personnel who are actually exposed to smoke, the time that they spend at the scene of fires, the number of structural fires that they attend, the number of SCBA cylinders that they use and the percentage of time spent at fires that respiratory protection is used. Figure 65 shows how this data can be used to identify six firefighter exposure groups. The Montréal Fire Department services a city of approximately one million people. Only 64% (1,211) of the 1,883 members of the fire department were 1st-line combat firefighters (see Tables 24). Another 20% (386 firefighters) were 2nd-line combat firefighters estimated to be exposed to smoke for less than half the time of the 1st-line. Taken together as one group, there were 1,404 exposed firefighters (1,211 + ½•386) accounting for 75% of fire

Figure 65. Diagram showing six of the eight identifiable firefighter exposure groups (the mean is not shown), the number of fires attended per year per exposed firefighter and the number of minutes per year per exposed firefighter spent at the scene of fires. Management, support and fire prevention account for 25% of fire department personnel. Firefighters from the 10 least busy firehalls spend only 28% of the time at fires compared to firefighters from the 10 busiest firehalls (total firehalls = 36). Second-line combat firefighters include division chiefs, operations chiefs and drivers and they were exposed to combustion products for less than half the time that 1st-line combat firefighters were exposed. Worst-case scenario cumulative exposure to benzene was calculated for firefighters wearing no respiratory protection and exposed to 10 ppm benzene while at the scene of fires. See text for details.


Increasing exposure levels to combustion products
Busiest firehalls (10/36)
25 structural fires/yr
62 fires/yr (all kinds)
3,244 min/yr/firefighter
1st-Line combat
262,764 ppm-min/yr Benzene
2nd-Line combat
Least busy firehalls (10/36)
25 structural fires/yr
19 fires/yr (all kinds)
906 min/yr/firefighter
1st-Line combat
73,386 ppm-min/yr Benzene
2nd-Line combat
Management, Technical support, Fire prevention
No fires
No current exposures
Past exposures
No past exposures
Locations
Fires per year
Time spent at fires
Exposure groups

department personnel. Twenty percent of all emergency calls were for fires (4,115 fires) and only 41% (1,684) of these were structural fires (see Table 26). Exposed firefighters spent 906-3,244 min/yr per firefighter at fires of all kinds, or 1,924 min/yr per firefighter, on average. They responded to 19-62 fires of all kinds per year per firefighter, or 37 fires of all kinds, on average. Firefighters responded to 8-25 structural fires per year per firefighter, or 15 structural fires, on average. During the time spent at fires (presumably, structural fires), firefighters used respiratory protection for 118 min/yr per firefighter, on average, being protected for 6% of the time spent at fires of all kinds (Figure 63). The fire department used a total of 10,911 SCBA cylinders in one 12-month period, each cylinder providing approximately 15 minutes of compressed breathing air to a firefighter working under conditions of maximum physiological and psychological stress.

There is reason to believe that Montréal firefighter exposure patterns are not significantly different from those of American cities, the number of firefighters for the size of the population, the number of fires for the size of the city and the accident rate amongst firefighters being comparable. The observation that 97% of Montréal fires were small, 1-alarm fires which were rapidly extinguished is consistent with the previously reported observation that approximately 90% of structural fires were either extinguished or abandoned and fought from the outside within 5-10 minutes (Gempel and Burgess, 1977; Gilman and Davis, 1992). It is likely that this fact is responsible for the apparent tendency of firefighters to avoid donning respiratory protection unless they perceive it to be absolutely necessary. There is no reason to believe that Montréal firefighters (who use respiratory protection for 6% of the time spent at fires) exercise better judgment as to when SCBA's must be worn than firefighters in large American cities. There is no question that the use of SCBA's has protected firefighters from the acute effects of combustion products and has saved lives. However, American studies found that 70% of firefighters wore their masks less than 100% of the time during knockdown and that firefighters who chose to wear their SCBA's for part of the time were exposed to similarly high levels of toxic contaminants as those who did not wear respiratory protection at all (Burgess et al., 1977; Brandt-Rauf et al., 1988; Jankovic et al., 1992).

The present study found that exposed Montréal firefighters spent 906-3,244 min/yr at fires depending on the geographical location of the firehall, translating to an average of only 5-17 minutes per day worked (188 days/yr). This does not seem excessive, whatever the exposures might be, especially in view of the fact that respiratory protection is worn for part of this time, albeit a small part (6%), but presumably during the periods of highest exposures, firefighters wearing their masks when they "see lots of smoke." However, given the fact, already discussed, that firefighters do not wear their masks for all of the time spent fighting fires during knockdown, this last point cannot be taken for granted.

Clearly, given firefighter intermittent exposures, determination of TWA's will result in calculated exposures far below the established TLV's for different substances, including benzene and 1,3-butadiene. In addition, this approach does not take into account peak exposures and possible unknown synergistic effects present in the case of firefighter exposures to multiple, potential toxicants. For example, CO may act synergistically with benzene in rats (Ponsold et al., 1978). Also, as was the case for the exposure of firefighters to CO in contaminated compressed breathing air, the absorbed dose of fire gases and smoke will be higher for firefighters than for most other workers due to the high levels of heat and physiological stress experienced by firefighters. Firefighter exposures are therefore not comparable to TLV's or to the exposures of other workers who function at light work loads.

An interesting exercise is provided by the example of firefighter exposure to benzene. Cumulative exposure equals the long-term arithmetic mean exposure level times the duration of exposure (Rinsky et al., 1987; Seixas et al., 1988; Smith, 1992). Cumulative exposure has been used as the measure of cancer risk in the case of benzene (Rinsky et al., 1987; Federal Register, 1987; Nicas et al., 1991). The worst-case scenario of an exposed firefighter from one of the 10 busiest firehalls who never wears respiratory protection and who is exposed to 10 ppm of benzene (see Table 22) for 3,244 minutes per year works out to 32,440 ppm•minutes per year. Multiplied by a factor of 8.1 to account for the increased ventilation rate of a firefighter (assuming a ventilation rate of 8 L/min for a worker at rest and 65 L/min for a firefighter engaged in heavy work), this translates to cumulative exposure of 262,764 ppm•minutes per year, 23-fold higher than the cumulative exposure of a worker (11,250 ppm-minutes per year) who is exposed to 0.1 ppm of benzene for 7.5 hours per day, 5 days per week, 50 weeks per year and for whom there has been calculated to be no excess leukaemic risk compared to a non-exposed worker (Rinsky et al., 1987). This firefighter's exposure would be 2.3-fold higher than that of a worker exposed to 1 ppm of benzene (112,500 ppm•min/yr) and for whom the excess leukaemic risk is 1.7 (Rinsky et al., 1987). Similarly, an exposed firefighter from one of the 10 least busy firehalls would experience a cumulative exposure of 73,386 ppm•min/yr benzene, 6.5-fold higher than the worker for whom there has been calculated to be no excess leukaemic risk. These estimates of cumulative exposure would be somewhat higher for 1st-line combat firefighters and lower for 2nd-line combat firefighters.

Given the limitations of the current exposure database from this and previous studies, multiplication of measured VOC levels by a factor of 8.1 to take into account higher absorbed doses due to higher ventilation rates is prudent but, perhaps not excessive. This is justifiable, particularly in view of the fact that measured VOC levels do not take into account possible synergistic effects, the possibility of desorption of VOC's from respirable particulate matter in the alveolar spaces, the fraction absorbed from dermal contact with benzene-containing soot and the fraction absorbed via the skin from body surface exposure to ambient air (Blank et al., 1985). In addition, equal cumulative exposures may not necessarily result in equal blood concentrations of VOC's. Studies of controlled exposures to xylene found that higher concentrations and shorter time periods generated a 2.7-fold increase in the blood concentration of VOC's compared with lower air concentrations and longer time periods (Tardiff et al., 1991; Kawai et al., 1992; Ashley and Prah, 1997). Although blood concentrations of VOC's have been found to be directly related to cumulative exposure, they are also a function of the blood/air partition coefficients, body mass, body fat, respiratory rate and metabolic rate (Pierce et al., 1996; Ashley and Pray, 1997). VOC's absorbed by inhalation are first distributed by the blood to peripheral tissues with slower metabolism and return to the liver, the major metabolic organ of the body. The accumulation of VOC's having tissue/blood partition coefficients greater than 1.0 in fat tissues results in continued internal exposure long after external exposure has ceased. The tissue/blood partition coefficient is found by dividing the tissue/air coefficient by the blood/air coefficient (Tardif et al., 1993). Higher blood/air partition coefficients are associated with a more rapid onset of central nervous system (CNS) effects a longer time to reach steady-state blood levels during constant exposure, and a more gradual loss through exhaled air after the cessation of external exposure (Pierce et al., 1996). Higher fat/air partition coefficients are associated with a longer time to reach adipose tissue steady-state levels during constant exposure and a more gradual loss from adipose tissue (and therefore longer internal exposure) after the cessation of external exposure. Results of a study by Pierce et al. (1996) indicate that these effects would be expected in the order styrene > xylenes > ethylbenzene > toluene > benzene, fat/air partition coefficients being 3184, 1919-2460, 1764, 962 and 334, respectively.

