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CHARCOAL CLOTH AS AN ADSORBENT
FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS
IN INDOOR AIR

By

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September, 1993

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements of the degree of Doctor of Philosophy

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Charcoal cloth as an adsorbent for the analysis of VOCs in indoor air

ABSTRACT

A comparison was made between NIOSH-type, prepacked nutshell charcoal tubes and layers of commercial charcoal cloth in a stainless steel cassette designed for the active sampling/adsorption of different concentrations of a mixture of volatile organic chemicals (VOCs) (benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene). Physicochemical parameters of the charcoal cloth including breakthrough times and volumes and adsorption capacities were determined for toluene and the VOC mixture. The quantitative removal of VOCs from the charcoal cloth by solvent desorption, by supercritical fluid extraction (SFE), and by thermal desorption was studied prior to analysis by gas liquid chromatography with photoionization detection. Optimal conditions were explored both in laboratory and industrial environments.

Charcoal cloth was comparable to the NIOSH tube, adsorbed VOCs being quantitatively removed at any time up to 32 days after sampling. Although solvent (pentane, hexane) desorption yielded accurate, reproducible results with a high percent recovery of the VOCs, a major disadvantage was the irreparable damage done to the cloth, preventing its repeated use. Desorption by SFE proved unreliable for these low molecular weight VOCs, both the collecting solvents and the VOCs being lost during extraction. Thermal desorption proved to be efficient, sensitive and reliable, repeated heating having no effect on the adsorptive properties of the cloth. Charcoal

cloth would appear to be a useful adsorbing medium for air sampling of both industrial and office building/home environments for either single chemicals or mixtures.

RÉSUMÉ

Une comparaison a été faite entre des tubes de charbon de noix de coco activés genre NIOSH et un tissu de charbon contenu dans une cassette d' acier inoxydable concue pour l'échantillonnage et l'adsorption de concentrations diverses de mélanges de composés organiques volatiles (COV) (benzène, trichloroéthylène, toluène, tetrachloroéthylène, chlorobenzène et o-xylène). Les paramètres physicochimiques du tissu de charbon tels les temps et volumes de claquage, les capacités d'adsorption ont été mesurés. La désorption quantitative des COV du tissu de charbon avec solvant et fluide supercritique ainsi que par désorption thermique suivie d'une analyse par chromatographie en phase gazeuse avec détection photoionique a été étudiée. Les conditions optimales ont été investiguées en laboratoire et sur le terrain.

Le tissu de charbon a donné des résultats comparables au tube de charbon NIOSH, les COV étant analysables quantitativement pour une période de 32 jours et plus après l'échantillonnage. La désorption avec solvant (pentane, hexane) a fourni des résultats précis et reproductibles avec une récuperation acceptable de COV. Cependant, un désavantage majeur est le dommage irreversible fait au tissu qui empêche sa réutilisation. La désorption avec fluide supercritique s'est avérée peu sûr pour les molécules à poids moléculaire moyen puisque le solvant et les COV ont été perdus pendant l'extraction. La désorption thermique s'est demontrée efficace, sensible et sûr. Le chauffage répeté du tissu n'a

pas affecté ses propriétés d'adsorption. Le tissu de charbon est, selon les résultats de cette étude, un matériel d'adsorption utile pour l' échantillonnage de COV en divers milieux environnementales.

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CLAIMS TO ORIGINALITY

Charcoal cloth, first developed by the Chemical Defence Establishment, Porton Down, UK for use in gas masks to adsorb chemical warfare agents, has been tested by only one investigator as a medium for active sampling of volatile organic chemicals (VOCs) (Evan et al., 1977). Charcoal cloth has been studied for use for passive sampling in a badge device. To the best of my knowledge, no one has explored the physicochemical properties of commercial charcoal cloth in relation to its usefulness as a medium for active sampling of environments contaminated by VOCs, present either as single compounds or as mixtures.

The original aspects of this thesis include:

1) the measurement of the adsorption capacities of charcoal cloth for the VOC components in a mixture;

2) the design and improvement of a cassette device for the active collection of VOCs and a cassette capable of being used for thermal desorption;

3) the comparison of three desorptive techniques (solvent, supercritical fluid, thermal) for the quantitative removal and recovery of VOCs from charcoal cloth;

4) the demonstration that charcoal cloth can be used as a medium for active sampling of airborne contaminants in an industrial setting, proving that this medium met the qualitative and quantitative expectations determined by laboratory experiments.