Rusch et al. (1977) estimated that humans absorb approximately 46% of the benzene that is inhaled. Assuming a respiratory rate of 8 L/min, approximately 7.5 μL (0.66 mg) can be expected to be absorbed each hour via the lungs by a person exposed to 10 ppm of benzene (Rusch et al., 1977). This translates to 5.4 mg absorbed benzene per hour in the case of a firefighter engaged in heavy work. The concentration of VOC's in exhaled air closely follows the fluctuations of the ambient air concentrations, VOC alpha half-lives ($t_{\frac{1}{2}}$) during the rapid, initial elimination alpha-phase being 5-20 minutes (Berlin, 1980; ACGIH, 1991b). This method is therefore of limited usefulness in the workplace, the method providing no information on the average exposure during an 8-hr work shift. It is distinctly advantageous, however, in the case of firefighters who enter burning structures for approximately 15-minutes at a time and who may or may not be using respiratory protection. In such cases, monitoring the initial VOC levels in breath immediately upon exit from structural fires will provide information on firefighter exposures (including both lung and dermal absorption). Monitoring during the second beta-elimination phase from storage compartments will provide information about body burdens (ACGIH, 1991b).

Although cumulative exposure is one of the most common summary measures for exposure used in occupational epidemiology, its usefulness is limited when assumptions of a linear relationship between cumulative exposure and tissue dose are violated (Rappaport, 1991b; Smith, 1992). With many inhaled lipid-soluble organic chemicals, there is an apparent biphasic, long-term elimination by exhalation. Berlin (1980) found that the alpha and beta half-lives for the elimination of benzene for experimental human subjects were 2.6 hr. and 24 hr., respectively. However, they found that, in the case of industrial workers, the decay was slower, the beta $t_{1/2}$=75 hr. This could also be interpreted as evidence of two slow-emptying compartments having half lives of 24 hr. and 175 hr, respectively (Berlin, 1980). The long beta half-life for benzene is consistent with the high fat/air partition coefficient found by Pierce et al. (1996). The fat/air partition coefficient found for styrene was 3184, 9.5-fold higher than that found for benzene and the reported half-life of styrene was 20 hours with an additional decay having a beta $t_{1/2}$=75 hr (ACGIH, 1991a; Pierce et al., 1996). Similarly, the beta half-lives for the elimination of toluene and hexane from fat depots are 77 hours and 64 hours, respectively (Engstrom et al., 1978; Cohr and Stockholm, 1979; Perbellini et al., 1986; ACGIH, 1991a). The lipophilic VOC's to which firefighters are exposed in the highest concentrations have initial beta half-lives of approximately 20 hours with elimination from adipose tissue having half-lives of the order of 70 hours. Even with intermittent exposures such as experience by firefighters, accumulation of a body burden of VOC's would, therefore, be expected.

Rappaport (1991a, b) has suggested that $t_{1/2}$>40 hr. constitute slow rates of elimination. When the rate of elimination is slow, relative to the duration of exposure, the effect of exposure variability is dampened and there is the possibility of an accumulation of body burden from shift to shift (ACGIH, 1991; Rappaport, 1991b). Cumulative exposure, therefore, may well be a better estimate of exposure than the mean, in the case of firefighters. However, if nonlinear kinetics were involved between tissue concentrations and incidence of effect, then peak exposures might contribute disproportionately to disease (Rappaport, 1991b). The use of cumulative exposure, in cases where exposure levels were sufficient to saturate the metabolic pathways producing the toxic metabolites, may result in overestimation of the risk (Smith, 1992). This is not expected to occur at the concentrations to which firefighters are exposed (<10 ppm), 1st-order kinetics being observed when exposures to VOC's are less than 200-300 ppm (ACGIH, 1991a). It is, however, conceivable that saturation of the metabolic pathways might occur for exposures to a mixture of VOC's due to competitive inhibition of the P450 enzyme system. On the other hand, the fact that firefighters generally operate at high work levels while exposed to VOC's alters the distribution of the chemicals absorbed, perfusion of the liver decreasing and perfusion of the muscles and brain increasing during exercise (ACGIH, 1991a). Although uptake of toxic chemicals is increased due to increased ventilation and cardiac output, metabolites do not necessarily increase proportionately because of the decreased liver perfusion. These issues require further research.

The question also arises whether, for the same cumulative exposure, there is a difference in risk between workers exposed to lower levels for longer periods of time and workers exposed to higher levels for shorter periods of time. In the case of 1,3-butadiene, lymphosarcomas were observed in the latter group (Koppikar, 1996). Melnick et al. (1990b) made a similar observation in the case of mice, suggesting that, for 1,3-butadiene and the occurrence of lymphomas, concentration is more important than duration of exposure. Welp et al. (1996) observed increased mortality from nonmalignant diseases of the genitourinary system associated with increased average exposure and with increased cumulative exposure to styrene, while no increase was seen for duration of exposure. Cox et al. (1996) found that the carcinogenic response of isoprene may be more closely linked to peak than to cumulative exposures. Such findings suggest that firefighter periodic exposures to VOC's may be associated with higher risks than equivalent cumulative exposures at lower levels and spread more evenly over time.

Further assessment of firefighter exposure to VOC's is warranted. However, based on the experience of this and previous studies, it is recommended that future exposure assessments not rely exclusively on firefighter personal sampling. An attractive alternative is the quantification of VOC's in firefighters' breath, the concentration of VOC's in breath being known to correlate well with exposures (Brugnone et al., 1976; Apostoli et al., 1982; Pellizzari et al., 1986a, b). This would avoid the complicated logistics of sampling inside burning buildings and would provide a true picture of firefighter exposures, eliminating the guess-work as to whether or not they were wearing their masks. Quantification of VOC's in alveolar breath has been used previously but it has not been applied to the case of firefighters (Raymer et al., 1989, 1991; Thomas et al. 1991; Raymer and Pellizzari, 1996). Raymer (1990) developed a Summa™ canister-based spirometer capable of rapidly collecting alveolar breath samples in the field and successfully used the device to monitor the elimination kinetics of VOC's from the body. Target compounds included benzene, toluene, ethylbenzene, xylenes, styrene and decane. Use of this device seems to be ideally suited to the case of firefighters whose job, task and location are unpredictable (but fully characterizable after the fact), who have highly unpredictable work schedules and whose absorbed dose is increased by virtue of the fact that they tend to work near maximum physiological stress when exposed to combustion products. There is the added advantage that results obtained for one of the most important of the combustion products, benzene, can be compared to the BEI's for mixed-exhaled and end-exhaled air, 0.08 ppm and 0.12 ppm, respectively (ACGIH, 1996). In addition, the device can be used in conjunction with personal sampling and area sampling using the same Summa™ canisters. Not only is the analytical method used identical in both cases thereby eliminating inter-method variability, but, as this study has shown, the TO-14 method is reliable for use in fire atmospheres.

Epidemiological studies have demonstrated associations between firefighting and increased risk for cancers, including cancer of the brain and nervous system, lymphatic and haematopoietic systems, oesophagus, colon, rectum, kidney, bladder and genitourinary systems and lymphoma (see pages 34-35). One study found that firefighters were at risk for liver disease (Beaumont et al., 1991). The results of epidemiological studies with respect to heart disease have been inconclusive (see Table 6) although half of the line-of-duty deaths are due to heart attacks (Green and Crouse, 1991) and the Occupational Disease Panel of Ontario has found that a probable connection exists between firefighting and cardiovascular disease (IDSP, 1994).

There has been no attempt made in any of the epidemiological studies to distinguished between exposed and non-exposed firefighters, years worked in a fire department having been used as a surrogate for cumulative exposure in all of the studies. Use of such nominal exposure information has undoubtedly resulted in significant misclassification: only 64% of fire department personnel are 1st-line combat firefighters, exposures vary widely depending on the geographical location of the firehall and many combat firefighters move into non-exposed jobs before the end of their careers (Table 24). The present study demonstrates that there are eight identifiable firefighter exposure groups (Figure 65): 1st- and 2nd-line firefighters from the busiest, intermediate and least busy firehalls, management and fire prevention personnel. The failure of epidemiological studies to sort firefighters into homogeneous groups for risk comparisons may have resulted in underestimates of the cancer risk to firefighters and in the failure to detect other chronic diseases. Years worked in one or the other of the exposure groups identified in this study might be a satisfactory surrogate for firefighter exposures to combustion products. Given the difficulties inherent in obtaining exposure data for firefighters, this may be the breakthrough needed by epidemiologists to identify exposure/response relationships for various disease outcomes related to firefighting using new ordinal exposure information. This may be improved further, in the future, with the use of firefighter VOC breath analysis providing proportional dose information based on actual, measured values enabling the investigation of dose/response relationships. Statistical variance analysis of such data will help determine if this is more useful than classification according to the number of fires attended and identification of 1st- and, 2nd-line combat firefighters and support personnel.

CONCLUSIONS

Diesel emissions in firehalls

Results of the present study do not support the mandatory installation of mechanical ventilation systems for the removal of diesel exhaust from firehall garages. Assuming 2-vehicle response to alarms, 20 alarms in 24 hours and operation of vehicles in garages for one minute, the expected 8-hour TWA for CO would be less than 0.1 ppm. Similarly, the expected 15 minute time weighted average for NO_2 would be 0.2 ppm. The levels of both CO and NO_2 were below the ACGIH occupational exposure limits of 25 ppm and 5 ppm, respectively.

Contamination of compressed breathing air

The results of the present study show that serious CO contamination can and does occur between currently mandated monitoring periods, CO levels initially found in 16 Montréal SCBA's being 60±38 ppm (95% CI) and, in one case, 250 ppm. Even with rigorous monitoring and maintenance procedures in place, H_2O and CO contamination arise (Figure 10). Although the data may be sparse, it is significant because contamination occurred precisely between currently mandated testing periods and there is no way of knowing for how long users had been exposed to the contaminated air. Furthermore, the frequency of occurrence is irrelevant when it is known that this does happen, that it is life threatening and that it is preventable.

Firefighter exposures to VOC's

The characterization of firefighter exposures to fire gases and smoke is an enormously challenging and interesting task due to a number of complicating factors:

(1) the unusual work schedules of 10- to 24-hour shifts for 188 days in a year;
(2) wide variations between firefighters' time spent at fires;
(3) exposures do not accurately reflect absorbed dosages when firefighters function at moderate to heavy work levels;
(4) intermittent exposures;
(5) prevalence of firefighters working overtime or holding down other hazardous occupations;
(6) exposure to a complex mixture of toxic gases, vapours and particulate matter;
(7) unknown effect of heat;
(8) gases and free radicals measured in the air may also be adsorbed onto the particulate matter of smoke; and,
(9) some of the SVOC vapours measured in the air may be distributed between the solid and vapour phase, this equilibrium shifting in either direction depending on the temperature and on the density of the smoke.

These difficulties are mitigated somewhat by the fact those substances responsible for the toxic effects of fire gases and smoke do not appear to be new, they appear to be relatively few in number, and that their levels are considerably higher than the remaining numerous combustion products. This study demonstrated that only 14 of the 123 VOC's found at municipal structural fires were present at comparatively high levels, that these are the substances likely responsible for many of the toxic effects and that these substances appear also in the combustion products of wood, a traditional building material. This study has also quantified VOC carcinogens not previously characterized in previous studies of fire atmospheres, 1,3-butadiene and isoprene, in particular.

In spite of the small number of fire samples collected, the consistency of the results obtained indicates that further such sampling is likely to do little more than confirm the results of the present study (Figure 52). Given the toxicity/carcinogenicity of those VOC's which were found in the highest concentrations however, further investigation of VOC exposures of firefighters is warranted. Suggested avenues for future research include:

(1) verification of the stability of aldehydes in Summa™ canister fire samples;

(2) the measurement of correlations between CO or benzene and other toxic VOC's present in combustion products for the identification of a marker which can be used in as-yet-to-be-developed models of chronic/carcinogenic toxicity of fire effluents;

(3) the distribution of VOC's which may be present in the vapour phase and/or adsorbed onto smoke particles;

(4) the determination of VOC's absorbed by firefighters following exposure at fires by measurement of exhaled, alveolar breath;

(5) the elimination kinetics of absorbed VOC's by firefighters, given their unusual exposure patterns and work schedules;

(6) Application of more rigorous identification criteria for exposed firefighters to past and future epidemiological studies; and,

(7) Investigation of dose/response relationships based on the firefighter exposure groups identified in the present study.

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Appendix 1

Coburn-Forster-Kane (CFK) Equation for CO Uptake

$$\frac{A \cdot [HbCO]_t \ - \ B \cdot Vco \ - \ pCO_i}{A \cdot [HbCO]_0 \ - \ B \cdot Vco \ - \ pCO_i} = \exp\ (-t \cdot A / V_b \cdot B) \quad \text{Eqn. 2}$$

A = $pO_2c / M\ [HbO_2]$ Eqn 2d

B = $(1 / DL_{CO}) + pL / V_A$ Eqn 2j

°C = degrees Celcius

CH_4 = methane

C_6H_6 = benzene

CO = carbon monoxide

CO_2 = carbon dioxide

%COHb = % carboxyhaemoglobin in the blood

%COHb = 0.8% for nonsmokers

%COHb > 2% for 80% of smokers

%COHb = 17% for heavy smokers

DL_{CO} = diffusivity of the lung for CO, mL/min · mmHg

$DL_{CO} = 35 \times Vo_2 \times \exp(0.33)$ Eqn 2k

DL_{CO} = 30 mL/min · mmHg (ranges from 10 to 50 mL/min · mmHg)

e = exp

eqn = equation

exp = 2.7182..., the base of the natural logs (e) raised to the power in the bracketed expression

f = respiratory frequency, breaths/min

$f = \exp(\ (0.0165 \times RMV) + 2.3293)$ Eqn 2n

Hb = haemoglobin

HbCO = carboxyhaemoglobin

HbO_2 = oxyhaemoglobin

[Hb] = grams haemoglobin per 100 mL blood

[Hb] = 15.94 g/100mL (ranges from 10 to 20 g/100mL)

[HbCO] = %COHb x $[HbO_2]_{max}$ / 100 Eqn 2a

$[HbCO]_0$ = mL of CO per ml of blood at the beginning of the exposure interval

$[HbCO]_t$ = mL of CO per ml of blood at time t

$[HbO_2]$ = $[HbO_2]_{max} - [HbCO]_t$ Eqn 2e

$[HbO_2]$ = ml of O_2 per mL of blood

$[HbO_2]_{max}$ = mL O_2 per mL blood (should equal approximately 0.22 mL O_2/mL blood)

$[HbO_2]_{max} = 1.38 \times [Hb] / 100$ Eqn 2b

L = litres

M = ratio of affinity of blood for CO to that for O_2

$M = 218$ (ranges from 150 to 250)

min = minute

mL = millilitre

mmHg = millimeter of mercury

O_2 = oxygen

$\%O_2i$ = percent oxygen in inspired air

P_{atm} = atmospheric (barometric) pressure, mmHg

$P_{atm} = 750$ mmHg

pCO_i = partial pressure of CO in inhaled air, mmHg

$pCO_i = ppmCO \times P_{atm} / 10^6$ **Eqn 2c**

pH_2O = vapour pressure of water at T_b

$pH_2O = 47$ mmHg

pL = Pressure in the lung

$pL = P_{atm} - pH_2O$ **Eqn 2l**

ppm = parts-per-million

pO_2c = average partial pressure of oxygen in lung capillaries, mmHg

$pO_2c = pO_{2i} - 49$, when $pO_{2i} \geq$ "normal" or 149 mmHg **Eqn 2f**

pO_2i = partial pressure of oxygen in inspired air, mmHg

$pO_2i = (\%O_2i / 100) \times (P_{atm} - pH_2O - pCO_i)$, or **Eqn 2g**

$pO_2i = 148.304 - (0.0208 \times pCO_i)$ **Eqn 2h**

RMV = respiratory minute volume (=volume of air breathed per minute), L/min

RMV = 8.5 L/min (at rest) RMV = 25 L/min (light work)

RMV = 60 L/min (heavy work) RMV = 117 L/min (maximum work)

sec = second

T_b = body temperature, °C

$T_b = 37$ °C

t = exposure duration, min

V_A = alveolar ventilation rate, mL/min

$V_A = (0.933 \times RMV \times 1000) - (132 \cdot f)$ **Eqn 2m**

V_b = total blood volume, mL (ranges from 1000 to 7000 mL)

$V_b = 74$ mL/kg body weight for men (approximately **5500 mL** for 70 kg man)

$V_b = 73$ mL/kg body weight for women

Vco = rate of endogenous CO production, mL/min

Vco = 0.007 mL/min (ranges from 0.000 mL/min to 0.070 L/min)

Vo_2 = oxygen consumption, L/min

$Vo_2 = (RMV / 22.274) - 0.0309$ **Eqn 2l**

Appendix 2 - Iterative solution of the Coburn-Forster-Kane (CFK) equation for CO uptake (Excel 5.0)