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Abbreviations and Symbols

ACC	activated charcoal cloth
ACGIH	American Conference of Governmental Industrial Hygienists
Acn	acrylonitrile
α	alpha
ATM	atmosphere
$\hat{B}$	mean bias
B_i	bias
Bz	benzene
°C	degree Celsius
C_1	one carbon atom in the molecule
C_2	two carbon atoms in the molecule
C_{10}	ten carbon atoms in the molecule
C_{12}	twelve carbon atoms in the molecule
Cl	chlorobenzene
cm	centimeter
cm^2	square centimeter
cm^3	cubic centimeter
CV	coefficient of variation
$\overline{CV}_T$	the precision of the sampling and analytical method
d	diameter
dia.	diameter
DMP	dimethyl phosphate
Dvb	divinylbenzene

E. coli	Escherichia coli
EPA	U.S. Environmental Protection Agency
f	degree of freedom
g	gram
g	gas
GC	gas chromatograph
GLC	gas-liquid chromatography
hr(s)	hour(s)
i.d.	inner diameter
IUPAC	International Union of Pure and Applied Chemistry
kg	kilogram
L	litre
log	logarithm
m	metre
m	mist
min	minute
MOE	The Ontario Ministry of Environment
m^2	square metre
N or n	number of replication
NIOSH	National Institute for Occupational Safety and Health
No	number
OP	orthophosphate
O.S.A.	overall system accuracy
OSHA	Occupational Safety and Health Administration

p	vapour pressure
PAC	Pittsburgh activated carbon
PCB's	polychlorinated biphenyls
PCL	Perchloroethylene
PDS	Porton diffusion sampler
PEL(s)	permissible exposure level
PID	photoionization detector
ppb(v)	part per billion (volume)
ppm(v)	part per million (volume)
ppt	part per trillion
psi	pound per square inch
r	radius
RH	relative humidity
s	second
SD	standard deviation
SFE	supercritical fluid extraction
Sty	styrene
TEAM	total exposure assessment methodology
Tb	Breakthrough time
TDI	toluene diisocyanate
TEP	triethyl phosphate
T4	tetrachloroethylene
TLV(s)	threshold limit value(s)
To	toluene
T3	trichloroethylene
TWA	time-weighted average

v	vapour
VOC(s)	volatile organic compound(s)
$\bar{X}$	arithmetic mean
Xy	o-xylene

Prefix

m	meta
m	milli
n	nano
n	normal
o	ortho
p	para
u	micro

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INTRODUCTION

Almost all work environments involve some exposure to potentially hazardous materials and the potential for exposure to these hazards cannot be eliminated completely. It becomes necessary to reduce the exposure level to protect the health and well-being of workers (Ayres and Taylor, 1989). There are three main routes by which workers can be exposed to these agents: a material can come in contact with skin (dermal exposure), it can be swallowed after contact with the mouth and oral cavity (oral exposure) and it can be breathed through the nose, mouth and into the lungs (inhalation exposure) (Kennedy, 1989). The skin is exposed to toxic chemicals in the form of vapours, liquids or solids, absorption via this route being extremely important. The skin is a reasonably impermeable barrier to chemicals although absorption can be enhanced by organic solvents (Timbrell, 1991). Occupational skin injuries account for 23 to 35 percent of all occupational injuries (Arndt and Bigby, 1988). Oral exposure to chemicals can be prevented in the workplace by instituting personal hygiene practices to prevent contamination. Exposure to and absorption of compounds through the lungs is toxicologically important and more significant than skin absorption (Timbrell, 1991). Absorption from the lungs is rapid and efficient because of the large surface area available for gas exchange with the blood supply. Therefore, inhalation is perhaps the most important route for exposure to solvent vapours in the workplace.

With inhalation, one can anticipate three scenarios. The first involves acute exposure to a high level of the toxicant, either immediate and/or delayed effects being observed. Solvent-abuse would be one example where both immediate mood-elevating and CNS-depressant effects would be observed followed by a persistent central or peripheral sensory or motor neuropathy. Subacute exposure to moderate levels of toxicant vapours would result in the development of similar toxic endpoints but the time interval to achieve these would be extended. The third scenario involves the prolonged, chronic exposure to low levels of toxicant vapours, with a delay of some years before biological effects become obvious. Sampling techniques for the analysis of toxicant vapours must be capable of quantitatively capturing high, moderate and low levels of the suspect toxicant, e.g. the entire dosage range, during both short- and long-term conditions of sample collection.

People divide their time between home and work. At home, people smoke, cook, clean, make repairs, conduct hobby activities, heat the air for comfort and carry out many other activities that can add harmful substances to indoor air. The house itself, even the soil beneath it can be a source of indoor air contaminants. Typical sources of indoor air pollution in home and office are summarized in Table 1. Some of these pollutants, sources and their health effects will be

Table.1 Typical Sources of Indoor Air Pollution in the Home and Office.

Environment	Sources and Pollutants
Home	Tobacco smoking: respirable particles, CO, VOCs Gas stoves: NO_2, CO Wood stoves, fireplaces: respirable particles,CO,PAH Building materials: formaldehyde, radon Earth underlying the home: radon Furnishings and household products: VOC, formaldehyde Gas-fueled space heaters:NO_2, CO Kerosene-fueled space heaters: NO_2, CO, SO_2 Insulation: asbestos Moist materials and surfaces: biological agents
Office	Tobacco smoking: respirable particles, CO, VOC Building materials: VOC, formaldehyde Furnishings: VOC, formaldehyde Copying machines: VOC Air conditioning systems:biological agents, CO, NO_2

VOC = Volatile organic compounds
PAH = Polycyclic aromatic hydrocarbons
Data from Samet et al., 1987

reviewed as examples of common air contaminants; e.g. combustion products and volatile organic compounds (VOCs).

This introduction is composed of five sections: health effects of selected contaminants in industries, homes and office buildings; overview of air sampling for gas and vapour; adsorbents and their properties; charcoal cloth and its applications and volatile organic compounds (VOCs).

HEALTH EFFECTS OF SELECTED CONTAMINANTS IN INDUSTRIES, HOMES AND OFFICE BUILDINGS

In industry, inhalation exposure to various contaminants can occur depending on the processes, work operations and the effectiveness of existing control measures (Table 2). Two types of industries were chosen as examples of common industrial operation: dry cleaning and painting.

Dry cleaning industry

Workers in the dry cleaning industry are exposed to tetrachloroethylene (perchloroethylene, PCL) a solvent used extensively for this type of operation (Solet et al., 1990). Commercial dry cleaning has existed in the United States since the 1800s. Early dry cleaning solvents such as gasoline, turpentine or benzene were flammable or explosive. Dry cleaning solvents have evolved since 1900 from petroleum solvents, carbon tetrachloride, tetrachloroethylene, trichloroethylene to fluorocarbons. Tetrachloroethylene,

Table.2 Selected Hazardous Operations and Air Contaminants.

Process type	Contaminant examples
Liquid operations	
Painting	Toluene (v), Xylene (v) Toluene diisocyanate (v)
Degreasing	Trichloroethylene (v) Methylene chloride (v) 1,1,1-trichloroethane (v)
Dry cleaning	Tetrachloroethylene (v)
Pickling	Hydrogen cyanide (g) Hydrogen chloride (g) Sulfuric acid (m)

(v) = vapour, (m) = mist, (g) = gas

introduced in the 1940s, has become the primary dry cleaning solvent in use today because of its nonflammability. Of the 600 million pounds of domestic demand for tetrachloroethylene in 1986, most (53%) was consumed by the dry cleaning industry. Approximately 139,000 workers were employed in 17,200 dry cleaning plants in the U.S. (Solet et. al., 1990).

The effects of short term exposure to tetrachloroethylene are shown in Table 3. Such effects are reversible on cessation of exposure, but increase in severity with both increasing concentration and duration of exposure. Direct contact of tetrachloroethylene with the skin can cause burns, blistering and erythema. Excessive exposure to tetrachloroethylene can cause severe depression of the central nervous system leading to coma ; death may occur from respiratory paralysis or circulatory failure (Ludwig et. al., 1983). Animal studies have clearly demonstrated tetrachloroethylene-related hepatic and renal toxicity. In humans, epidemiologic investigations have linked dry cleaning employment with excess risk of bladder, liver or kidney cancer (Solet et al., 1990).

Recently, the Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit (PEL) for tetrachloroethylene from 100 to 25 ppm (TWA). The standard was promulgated March 1, 1989, but the industry had until January 1, 1993, to come into compliance with engineering controls. In addition, the National institute for

Table 3. Effect of Short Term Exposure to Tetrachloroethylene

Conc.(ppm)	Duration	Effects
21	short term	No effect
100	4 hrs	Slight eye irritation
216	2 hrs	Light headedness, burning in the eyes and difficulty in motor coordination
500	50 min	Increased salivation metallic taste, eye irritation and tightness of the frontal sinuses
2,000	>1.5 min	Unconscious

Data from ACGIH, 1986

Occupational Safety and Health (NIOSH) has recommended that tetrachloroethylene be handled as if it were a human carcinogen and that exposure be kept as low as possible (Solet et. al., 1990).

The dry cleaning process involves three stages: cleaning, extracting and drying. During the cleaning cycle, textiles are cleaned by mechanical agitation in a solvent bath. They are rinsed, spun to remove excessive solvent (extraction). Drying is accomplished by tumbling garments in a heated air to evaporate any remaining solvent (Materna, 1985). Solvent vapours are recovered by condensation and purified by redistillation for reuse. Dry cleaning may be one of the two types: transfer or dry to dry process. With transfer equipment, garments are cleaned in an extractor unit and must be physically transferred to a separate dryer. During transfer operations, exposure occurs through inhalation and skin contact each time garments are removed from the extractor to the dryer (Materna, 1985). The dry to dry process is a closed system with three steps taking place within one machine. The dry to dry system is preferable because it minimizes employee exposure.