	A	B	C	D	E
1	SYMBOL	VARIABLE	UNITS	DESCRIPTION	ALGORITHM
2		Work level			='[COHB.XLS]%COHb'!E8
3	RMV	Breathing rate	L/min		='[COHB.XLS]%COHb'!E9
4	[CO]	Ambient concentration of CO	ppm		='[COHB.XLS]%COHb'!E10
5	Time	Exposure time	minutes		='[COHB.XLS]%COHb'!E11
6		Accuracy		Left side - Right side of eqn.	=E35-E36
7	**%COHb**	**Coburn equation**		**Result of iterative procedure**	**0.835506618455763**
8	%COHb	Stewart Eqn		%COHb=(3,317x0,00001)(ppmCO^1,036)(RMV)(t)	=3.317*0.00001*(E4^1.036)*E3*E5
9	Patm	Atmospheric pressure	mmHg		='[COHB.XLS]%COHb'!E12
10	%O2	% oxygen in ambient air	mmHg		='[COHB.XLS]%COHb'!E13
11	pH2O at 37 C	Vapor press. H2O	mmHg		='[COHB.XLS]%COHb'!E14
12	DLco	Diffusivity of lung	mL/min.mmHg		='[COHB.XLS]%COHb'!E15
13	Vco	Endogenous CO	ml/min		='[COHB.XLS]%COHb'!E16
14	Vb	Blood volume	ml		='[COHB.XLS]%COHb'!E17
15	[Hb]	Hemoglobin concentration	g/100mL		='[COHB.XLS]%COHb'!E18
16	(%COHb)o	Pre-exposure COHb			='[COHB.XLS]%COHb'!E19
17	VO2	Oxygen consumption	L/min	VO2=(RMV/22,274)-0,0309	=(E3/22.274)-0.0309
18	f	Respiratory frequency	breaths/min	f = exp(0,0165 x RMV + 2,3293)	=EXP(0.0165*E3+2.3293)
19	VA	Alveolar ventilation rate	ml/min	VA=(0,933 x RMV x 1000) - 132f	=(933*E3)-(132*E18)
20				DLco=35*VO2 x exp(0,33)	=35*E17*EXP(0.33)
21	PL		mmHg	PL=Patm-pH2O	=E9-E11
22	B	Use this one		(1/DLco) + (PL/VA)	=(1/E12)+(E21/E19)
23	B			From calculated DLco	=(1/E20)+(E21/E19)
24	PICO	pCO in air	mmHg	PIco = ppmCO x Patm/1000000	=E4*E9/1000000
25	[HbO2]max		mL O2 per mL blood	[HbO2]max=1,38[Hb]/100	=1.38*E15/100
26	[HbCO]o		mL CO per mL blood at t=0	[HbCO]o=%COHbo x [HbO2]max/100	=E16*E25/100
27	[HbCO]t		mL CO per mL blood at t	[HbCO]t=%COHbt x [HbO2]max/100	=E7*E25/100
28	[HbO2]		ml O2 per ml blood	[HbO2]=[HbO2]max - [HbCO]t	=E25-E27
29	PIO2	pO2 in air	mmHg	PiO2=(%oxygen/100)(Patm-pH2O-PiCO)	=(E10/100)*(E9-E11-E24)
30	Pco2	pO2 in capillaries	mmHg	Pco2=PiO2-49	=E29-49
31	A	Use this one		A=PCO2/(M[HbO2]) ; M=218	=E30/(218*E28)
32	A		Assuming Pco2=100	A=Pco2/(M[HbO2]) ; M=218	=E34/(218*E28)
33	PIO2	pO2 in air	mmHg	PIO2=148,304-0,0208 x PICO	=(148.304-0.0208*E24)
34	Pco2	Partial press. O2 in lung capillaries	mmHg	Pco2=Pi02-49 when PiO2>149mmHg	100
35	Left side of eqn.	Left		(A[HbCO]t-BVco-PiCO)/(A[HbCO]o-BVco-PiCO)	=(E31*E27-E22*E13-E24)/(E31*E26-E22*E13-E24)
36	Right side of eqn.	Right		exp(-tA/VbB)	=EXP(-(E5*E31)/(E14*E22))

Appendix 2 (Cont'd) - Results

	A	B	C	D	E
1	SYMBOL	VARIABLE	UNITS	DESCRIPTION	RESULT
2		Work level			Rest
3	RMV	Breathing rate	L/min		8.5
4	[CO]	Ambient concentration of CO	ppm		5
5	Time	Exposure time	minutes		60
6		Accuracy		Left side - Right side of eqn.	-0.00079
7	%COHb	**Coburn equation**		**Result of iterative procedure**	0.84
8	%COHb	Stewart Eqn		%COHb=(3,317x0,00001)(ppmCO^1,036)(RMV)(t)	0.09
9	Patm	Atmospheric pressure	mmHg		750.0
10	%O2	% oxygen in ambient air	mmHg		21
11	pH2O at 37 C	Vapor press. H2O	mmHg		47
12	DLco	Diffusivity of lung	mL/min.mmHg		30
13	Vco	Endogenous CO	ml/min		0.007
14	Vb	Blood volume	ml		5500
15	[Hb]	Hemoglobin concentration	g/100mL		15.94
16	(%COHb)o	Pre-exposure COHb			0.8
17	VO2	Oxygen consumption	L/min	VO2=(RMV/22,274)-0,0309	0.3507
18	f	Respiratory frequency	breaths/min	f = exp(0,0165 x RMV + 2,3293)	11.8171
19	VA	Alveolar ventilation rate	ml/min	VA=(0,933 x RMV x 1000) - 132f	6371
20				DLco=35*VO2 x exp(0,33)	17
21	PL		mmHg	PL=Patm-pH2O	703
22	B	Use this one		(1/DLco) + (PL/VA)	0.1437
23	B			From calculated DLco	0.1689
24	PICO	pCO in air	mmHg	PIco = ppmCO x Patm/1000000	0.0038
25	[HbO2]max		mL O2 per mL blood	[HbO2]max=1,38[Hb]/100	0.2200
26	[HbCO]o		mL CO per mL blood at t=0	[HbCO]o=%COHbo x [HbO2]max/100	0.0018
27	[HbCO]t		mL CO per mL blood at t	[HbCO]t=%COHbt x [HbO2]max/100	0.0018
28	[HbO2]		ml O2 per ml blood	[HbO2]=[HbO2]max - [HbCO]t	0.2181
29	PIO2	pO2 in air	mmHg	PiO2=(%oxygen/100)(Patm-pH2O-PiCO)	147.6292
30	Pco2	pO2 in capillaries	mmHg	Pco2=PiO2-49	98.6292
31	A	Use this one		A=PCO2/(M[HbO2]) ; M=218	2.0741
32	A		Assuming Pco2=100	A=Pco2/(M[HbO2]) ; M=218	2.1029
33	PIO2	pO2 in air	mmHg	PiO2=148,304-0,0208 x PiCO	148.3039
34	Pco2	Partial press. O2 in lung capillaries	mmHg	Pco2=Pi02-49 when PiO2>149mmHg	100.0000
35	Left side of eqn.	Left		(A[HbCO]t-BVco-PiCO)/(A[HbCO]o-BVco-PiCO)	0.85351
36	Right side of eqn.	Right		exp(-tA/VbB)	0.85430

Appendix 3

Calibration Standard Mixture (Canmix)

Compound	Env. Can.[a]	TO-14[b]	TO-15[c]	ng/L
Acetaldehyde (Ethanal)			x	
Acetonitrile (cyanomethane)			x	
Acetophenone			x	
Acrolein (2-Propenal)			x	
Acrylamide			x	
Acrylic acid			x	
Acrylonitrile (2-Propenenitrile)			x	
Allyl chloride (3-Chloropropene)			x	
Aniline (Aminobenzene)			x	
Benzene	x	x	x	8.112
Benzyl chloride (alpha-Chlorotoluene)	x	x	x	6
1- Bromo-4-Fluorobenzene[d]	x			5.533
Bromochloromethane[d]	x			5
Bromodichloromethane	x			10.8
Bromoform	x		x	7.1
Bromomethane (Methylbromide)	x	x	x	22.708
Bromotrichloromethane	x			2.2
1,3- Butadiene	x		x	8.806
Butane	x			28.232
c-2- Butene	x			8.956
t-2- Butene	x			9.146
1- Butene/2-Methylpropene	x			27.426
n- Butylbenzene	x			4.082
tert- Butylbenzene	x			4.08
sec- Butylbenzene (1-Methylpropylbenzene)	x			3.954
iso- Butylbenzene (2-Methylpropylbenzene)	x			4.052
1- Butyne	x			8.48
Carbon disulphide			x	
Carbontetrachloride (Tetrachloromethane)	x	x	x	8.1
Carbonyl sulphide			x	
Catechol (o-Hydroxyphenol)			x	
Chloroacetic acid			x	
Chlorobenzene	x	x	x	6.1
Chlorobenzene-d_5[d]	x			3.974
Chloroethane (Ethylchloride)	x	x	x	12.952
bis-2- Chloroethylether			x	
Chloroform (Trichloromethane)	x	x	x	6
Chloromethane (Methylchloride)	x	x	x	13.43
bis- Chloromethylether			x	
Chloromethyl methyl ester			x	
Chloroprene (2-Chloro-1,3-butadiene)			x	
o- Cresol			x	
Cresylic acid (Cresol isomer mixture)			x	
Cyclohexane	x			2.48
Cyclohexene	x			13.596
Cyclopentane	x			2.07
Cyclopentene	x			10.838
p- Cymene (Isopropyltoluene)	x			4.054
Decane	x			2.422

Compound	Env. Can.[a]	TO-14[b]	TO-15[c]	ng/L
1- Decene	x			4.792
Diazomethane			x	
Dibromochloromethane	x			10.7
1,2- Dibromo-3-chloropropane			x	
1,2- Dibromoethane (Ethylene dibromide)	x	x	x	5.4
Dibromomethane (Methylene bromide)	x			13.2
1,2- Dichlorobenzene	x	x		7.1
1,3- Dichlorobenzene	x	x		7.1
1,4- Dichlorobenzene	x			3.1
1,4- Dichlorobutane	x			4.9
1,1- Dichloroethane (Ethylidene dichloride)	x	x	x	6.3
1,2- Dichloroethane (Propylene dichloride)	x	x	x	6.6
1,1- Dichloroethene (Vinylidene chloride; 1,1-dichloroethylene)	x	x	x	11
c-1,2- Dichloroethene	x	x		6.3
t-1,2- Dichloroethene	x			5.4
Dichloromethane (Methylene chloride)	x	x	x	6.3
1,2- Dichloropropane	x	x		6.1
c-1,3- Dichloropropene	x	x		5.172
c/t-1,3- Dichloropropene	x		x	4.6
1,2- Diethylbenzene	x			4.168
1,3- Diethylbenzene	x			4.088
1,4- Diethylbenzene	x			8.234
Diethylsulphate			x	
1,4- Difluorobenzene[d]	x			3.984
N,N- Dimethylaniline			x	
2,2- Dimethylbutane	x			14.984
2,3- Dimethylbutane	x			1.856
Dimethylcarbamyl chloride			x	
c-1,2- Dimethylcyclohexane	x			378.2
c-1,3- Dimethylcyclohexane	x			2.716
c-1,4/t-1,3- Dimethylcyclohexane	x			2.352
t-1,2- Dimethylcyclohexane	x			0.946
t-1,4- Dimethylcyclohexane	x			1.292
N,N- Dimethylformamide			x	
2,2- Dimethylhexane	x			3.194
2,4- Dimethylhexane	x			4.664
2,5- Dimethylhexane	x			2.26
1,2- Dimethylhydrazine			x	
3,6- Dimethyloctane	x			1.288
2,2- Dimethylpentane	x			3.05
2,3- Dimethylpentane	x			4.474
2,4- Dimethylpentane	x			2.13
2,2- Dimethylpropane	x			13.474
Dimethylsulphate			x	
1,4- Dioxane (1,4-Diethylene oxide)			x	
Dodecane	x			2.49
Epichlorohydrin (1-Chlro-2,3-epoxy propane)			x	
1,2- Epoxybutane (1,2-Butylene oxide)			x	
Ethylacrylate			x	
2- Ethyl-1-Butene	x			1.67
Ethylbenzene	x	x	x	4.094

Compound	Env. Can.[a]	TO-14[b]	TO-15[c]	ng/L
Ethylbromide (Bromoethane)	x			6.434
Ethyleneimine (Aziridine)			x	
Ethylene oxide			x	
2- Ethyltoluene	x			4.176
3- Ethyltoluene	x			4.1
4- Ethyltoluene	x			8.186
Formaldehyde			x	
Freon11 (Trichlorofluoromethane)	x	x		5.956
Freon113 (1,1,2-Trichlorotrifluoroethane)	x	x		5.2
Freon114 (1,2-Dichlorotetrafluroethane)	x	x		29.904
Freon12 (Dichlorodifluoromethane)	x	x		21.696
Freon22 (Chlorodifluoromethane)	x			20.128
Heptane	x			20.754
1- Heptene	x			5.65
c-2- Heptene	x			5.838
c-3- Heptene	x			2.588
t-2- Heptene	x			5.728
t-3- Heptene	x			0.862
Hexachlorobutadiene	x	x	x	5.7
Hexachloroethane			x	
Hexane	x		x	16.258
c-2- Hexene	x			1.938
t-2- Hexene	x			3.284
1- Hexene/2-Methyl-1-Pentene	x			23.112
Hexylbenzene	x			4.052
Indane	x			4.552
Isobutane (2-Methylpropane)	x			18.956
Isophorone			x	
Isoprene (2-Methyl-1,3-Butadiene)	x			3.018
Methanol			x	
2- Methyl-1-Butene	x			2.278
3- Methyl-1-Pentene	x			4.756
4- Methyl-1-Pentene	x			4.728
2- Methyl-2-Butene	x			5.724
c-3- Methyl-2-Pentene	x			3.1
c-4- Methyl-2-Pentene	x			1.79
t-3- Methyl-2-Pentene	x			2.368
t-4- Methyl-2-Pentene	x			2.788
2- Methylbutane	x			12.08
Methylcyclohexane	x			2.552
1- Methylcyclohexene	x			15.918
Methylcyclopentane	x			2.394
1- Methylcyclopentene	x			13.596
Methylethylketone (MEK)			x	
2- Methylheptane	x			4.66
3- Methylheptane	x			2.27
4- Methylheptane	x			1.18
2- Methylhexane	x			2.22
3- Methylhexane	x			2.24
Methylhydrazine			x	
Methyliodide			x	
Methylisobutylketone (Hexone)			x	
Methylisocyanate			x	

Compound	Env. Can.[a]	TO-14[b]	TO-15[c]	ng/L
Methylmethacrylate			x	
2- Methylpentane	x			14.288
3- Methylpentane	x			14.304
Methyl-tert-butyl ester			x	
Naphthalene	x			2.768
Nitrobenzene			x	
2- Nitropropane			x	
N- Nitroso-N-methylures			x	
N- Nitrosodimethylamine			x	
N- Nitrosomorpholine			x	
Nonane	x			2.406
1- Nonene	x			3.858
Octane	x			4.72
1- Octene	x			4.544
c-2- Octene	x			3.788
t-2- Octene	x			6.23
Pentane	x			12.94
1- Pentene	x			12.972
c-2- Pentene	x			9.13
t-2- Pentene	x			3.316
Phenol			x	
Phosgene			x	
Propane	x			14.532
1,3- Propane sulphone			x	
Propene	x			13.326
Propionaldehyde			x	
Propylene oxide			x	
beta- Propyliolactone			x	
n- Propylbenzene	x			4.072
iso- Propylbenzene (1-Methylethylbenzene; Cumene)	x		x	4.102
1,2- Propyleneimine (2-Methylaziridine)			x	
Propyne	x			5.3
Styrene	x	x	x	4.252
Styrene oxide			x	
1,1,2,2- Tetrachloroethane	x	x	x	8.7
Tetrachloroethene (Tetrachloroethylene)	x	x	x	8.8
Toluene	x	x	x	8.142
1,2,4- Trichlorobenzene	x		x	8
1,1,1- Trichloroethane (Methylchloroform)	x	x	x	6.7
1,1,2- Trichloroethane	x	x	x	7.8
Trichloroethene (Trichloroethylene)	x	x	x	7.6
Triethylamine			x	
1,2,3- Trimethylbenzene	x			4.258
1,2,4- Trimethylbenzene	x	x		8.302
1,3,5- Trimethylbenzene	x	x		4.108
2,2,3- Trimethylbutane	x			1.048
2,2,5- Trimethylhexane	x			1.626
2,2,4- Trimethylpentane	x		x	4.458
2,3,4- Trimethylpentane	x			2.38
Undecane	x			2.466
Urethane (Ethylcarbamate)			x	
Vinyl acetate			x	
Vinyl bromide (Bromoethene)			x	

Compound	Env. Can.[a]	TO-14[b]	TO-15[c]	ng/L
Vinylchloride (Chloroethene)	x	x	x	6.826
Vinylidene chloride (1,1-Dichloroethylene)			x	
m- Xylene			x	
m/p- Xylene	x	x	x	8.186
p- Xylene			x	
o- Xylene (1,2-Dimethylbenzene)	x	x	x	4.172

[a] Environment Canada target compounds.

[b] EPA TO-14 method target compounds (EPA, 1988).

[c] EPA TO-15 method target compounds (EPA, 1997).

[d] Internal Standard.

Appendix 4

VOC Pre-concentration Standard Operating Procedures (SOP's)

Sample loop method (1 mL or 10 mL aliquots)

Turn valve "4" to sample and valve "1" to off to evacuate the lines. Cool the trap in liquid oxygen and switch valve "4" to "Sample". Attach a needle valve to the canister and connect to the 1 mL or 10 mL sample loop. Open the canister and allow the sample loop to fill for 2 minutes at 50 mL/min. Close the canister and when the sample loop rotameter falls to zero, inject the contents of the loop. Allow the sample loop to flush with air for 3 minutes. Leave valve "4" on "sample" and open the internal standard canister. Allow the 10 mL loop to fill for 2 min. at 50 mL/min. Close the internal standard canister and when the sample has equilibrated to atmospheric pressure (the sample loop rotameter falls to zero), flush the contents of the loop into the sample line with humid air (Valve 3). Allow the sample loop to flush with air for 3 minutes. The sample can be injected after 3 minutes and when the GC reaches -60 °C.