The dry cleaning operator's task is to load and unload garments from machines. Periodically, the operator may be required to perform other operations: replacing filter media, transferring solvent from a storage tank to the cleaning machine and performing equipment maintenance. Other conditions which may increase exposure of tetrachloroethylene concentration in the workroom air include: liquid or vapour solvent leaks due to poor maintenance and residual levels of solvent in incompletely dried garments. Dry cleaning equipment is usually supplied with local exhaust ventilation. An exhaust fan is activated when opening the door of the machine. The local exhaust should draw vapours away from the operators'breathing zone during handling of garments. In field surveys conducted in 67 dry cleaning establishments to assess working conditions and potential exposure to tetrachloroethylene, the mean time-weighted average (TWA) exposure of the operators for dry to dry process were lower (28.3 ppm) compared to 86.6 ppm for transfer operations. Five-minute peak samples taken during clothing transfer demonstrated significant exposure levels ranging from 11.3 to 533.8 ppm (Materna, 1985). The National Institute for Occupational Safety and Health (NIOSH) conducted surveys at 44 commercial dry cleaning facilities to assess the health effects of long term, low-level exposure to tetrachloroethylene. The results showed that the TWA exposure of machine operators ranged from 4.0 to 149.0 ppm tetrachloroethylene. The geometric mean tetrachloroethylene exposure of the machine operators (22 ppm) differed significantly from the mean exposures of the pressers (3.3 ppm) and seamstresses (3.0 ppm) (Ludwig et. al., 1983). Solet et. al. (1990) carried out the exposure assessment in 13 dry cleaning plants using tetrachloroethylene. On average, operators of dry cleaning equipment (46.5 ppm) experienced significantly more exposure than non-operators (12.9 ppm). Also, employees working in shops that use transfer equipment showed significantly higher exposure (29.5 ppm) than those in shops utilizing dry to dry machinery (7.1 ppm).

Painting

Paint products are used widely in industry to provide a surface coating for protection against corrosion, for appearance, for electrical insulation, and for a number of special purposes (Burgess, 1981). Solvent-based paints consist of the vehicle, filler and additives as shown in Table 4. The vehicle represents the total liquid content of the paint including the binder and the solvent. The binder may be a naturally occurring oil or resin or a synthetic material. Examples of resins are alkyd resins, amino resins, acrylates, polyurethane resins and epoxy resins. The uncured polyurethane resin contains small amounts of unreacted monomer, toluene diisocyanate (TDI) monomer. TDI vapour is extremely irritating to eyes, skin, and the upper respiratory tract (Krivanek, 1982). Another example of toxic resins is epoxy resin. It offers excellent adhesive properties, resistance to abrasion and chemicals, and stability at high temperatures but it consists of a resin based on the reaction products of bisphenol A and epichlorohydrin. Epichlorohydrin

Table 4 Paint Constituents

Major Component	Constituents	Purpose
Vehicle	Binder	Resin that forms film
	Solvent	Thinner for adjustment of viscosity
Filler	General filler	Hiding ability, body, colour
	Pigment	Opaqueness, colour
	Extender	Fillers that build body
Additives	Driers	Speed drying or curing
	Biocide	Prevent growth of mold and fungus
	Flatting agents	Provide low luster
	Stabilizers	Protect against heat and UV radiation
	Antiskinning	Prevent skin formation in can

Data from Burgess, 1981

is considered to be a potential (respiratory) human carcinogen (Ringen,1982). In addition, epoxy resins are not completely cured materials and have been associated with skin reactions and eye irritation (Krivanek,1982). The solvent used in conventional paints may be chosen from a wide range of solvents in Table 5. The acute effects of paint solvents on humans have been known for a long time. They include general depression of the nervous system, irritation of the skin, eyes, nose, throat and lungs, gastrointestinal disturbances, and damage to liver and kidney (Mehlman and Smart, 1982). The routes of exposure are by inhalation, ingestion, eye or skin contact, or a combination of these. It appears that aromatic hydrocarbon solvents (toluene, xylene and styrene/ ethyl benzene) are the most hazardous and may be carcinogenic in addition to affecting the central nervous system (Ringer, 1982). The aromatic solvents are more irritating to the eye and skin than the aliphatic solvents. Of the aliphatic hydrocarbons, hexane is the most toxic. Chronic inhalation of hexane can cause peripheral neuritis that can progress to neuropathy (death of sensory nerves in the fingers, toes, etc.) (Peterson, 1982). Among ketones, methyl n-butyl ketone and methyl ethyl ketone appears to be most hazardous. The health effects may be extreme neurotoxic depression (Ringen, 1982).

The fillers contain pigments that historically have presented a major hazard in painting. The use of common heavy

Table 5 Partial List of Paint Solvents-Thinners

Aromatic	**Chlorinated Solvent**	**Acetates**
Benzene	Methyl chloride	Ethyl
Toluene	Chloroethane	Isopropyl
Xylene	Carbon tetrachloride	n-Propyl
Aromatic naphthas	Ethylene dichloride	Secondary butyl
Aromatic petroleum	Trichloroethylene	n-Butyl
Aliphatic	Perchloroethylene	Amyl
Petroleum ether	**Ketones**	**Alcohols**
Lacquer diluent	Acetone	Methanol
VM and P naptha	Methyl ethyl ketone	Ethanol
Mineral spirits	Methyl acetone	Isopropyl alcohol
Kerosene	Methyl isobutyl ketone	n-Propyl alcohol
High flash napthas		n-butyl alcohol
Glycol Ethers	Cyclohexanone	sec-Butyl alcohol
Terpenes	Isophorone	Amyl alcohol
Turpentine	Diisobutyl ketone	Cyclohexanol
Dipentine	Diacetone	
Pine oil		

Data from Burgess, 1981

metal compounds includes cadmium compounds, lead carbonate, sulfates and oxides. Lead compounds are very toxic and many people have suffered lead poisoning mainly from inhalation of dry pigment dust during paint manufacture. In homes painted with lead pigment formulation, children have suffered lead poisoning because they ate paint chips or gnawed on objects coated with paints containing lead pigments. Lead pigments are no longer used in home construction paints and have been replaced by titanium dioxide. Titanium dioxide has very low oral, dermal and inhalation toxicity (Krivanek, 1982). Other types of pigments include calcium carbonate, barium sulfate, aluminium silicate, zinc oxide, Iron oxide etc.