Syringe method (20 mL to 50 mL aliquots)

Replace the cap on the sample line with a septum (Figure 4). Screw on gently with the fingers (no wrench). The septum should be replaced every day or every 5 injections. Replace the canister cap with a septum. Open the canister valve and bleed briefly with a needle to flush out the dead-space between the valve and the septum. Insert the syringe taking care to hold the plunger and rinse 5 or 6 times. Withdraw the desired sample aliquot.

Turn valve "4" to sample and valve "1" to off to evacuate the lines. Cool the trap in liquid oxygen and switch valve "4" to "Helium". So as to not inject against too high a pressure, turn the helium flow down to approximately 5 mL/min. and insert the syringe through the septum into the sample line leading to the Nafion dryer. Inject slowly (i.e. 25 mL/min.) taking care not to apply excessive pressure on the plunger. When the syringe is nearly empty, slowly increase the helium flow so as to avoid creating a vacuum in the line which would result in sucking lab air through the septum around the outside of the needle. Withdraw the needle the moment the plunger makes contact with the bottom of the syringe. Open the internal standard canister. Allow the 10 mL loop to fill for 2 min. at 50 mL/min. Close the internal standard canister and when the sample has equilibrated to atmospheric pressure (the sample loop rotameter falls to zero), flush the contents of the loop into the sample line with humid air (Valve 3).

Mass flow controller method (250 mL to 1250 mL aliquots)

If the canister pressure exceeds 20 psi attach a needle valve to the canister and adjust the flow rate to 50 mL/min. with a rotameter. With valve "1" set to "air", attach the canister to the pre-concentrator at valve "1". Turn valve "4" to "sample" and valve "1" to "canister" to evacuate the lines. When mass flow controller "B" reads a negative value, turn valve "1" to air and open the canister. Start the stop-watch as valve "1" is turned back to "canister". This method minimizes the variation in mass flow controller readings due to the initial pressure surge. Open the internal standard canister one minute before the end of the sample collection time. Close the canister 5 seconds before the end of the collection time. At the end of the collection time turn valve "1" to air.

Sample injection

Enter the sample information in the "sample log table" found under the "sequence" menu in the HPChem "Instrument 1 Top" software. Enter the sequence information found under the "sequence/run" menu and enter "OK". Approximately 10 minutes before the desired sample injection time, download the acquisition method parameters to the GC/MSD. To do this, enter "Run sequence" found under the "sequence/run" menu. It takes approximately 10 minutes for the GC to cool to -60 °C. Wait until the "not ready" light goes OFF before injecting the sample. Wait also for the GC window to appear before injecting.

Appendix 5

Mass Spectral Acquisition Parameters

Acquisition Window	Group Start Time (min.)	Dwell Time per Ion (msec.)	Ions in Group	Plot Ion (Real time)
1	5.00	40	29 39 41 42 43 51 67 85	43
2	7.90	50	39 40 50 52	50
3	9.40	45	41 42 43 62 64 85 87	43
4	10.80	50	29 39 41 43 53 54 56	43
5	11.80	25	29 39 41 53 54 55 56 57	41
6	14.00	50	41 42 57 101 103	101
7	15.30	20	27 41 42 43 53 55 61 63	43
8	16.46	50	41 42 49 55 70	55
9	16.96	50	43 57 71 101 103 151	101
10	17.60	20	41 42 43 55 61 63 65 67	43
11	18.80	20	41 42 43 47 49 55 56 57	43
12	20.40	20	41 43 55 56 57 61 62 64	43
13	21.30	25	41 56 57 71 77 78 84 85	78
14	22.50	20	42 43 57 62 63 70 83 85	43
15	23.04	20	41 43 55 56 57 69 71 75	43
16	24.58	40	43 61 71 83 91 92 97	91
17	25.20	20	41 43 55 57 70 71 81 85	43
18	27.00	50	77 97 112 114 117 119	112
19	27.70	50	91 106 171 173	171
20	28.48	25	43 55 57 70 78 83 85 90	91
21	29.30	50	75 95 105 120	105
22	29.90	50	43 57 71 91 105 120	91
23	31.30	20	43 55 56 57 69 71 91 92	91
24	32.15	30	91 92 105 111 117 118	146
25	33.70	50	43 57 71	57
26	35.00	50	43 57 71 127 128 180	128
27	36.70	50	91 92 162 223 225 227	225

Appendix 6

Target Compound Acquisition Window Assignments and Qualifier Ions

	Compound	Expected Retention Time	Acquisition Window	Target Ion	Qualifier Ion	Qualifier Ion Ratios Min.	Max.
1	1,4-Difluorobenzene[a]	21.99	XIII	114.00	88	13.1	19.6
2	Propene	6.45	I	39.00	41	80.9	121.4
3	Propane	6.67		29.00	39	68.2	102.3
4	Freon22 (Chlorodifluoromethane)	7.08		51.00	67	14.5	21.8
5	Freon12 (Dichlorodifluoromethane)	7.47		85.00	87	26.2	39.3
6	Propyne	8.23		39.00	40	81.2	121.7
7	Chloromethane	8.77	II	50.00	52	25.4	38.1
8	Isobutane (2-Methylpropane)	9.80		43.00	42	0.1	0.1
9	Freon114 (1,2-Dichlorotetrafluroethane)	10.15	III	85.00	135	41.9	62.8
10	Vinylchloride (Chloroethene)	10.44		62.00	64	25	37.5
11	1-Butene/2-Methylpropene	11.10		41.00	56	34.3	51.4
12	1,3-Butadiene	11.27	IV	39.00	54	66.2	99.3
13	Butane	11.49		43.00	41	25.5	38.2
14	t-2-Butene	12.03		41.00	56	40.2	60.3
15	2,2-Dimethylpropane	12.11	V	57.00	41	33.3	50
16	Bromomethane	12.20		94.00	96	81.2	121.7
17	1-Butyne	12.40		54.00	39	61	91.5
18	c-2-Butene	12.68		41.00	56	38.3	57.4
19	Chloroethane (Ethylchloride)	13.01		64.00	66	25.5	38.2
20	2-Methylbutane	14.81		42.00	57	63.7	95.5
21	Freon11 (Trichlorofluoromethane)	15.09	VI	101.00	103	53.9	80.8
22	1-Pentene	15.45		42.00	55	65.3	98
23	2-Methyl-1-Butene	15.74	VII	55.00	70	25.1	37.6
24	Pentane	15.90		43.00	41	53.2	79.7
25	Isoprene (2-Methyl-1,3-Butadiene)	16.09		67.00	68	52.1	78.1
26	Ethylbromide (Bromoethane)	16.21		108.00	110	84.5	126.8
27	t-2-Pentene	16.25		55.00	42	37.1	55.6
28	1,1-Dichloroethene	16.30		61.00	96	51.3	77
29	c-2-Pentene	16.54		55.00	42	35.2	52.7
30	Dichloromethane (Methylene chloride)	16.63	VIII	49.00	84	71.4	107.1
31	2-Methyl-2-Butene	16.72		55.00	41	20	29.9
32	Freon113 (1,1,2-Trichlorotrifluoroethan	17.13		151.00	101	106.7	160
33	2,2-Dimethylbutane	17.29	IX	57.00	71	80.1	120.1
34	Cyclopentene	17.93		67.00	68	33.7	50.5
35	t-1,2-Dichloroethene	18.05	X	61.00	96	58.9	88.3
36	4-Methyl-1-Pentene	18.12		43.00	0	0	0
37	3-Methyl-1-Pentene	18.15		55.00	69	56.6	84.9
38	1,1-Dichloroethane	18.31		63.00	65	23.8	35.7
39	Cyclopentane	18.34		42.00	55	22.8	34.2
40	2,3-Dimethylbutane	18.44		43.00	42	95.3	142.9
41	t-4-Methyl-2-Pentene	18.56		69.00	84	26.8	40.1
42	2-Methylpentane	18.61		43.00	42	42.3	63.4
43	c-4-Methyl-2-Pentene	18.68		69.00	84	24.3	36.4