Additives include driers, thickeners, catalysts, plasticizers, surfactants, biocides and anti-skinning agents. Additives are presented in the paint at low concentrations. The biocides are the most toxic of the additives since their functions are to retard mold and bacterial growth in paint.

Paints can be applied to parts by a number of processes including brush, roller, dip, compressed air spray, airless spray, electrostatic spray and powder coating. The operator is exposed to the solvent or thinner in the process in which the paint is applied during brushing, dipping and the drying of the parts. Compressed air spraying is the most common method encountered in industry and presents the principal hazards due to overspray and rebound. Compressed air spray is done by mixing the compressed air either inside the spray nozzle or outside of it. During atomization techniques, the exposure is to both the solvent and the paint mist. Airless spraying applies the coating with a gun at quite high pressure and by forcing it through a very small orifice. This method was reported to produce less wasted overspray than did electrostatic spraying (Burgess, 1981). The electrostatic technique places a charge on the paint mist particle so that it is attracted to the part to be painted.

Homes

Air pollutants in homes originate from combustion, outgassing, etc. Combustion products are primarily released in the home by gas stoves, unvented kerosene heaters, furnaces, fireplaces and by cigarette smoking. The combustion products of concern comprise aldehydes, carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, particulate and sulfur dioxide. Their health effects are shown in Table 6.

There are some studies reporting the health effect ot combustion products in homes. Nitrogen dioxide at the concentration of 0.05 ppm, in homes with gas cooking or unvented kerosene heaters may affect sensory perception and may produce eye irritation. Turiel (1985) concluded that there might be some increase in respiratory illness and a small decrease in lung function among young children living in homes with gas stoves compared to those living in homes with

Table 6 Health Effects Related to Various Combustion Products.

Contaminant	Health effect
Aldehyde	Irritation of eyes, nose and throat
Carbon monoxide	Headaches, impairment of visual acuity and brain functioning; irregular heart functioning
Carbon dioxide	Headaches, dizziness, shortness of breath and drowsiness
Nitric oxide	At high concentrations, irritation of eyes, nose and throat
Nitrogen dioxide	Damage to lung tissue and increase airway resistance
Particulates	Varies according to chemical and physical properties; for example, benzo-a-pyrene is carcinogenic, other particulates may not have adverse health effects
Sulfur dioxide	Irritation of skin, eyes, and mucous membranes; at high concentration, constriction of upper airways

Data from Turiel, 1985

electric stoves. In nine typical Canadian homes, the level of carbon monoxide after 20 minutes of gas stove operation ranged from 35 to 120 ppm which was above the maximum allowable 8-hr average outdoor concentration of 9 ppm (Sterling and Sterling, 1979). The experiments also indicated that the carbon monoxide concentration was highly dependent on the number of burners in operation and whether or not the burners were covered with cookware.

Office Buildings

Those who work in office buildings may experience building-related illness. Typical symptoms found in a low percentage of employees are eye and throat irritation, shortness of breath, headache, dizziness, chest tightness and fatigue. NIOSH investigated 365 office buildings across the United States. Indoor contaminants were the primary cause of building-related illness in 19% of cases (Table 7) (Samet et. al., 1988). These contaminants included all chemicals generated by indoor sources. Contaminants from outdoor sources such as motor vehicles exhaust may be drawn into a building through intake vents. In 4% of cases, contaminants from building materials such as formaldehyde were the causal agents. In 179 of the 356 investigations, no specific causal agent other than inadequate ventilation could be identified (Samet et al., 1988). Healthy Buildings International, Inc. has investigated causes of building-related illness in 412

Table 7 The Etiology of Building Related Illness in 356 Office Buildings Conducted by NIOSH.

Etiology	n	%
Inside contaminants	67	19
Outside contaminants	38	11
Contaminants from building materials	14	4
Biological contaminants	19	5
Inadequate ventilation	179	50
Unknown	39	11

Data from Samet et. al., 1988

buildings during 1980 to 1988. The results showed that the major causes of sick building syndromes were poor ventilation, inefficient filters and dirty air handlers (Table 8) (Robertson, 1989). Poor ventilation was the result of the energy crisis in the early 1970s. Many building owners and operators reduced the quantity of fresh air entering into their buildings, used cheap and low efficiency filters and did not have good maintenance of air conditioning systems in their buildings. Major pollutants found were allergenic fungi, dust particles, pathogenic bacteria, formaldehyde and low humidity in buildings (Robertson, 1989).