	Compound	Expected Retention Time	Acquisition Window	Target Ion	Qualifier Ion	Qualifier Ion Ratios	
						Min.	Max.
44	3-Methylpentane	19.13		57.00	56	60.5	90.8
45	1-Hexene/2-Methyl-1-Pentene	19.36	XI	56.00	55	53.2	79.7
46	c-1,2-Dichloroethene	19.44		61.00	96	59.3	88.9
47	**Bromochloromethane**[a]	19.65		130.00	128	68.3	102.4
48	Hexane	19.76		57.00	41	61.8	92.7
49	Chloroform (Chloromethane)	19.83		83.00	85	0.1	0.1
50	t-2-Hexene	19.93		55.00	42	45.4	68.1
51	2-Ethyl-1-Butene	20.02		69.00	41	55.1	82.6
52	t-3-Methyl-2-Pentene	20.13		69.00	41	100.4	150.5
53	c-2-Hexene	20.26		55.00	42	47.3	70.9
54	c-3-Methyl-2-Pentene	20.47		41.00	69	64	95.9
55	2,2-Dimethylpentane	20.62	XII	57.00	43	58.2	87.3
56	1,2-Dichloroethane	20.69		62.00	64	25.3	37.9
57	Methylcyclopentane	20.72		56.00	69	26	38.9
58	2,4-Dimethylpentane	20.84		43.00	57	58.7	88
59	1,1,1-Trichloroethane	21.00		97.00	61	31.8	47.7
60	2,2,3-Trimethylbutane	21.03		57.00	43	56.4	84.5
61	1-Methylcyclopentene	21.49		67.00	82	35.1	52.6
62	Benzene	21.55	XIII	78.00	77	12.5	18.7
63	Carbontetrachloride (Tetrachloromethan	21.73		117.00	119	85.7	128.5
64	Cyclohexane	21.88		56.00	84	56.5	84.7
65	2-Methylhexane	22.12		85.00	57	64.6	96.9
66	2,3-Dimethylpentane	22.20		56.00	71	28.1	42.2
67	Cyclohexene	22.42		82.00	67	218.9	328.3
68	3-Methylhexane	22.41	XIV	70.00	43	247.6	371.3
69	Dibromomethane (Methylene bromide)	22.48		174.00	93	95.5	143.2
70	1,2-Dichloropropane	22.52		63.00	62	56.5	84.8
71	Bromodichloromethane	22.74		83.00	85	51.6	77.3
72	Trichloroethene (Trichloroethylene)	22.81		130.00	132	75	112.5
73	1-Heptene	22.82		70.00	42	112.8	169.1
74	2,2,4-Trimethylpentane	22.88		57.00	43	19.2	28.7
75	t-3-Heptene	23.11		41.00	56	57.2	85.7
76	c-3-Heptene	23.21	XV	69.00	98	40.1	60.1
77	Heptane	23.19		43.00	57	38.1	57.1
78	t-2-Heptene	23.32		55.00	56	88.1	132.1
79	c-2-Heptene	23.61		56.00	55	54.1	81.2
80	c-1,3-Dichloropropene	23.84		75.00	77	24.9	37.4
81	2,2-Dimethylhexane	23.93		57.00	41	21.8	32.7
82	Methylcyclohexane	23.97		83.00	98	35.3	52.9
83	2,5-Dimethylhexane	24.23		57.00	43	66.2	99.3
84	2,4-Dimethylhexane	24.31		85.00	57	124.1	186.1
85	c/t-1,3-Dichloropropene	24.45		75.00	77	26.7	40
86	1,1,2-Trichloroethane	24.67		97.00	83	66.8	100.1
87	Bromotrichloromethane	24.85	XVI	117.00	119	77.5	116.2
88	2,3,4-Trimethylpentane	24.86		43.00	71	45.7	68.6
89	Toluene	25.03		91.00	92	58.1	87.2
90	2-Methylheptane	25.28		57.00	43	87.9	131.8
91	4-Methylheptane	25.33	XVII	70.00	71	91.5	137.2
92	1-Methylcyclohexene	25.36		81.00	96	34.5	51.7

	Compound	Expected Retention Time	Acquisition Window	Target Ion	Qualifier Ion	Qualifier Ion Ratios	
						Min.	Max.
93	Dibromochloromethane	25.54		129.00	127	64.6	96.9
94	3-Methylheptane	25.51		43.00	57	59.7	89.6
95	c-1,3-Dimethylcyclohexane	25.75		97.00	55	75.2	112.7
96	t-1,4-Dimethylcyclohexane	25.81		97.00	55	87.8	131.7
97	EDB (1,2-Dibromoethane)	25.86		107.00	109	75.2	112.7
98	2,2,5-Trimethylhexane	25.86		57.00	71	14	20.9
99	1-Octene	26.18		41.00	55	78.2	117.3
100	Octane	26.28		43.00	57	24.3	36.4
101	t-1,2-Dimethylcyclohexane	26.37		97.00	0	0	0
102	t-2-Octene	26.36		41.00	0	0	0
103	Tetrachloroethene (Tetrachloroethylene)	26.48		166.00	164	65.5	98.2
104	c-1,4/t-1,3-Dimethylcyclohexane	26.57		97.00	55	64.5	96.7
105	c-2-Octene	26.64		55.00	41	65.3	98
106	c-1,2-Dimethylcyclohexane	27.30		97.00	112	39.8	59.7
107	**Chlorobenzene-d5**[a]	27.30	XVIII	117.00	119	26.3	39.4
108	Chlorobenzene	27.36		112.00	77	50.2	75.3
109	Ethylbenzene	27.87		91.00	106	25.8	38.7
110	m/p-Xylene	28.11	XIX	91.00	106	39.7	59.6
111	Bromoform	28.22		173.00	171	0.1	0.1
112	1,4-Dichlorobutane	28.62		55.00	90	20.9	31.4
113	Styrene	28.63	XX	104.00	103	32.9	49.2
114	1,1,2,2-Tetrachloroethane	28.75		83.00	85	50.8	76.1
115	o-Xylene (1,2-Dimethylbenzene)	28.79		91.00	106	32	47.9
116	1-Nonene	28.91		55.00	43	120.8	181.1
117	Nonane	29.09		43.00	57	53.7	80.6
118	**1-Bromo-4-Fluorobenzene**[a]	29.44		95.00	75	33.9	50.8
119	iso-Propylbenzene (1-Methylethylbenzen	29.65	XXI	105.00	120	20.4	30.5
120	3,6-Dimethyloctane	30.24		57.00	71	45.1	67.6
121	n-Propylbenzene	30.45	XXII	91.00	120	16.9	25.3
122	3-Ethyltoluene	30.62		105.00	120	25.5	38.2
123	4-Ethyltoluene	30.69		105.00	120	23.2	34.7
124	1,3,5-Trimethylbenzene	30.81		105.00	120	51.1	76.6
125	2-Ethyltoluene	31.13		105.00	120	23.9	35.8
126	1-Decene	31.47		55.00	56	81.4	122.1
127	tert-Butylbenzene	31.50	XXIII	134.00	0	0	0
128	1,2,4-Trimethylbenzene	31.50		105.00	120	44.9	67.3
129	Decane	31.68		57.00	43	89	133.5
130	Benzyl chloride (alpha-Chlorotoluene)	31.72		91.00	126	16.1	24.1
131	1,3-Dichlorobenzene	31.76		146.00	148	51.7	77.5
132	1,4-Dichlorobenzene	31.88		146.00	148	50.1	75.1
133	iso-Butylbenzene (2-Methylpropylbenzen	31.90		91.00	92	53.3	80
134	sec-Butylbenzene (1-Methylpropylbenzen	31.98		105.00	134	12.4	18.5
135	1,2,3-Trimethylbenzene	32.25		105.00	120	39.7	59.6
136	p-Cymene (Isopropyltoluene)	32.26	XXIV	134.00	0	0	0
137	1,2-Dichlorobenzene	32.50		146.00	148	49.3	74
138	Indane	32.63		117.00	118	62.6	93.9
139	1,3-Diethylbenzene	32.82		105.00	119	86.6	129.9
140	1,4-Diethylbenzene	33.01		119.00	105	60.2	90.3
141	n-Butylbenzene	33.04		92.00	91	146.6	219.9

Compound	Expected Retention Time	Acquisition Window	Target Ion	Qualifier Ion	Qualifier Ion Ratios Min.	Qualifier Ion Ratios Max.
142 1,2-Diethylbenzene	33.19		105.00	119	64.5	96.8
143 Undecane	34.07	XXV	57.00	43	93.2	139.7
144 1,2,4-Trichlorobenzene	35.96		180.00	182	77.8	116.7
145 Naphthalene	36.21	XXVI	128.00	127	9.3	13.9
146 Dodecane	36.29		57.00	43	77.7	116.5
147 Hexachlorbutadiene	36.99		225.00	223	53.1	79.6
148 Hexylbenzene	37.63	XXVII	91.00	92	61.6	92.3

[a] Internal Standard

Appendix 7

Data Management and Processing

1. Archiving

(1) Raw data files are backed up as YrMoData onto a data files tape identified as DxA.

(2) Processed data files are backed up as DescrData onto a data files tape identified as DxB.

(3) Raw Excel reports are backed up as ExcelRpt onto a data files tape identified as DxA.

(4) Updated Excel reports are backed up as ExcelRpt onto a data files tape identified as DxB.

(5) Methods created to monitor data acquisition are backed up as YrMoMethod onto a method files tape identified as MxA.