AIR SAMPLING

The need for sampling air in workrooms and ambient environments is to ensure a safe atmosphere which will not cause any diseases. Air sampling is defined as the collection of air from an atmosphere, followed by transfer of these volumes to the place and into the form in which the analysis can be made (Weurman, 1974). Air sampling can be taken for several purposes: (1) assurance of adequate health protection for all workers by initial and ongoing assessment of risk for developing occupational diseases; (2) establishment of historical records of exposure levels for epidemiologic and worker's compensation purposes; (3) compliance with governmental standards; (4) evaluation of new types of equipment, process and control and (5) correlation of

Table 8 Sick Building Syndrome Causes: Healthy Buildings International, Inc. Experience, 1980-1988

Total building studies	412
Poor ventilation	62%
Including no ventilation	33%
Inefficient filters	61%
Including careless installation	18%
Dirty air handlers	58%
Including contaminated ductwork	22%

Summary of Most Significant Pollutants Found

Major Pollutants in Air	% of Buildings
Allergenic fungi	31
Dust particles	29
Low humidity	26
Allergenic bacteria	8
Formaldehyde	7
Vehicles exhaust gases	6
Tobacco smoke	3
VOCs	3
Fibrous particles	2
Ozone	1

Data from Robertson, 1989

environmental conditions with medical findings in order to establish the threshold limit value.

The decision to sample an atmosphere for particular contaminants is often based on the results of preliminary surveys. Surveys are sometimes initiated as a result of complaints received from workers, neighbors or other sources suggesting that a hazardous or annoying air contamination exists. The type of contaminants occurring in a workplace depends on the process employed. It can be particulate matter, gases, vapours, mists or mixtures. This overview is focused only on air sampling for gases and vapours.

Air sampling devices for industrial purposes have been divided into two groups, one called "instantaneous" or "grab" samples, and the other integrated or continuous samples (Silverman, 1956).

Instantaneous sampling

Butterfield (1909) developed an instantaneous sampling device to collect air for the assessment of moisture, carbon dioxide, methane or other combustible gases. The sampling device used was a narrow-mouthed bottle of about 56 ml, with a well-fitting glass stopper. A piece of rubber tubing was used to draw air into the bottle; one end of the tube being attached to the bottom of the bottle, the other was put in the mouth of investigator. A full inspiration of air was taken, thus drawing the air of the room into the bottle, following which the bottle was stoppered.

Instantaneous samples could be collected by means of evacuated flasks, with volumes ranging from a few milliters to 300 ml. These flasks were constructed of glass, metal or plastic. In practice, the evacuation was done in the laboratory or the flask was purged in the field by pump. Bottles were commonly used to collect grab samples. In one instance, the bottles had a mercury pool at the bottom to form an air-tight seal over the porcelain stopper when the bottles were inverted during transportation (Silverman, 1956). Instantaneous sampling devices also included direct reading instrumentation for air contaminants. These devices collected gases and vapours on a solid adsorbent, impregnated papers or cellulose. The adsorbents used were either granular adsorbent gels, such as activated alumina or silica gel, or inert granules, such as pumice or sand coated with the detecting materials. Detector tubes or impregnated papers became popular devices (Silverman, 1956).

Plastic bags of varying chemical composition sometimes are used for the collection of air samples. This is the preferred method for sampling gases and high vapour pressure compounds which have low breakthrough volumes for adsorption methods. A variety of bags have been used, such as aluminized, Halar^{R}, Saran^{R}, Tedlar^{R}, Teflon^{R} and Mylar^{R}. Possible sources of loss of substances from such bags include adsorption of the analyte on the walls of the bags, chemical reactions among the collected substances and permeation of the substances through walls of the bag (Tombe et. al., 1991). Posner and Woodfin (1986) performed a study on the losses of butene and 1,3-butadiene with time on some of the gas bags. Tedlar bags appeared to be the best choice for short term storage although Tedlar bags have been found to contaminate air samples with acetaldehyde and acetone (Tombe et. al., 1991). Tedlar bags have been used to collect gases and vapours for the exposure assessment of firefighters (Trietman et. al., 1980 and Jankovic et. al., 1991) and for source emission sampling (Pau et. al., 1991).

Another type of instantaneous sampling uses a canister. Miller (1976) used partially evacuated steel containers, Vacu-Samplers, for collecting gases and vapours. Recently, the SUMMA passivated stainless steel canister has been the recommended sampling method by U.S. Environmental Protection Agency (EPA) for the collection of volatile organic compounds in ambient air (Tombe et al., 1991). These devices provided very satisfactory performance for aliphatic and aromatic hydrocarbons (C_1-C_{12}). The inertness of the SUMMA canister surface has been demonstrated by storing parts per trillion (ppt) levels of trace gases for several months or longer without any appreciable losses of the stored substances (Tombe et. al., 1991). The advantages of canister use in monitoring VOCs in ambient air include easy cleanup procedure, repeated or multiple analysis, good storage stability, no breakthrough of target compounds and no electrical power needed for filling canister (McClenny et.al., 1991; Hsu et. al.,1991). However, the canisters are costly, bulky and have limited sampling volumes and are not generally applicable to polar compounds (McClenny et al., 1991). The analysis of VOCs collected by the canisters is difficult and costly.

Integrated sampling

Initially, integrated sampling used adsorbers containing collecting agents, such as water, acid, alkali or organic solvent, to trap contaminants. Adsorbers for gases and vapours varied in characteristics depending upon the gas and vapour encountered. Simple wash bottles with ground glass joints or with multi-hole dispensers were used for collecting readily soluble adsorbed gas and vapours. For poorly adsorbed gases and vapours, sintered micro-gas washing flasks or midget impinger flasks fitted with a glass-filter stick were used. These filters dispersed the gas into fine bubbles or spread the liquid onto a large surface area (Silverman, 1956). The pumps used for drawing air contaminants into adsorbers could be an aspirator (bottle), a hand pump or a motor-driven pump. The flow rate of contaminants in air could be drawn through adsorbers ranging from 0.5 to 15 liters per minute (Silverman, 1956).

At present, liquid adsorbents and impingers, may be useful for some reactive gas and vapours such as formaldehyde and ammonia. The spill-proof impinger for personal samples is also available (Heitbrink and Doemeny, 1979).

When collected contaminants are insoluble or non-reactive vapours, adsorption or condensation is the method of choice. Adsorbents commonly used in practice include: (1) activated charcoal, (2) silica gel and (3) special impregnated gels which contained a reactant for specific gases. Sometimes, highly volatile contaminants must be condensed at low temperature with a mixture of dry ice and acetone.

Rushing (1958) proposed methods coordinating the process of sampling on adsorbents and subsequent gas chromatographic analysis (Cited by Reid and Halpin, 1968). Reid and Halpin (1968) used small glass tubes containing activated charcoal to collect organic vapours. Sampling was accomplished by drawing vapour-containing air, at desired flow rate, through these tubes. Altshuller et. al. (1962) and Feldstein et. al. (1967) did essentially the same thing except that a silica gel adsorbent was employed. They desorbed contaminants by solvent desorption and analyzed by gas liquid chromatography.

The use of small charcoal tubes connected to a small portable pump was introduced in 1970 (White et. al., 1970). Charcoal has gained the status of the almost universal adsorbent because of the large surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. Activated charcoal is extensively used to purify, decolorize and detoxify potable waters; for air purification in inhabited spaces such as chemical industries; and in a variety of gas phase applications (Bansal et. al., 1988). Many types of raw materials are used for industrial-scale production of activated charcoal such as wood, coal, lignite, coconut shell and peat. Granular activated charcoal is the type of charcoal commonly used for the adsorption of gases and vapours. Nutshell charcoal tube sampling was the recommended method for organic solvents in air in 1974. NIOSH adapted this technique to more than one hundred individual chemicals including compounds with low exposure limits such as acrylonitrile, benzene and vinyl chloride in 1977. Activated charcoal has some limitations, including sensitivity to humidity and low sensitivity due to solvent desorption. These limitations have led to the development of other adsorbents, such as porous polymers. The use of sampling tubes packed with porous polymer adsorbents, such as Porapak Q, Tenax GC or Chromosorb 101,102 or 103, offered an excellent means for trapping organic contaminants present in air (Tanaka, 1978). Subsequently, the contaminants are thermally desorbed into a gas chromatograph for analysis. The advantages of thermal desorption include high sensitivity, the absence of a solvent peak in a gas chromatographic analysis and the reuse of the adsorbent (Crisp, 1980). However, thermal desorption does not permit multiple analysis of a single sample. Tenax GC has been widely used porous polymers for the assessment of VOCs in ambient environment (Crisp, 1980).

The approach of using more than one adsorbent to enhance the adsorption for low molecular weight compounds has been studied. The Oil Companies'International Study Group used a sampling system composed of two types of solid sorbents for monitoring gasoline vapour. The sampling tube consisted of a front bed of Chromosorb^R 106 and a back bed of charcoal. The low molecular weight hydrocarbons passed through the front bed and were trapped on the charcoal. The tube was thermally desorbed in the reverse direction from that used for collection (Coke et. al., 1989). The Ontario Ministry of Environment (MOE) currently uses a sorbent tube of Carbotrap/Carbosieve that has been found to be very effective for retaining C_2 to C_{12} components (Tombe, 1991). Multi-sorbent samplers containing a series of Tenax, Ambersorb XE-340 and activated charcoal have been used to increase the breakthrough volume of low-boiling compounds. With a 10-L collected sample volume, limits of quantitation were < 1 ppb (Hodgson et al., 1988). In a field study evaluating the ability of a multi-sorbent sampling tube to identify organic contaminants in 12 Canadian homes, the results indicated that the recoveries were more than 70%, with the precision being better than 15% (Chan et al.,1990).