(6) Processed calibration files are backed up as YrMoCANMIX onto a method files tape identified as MxB.

(7) Updated methods are backed up as YrMoMethod onto a method files tape identified as MxB.

(8) The thesis is found on the hard drive of the Packard Bell computer. Preliminary versions of the thesis are backed up onto diskette and onto a method files tape identified as MxA. The final version of the thesis is backed up onto diskette and onto a method files tape identified as MxB.

2. Transferring data

(1) Back up raw data from GC/MSD computer to Connor tapes DxA and MxA.

(2) Back up a second copy of raw data from GC/MSD computer to Irwin tape.

(3) Restore data to be processed from Connor tape to Packard Bell computer drive C:\.

(4) Process the data on drive C:\ with HPEnviroquant software.

(5) Backup the final processed data and methods from C:\ to Connor tapes DxB and MxB.

(6) Move updated methods and processed data to E:\finaldata and E:\finalmethod.

(7) Restore final processed data and methods from Connor tapes DxB and MxB to Everex computer.

(8) To recover space on drive E:\ of the Packard Bell computer, delete sample data files before calibration data files and methods files.

(9) To recover space on the GC/MSD C:\ drive, delete files which have been processed and archived before those which have not.

3. Update (calibrate) the method

(1) Load the last updated method.

(2) Run Excel and Custom Reports and make the method default template which corresponds to the sample volume (eg. CAL500.XLS).

(3) Rename the method and Save with the format YrMonDy.M.

(4) Load calibration data file and integrate.

(5) CALCULATE REPORT and save results to the DETAIL.XLS quantitation file.

(6) Shift the retention times (do not use replace retention times since the software may choose the wrong peaks). If ΔRT is negative, shift the retention times by +ΔRT. If ΔRT is positive, shift the retention times by -ΔRT; Pause the printer.

(7) EASY ID. Correct the retention times and the extraction windows, where necessary, in the calibration table.

(8) Recalculate report and overwrite the DETAIL.XLS quantitation file. Do not print.

(9) UPDATE LEVELS. Replace the levels in the calibration table for the corresponding sample volume (calibration level).

(10) Recalculate report and overwrite the DETAIL.XLS quantitation file. Do not print.

(11) QEDIT. Check the integration for each peak and do a manual integration where necessary. Update the corrections in the DETAIL.XLS quantitation file.

(12) UPDATE levels in the calibration table.

(13) Repeat steps 4 and 9-12 for each calibration level.

(14) Update qualifier ion ratios in the calibration table.

(15) Check each calibration curve and delete outliers. Do this only if the resulting correlation coefficient meets the data quality objectives at the 95% confidence level. Note: the software retains the previous response level for peaks which are not found in the current calibration data file. SAVE the method.

(16) Update the correlation coefficients database , CORRCOEF.XLS.

(17) Recalculate report and overwrite the DETAIL.XLS quantitation file. Do not print.

(18) QEDIT. Check the integration for each peak and do a manual integration where necessary. Update the corrections in the DETAIL.XLS quantitation file.

(19) GENERATE REPORT. Transfer the quantitation results from DETAIL.XLS to the CUSTOM REPORT template. Print.

(20) Update Continuing Calibration Report Criteria for each calibration level.

(21) Print Evaluate Continuing Calibration Report for each calibration level.

(22) Print Compound List Report.

(23) Print Response Factor Report.

(24) Print Calibration table (Viewmethod\QuantDatabase).

(25) Save updated method.

(26) Archive the updated method.

4. Process data files

(1) Load the updated method.

(2) Run excel and Custom Reports. Make the default method template FIREVOC.XLS and the default method database AMOUNTS.XLS.
CustRpt\RunExcel\CustRpt

(3) Load the data file.

(4) Quantitate the data file (calculate report); don't print; don't update the database.

(5) QEDIT. Check selection and integration of all peaks, manually integrate and enter corrected responses in the quantitation file. EXIT & SAVE changes. Generate report; print.

(6) Transpose amounts (ng/sample) from AMOUNTS.XLS to REPORT.XLS.

(7) Transpose 5-point calibration Correlation Coefficients from CORRCOEF.XLS to REPORT.XLS.

(8) Transpose dilution factors to REPORT.XLS.

(9) Indicate estimated amounts according to the data quality objectives.

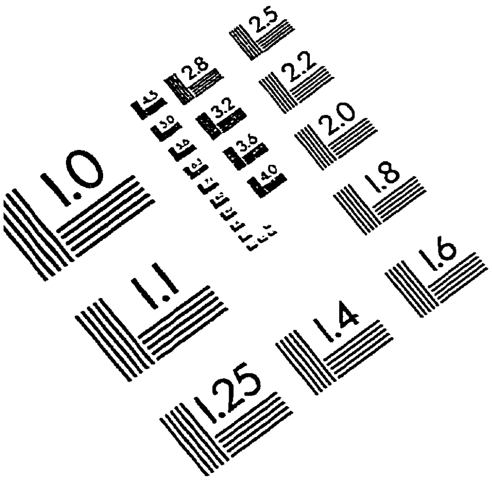
(10) Subtract blank values from sample values.

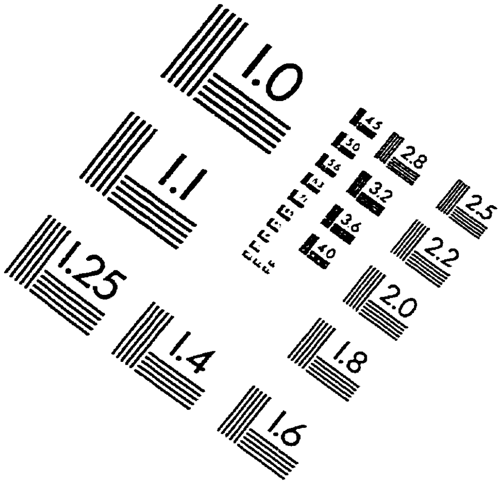
(11) Delete values which are less than the LLQ.

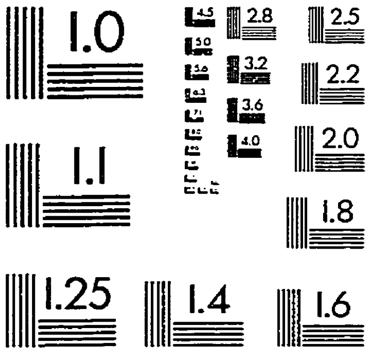
(12) Archive the processed data.

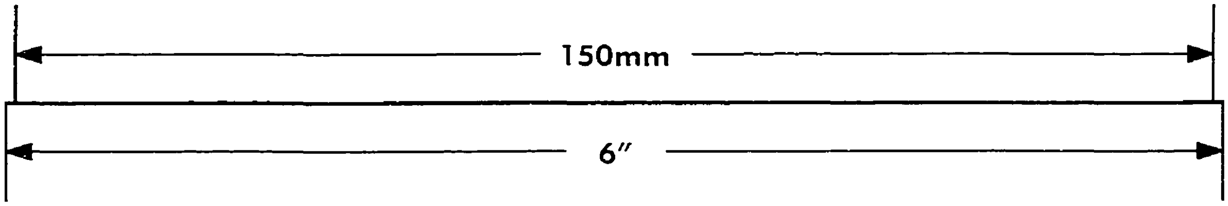
THE END

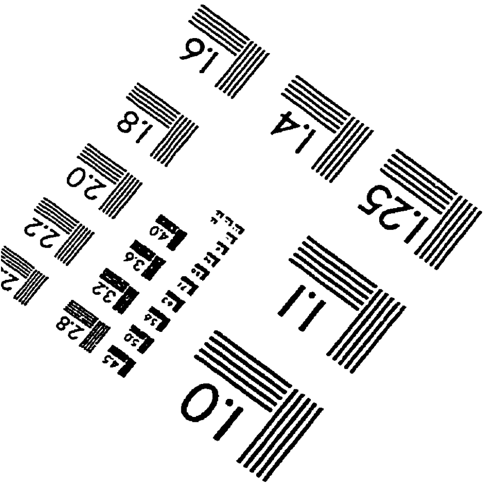
IMAGE EVALUATION
TEST TARGET (QA-3)

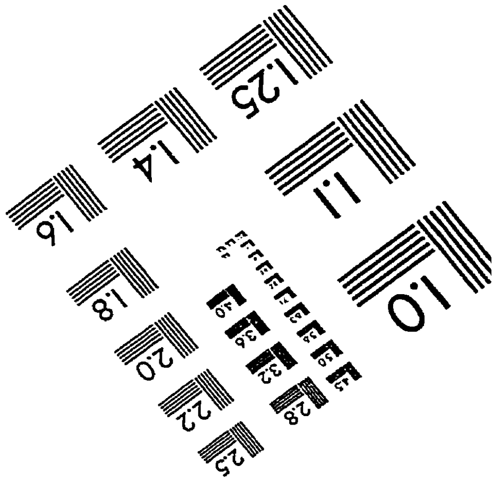












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