In 1973, Palmes introduced a passive sampling unit for monitoring sulfur dioxide based on the molecular diffusion of a gas through an orifice into a small chamber containing mercuric chloride (Palmes et. al., 1973). This approach was intended to obviate the need for pumps and flow control devices as parts of the sampler. This sampling principle could be applicable to any gaseous airborne contaminant. Another passive sampling unit for nitrogen dioxide, containing stainless steel grids coated with triethanolamine, was developed in 1976 (Palmes et. al.,1976). Similar passive sampling devices have been developed for organic vapour monitoring because they were small and light, simple in structure and required no source of power. Examples were the Walden GASBADGE^{TM} dosimeter for industrial pollutants (Tompkins and Goldsmith, 1977); the Abcor GASBADGE^{TM} for acrylonitrile (Silverstein, 1977); the 3M monitor for mercury vapour (McCammon and Woodfin, 1977); and the Porton diffusion sampler for volatile organic substances (Evans et.al., 1977). The passive samplers were initially developed for monitoring relatively high-level TWA exposures because OSHA was promulgating TLV-TWA for employee exposure to toxic substances in that period. The development of passive sampling increased dramatically because of the simplicity of sampling without a personal pump. The technique was commonly applied using charcoal or porous polymer adsorbents to the collection of organic vapours. With charcoal adsorbents, the adsorbed vapours were eluted with solvent, usually carbon disulfide. In some studies, the investigator reported poor recovery and precision when thermal desorption was used to remove the adsorbed vapour (Gonzalez and Levine, 1986). If a porous polymer adsorbent was employed, the analyte could be efficiently desorbed by thermal techniques. This technique could also be used for low sample loadings such as short-term exposure and low concentration monitoring of organic vapours. Such passive samplers require validation before use in analyzing low concentrations of organic vapours in indoor air.

ADSORPTION PRINCIPLES

Adsorption at a surface or interface is largely the result of binding forces between individual atoms, ions or molecule of an adsorbate and the surface of the adsorbent. The four principle types of adsorption are exchange, physical, chemical and specific adsorption (Weber, 1985).

Exchange adsorption, or ion exchange, involves the electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent, with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity.

Physical adsorption results from the action of van der Waals forces, which are composed of both London dispersion forces and dipole-dipole interactions. London forces is a result of momentarily unequal distributions of electron density in molecules, even nonpolar molecules (Boikess and Edelson, 1981).

Chemical adsorption involves a reaction between an adsorbate and adsorbent resulting in a change in the chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical van der Waals forces.

Specific adsorption results from the attachment of adsorbate molecule at functional groups on adsorption surfaces. These interactions do not result in adsorbate transformation. They exhibit binding energies ranging from a value commonly associated with physical adsorption to the higher energies involved in chemisorption.

The net electrostatic, physical, chemisorption and functional-group interaction broadly define the affinity of an adsorbent for a specific adsorbate.

Polar organic vapours will be strongly adsorbed by a polar adsorbent and a nonpolar organic will prefer a non polar adsorbent. The polarity of organic compounds is a function of charge separation within the molecule. Almost any asymmetric compound will be more or less polar, but several types of functional groups such as hydroxyl, carbonyl, nitro, nitrile, carboxyl, sulfonate and amine tend to produce fairly high polarities in compounds. Thus, ethanol (C_2H_5OH) is polar, being partially negative at the hydroxyl group and correspondingly positive at the ethyl group.

The surface chemistry of adsorbents is important in determining its activity or capacity for adsorption of a specific organic substance. The chemical properties of the surface depend on raw material used, the type of activation process and the conditions employed in activation. Activated carbon surfaces consist of essentially two different types. The bulk of the surface is composed of basal plane areas which are largely uniform, nonpolar surfaces. These surfaces support hydrophobic and physical adsorptions. The other surface is composed of the heterogeneous edges of carbon planes. The carbon-oxygen functional groups formed by oxidation are attached to the edges of carbon planes. These groups enable activated carbon to form halogenation, hydrogenation and oxidation. They provide for a range of electrostatic, hydrogen bonding, functional group and chemisorption interaction. They greatly extend the spectrum and degree of adsorbability of adsorbates on activated carbon (Weber, 1985).

ADSORPTION CAPACITY

Adsorption is a surface phenomenon which can be described as a concentration of material on a solid surface. Surface area and pore size are primary determinants of adsorption capacity. The adsorption capacity in a given system is generally found to increase with decreasing temperature (Weber, 1985). Conversely, because adsorptions are generally controlled by diffusive mass transfer, rates of approach to equilibrium normally increase with increasing temperature. The adsorption of more than one substance generally reduces the number of surface sites available to each. However, in certain circumstances, chemicals act relatively independently or can interfere with one another. Mutual reduction of both adsorption rates can be expected.

Measurement of adsorption capacity

The breakthrough test is commonly used for estimating adsorption capacity of solid adsorbents for organic vapours in air. When air containing an organic compound at concentration C_i, is pulled to a tube containing a solid adsorbent, the compound is distributed through a section of the adsorbent as shown by curve 1 (Fig.1). With continued collection, the front section becomes saturated (curve 2). If collection continues, the compound begins to break through the collection tube at time Tb as shown by curve 3. The breakthrough curve (#4) is generated by monitoring concentration of the compound in the effluent. When all the adsorbent is saturated, the effluent concentration approaches the input concentration C_i (Melcher et. al., 1978).

Breakthrough is defined as the detection of the compound in effluent as percentage of C_i. As a practical guide in air sampling, this is often set at 5%. The breakthrough volume which is more indicative of the collection efficiency, is the product of the sampling flow rate and the sampling time (Tb). The breakthrough capacity equals C_i multiplied by the breakthrough volume. The adsorption capacity is the ratio of trapped contaminant and weight of adsorbent (Guenier and

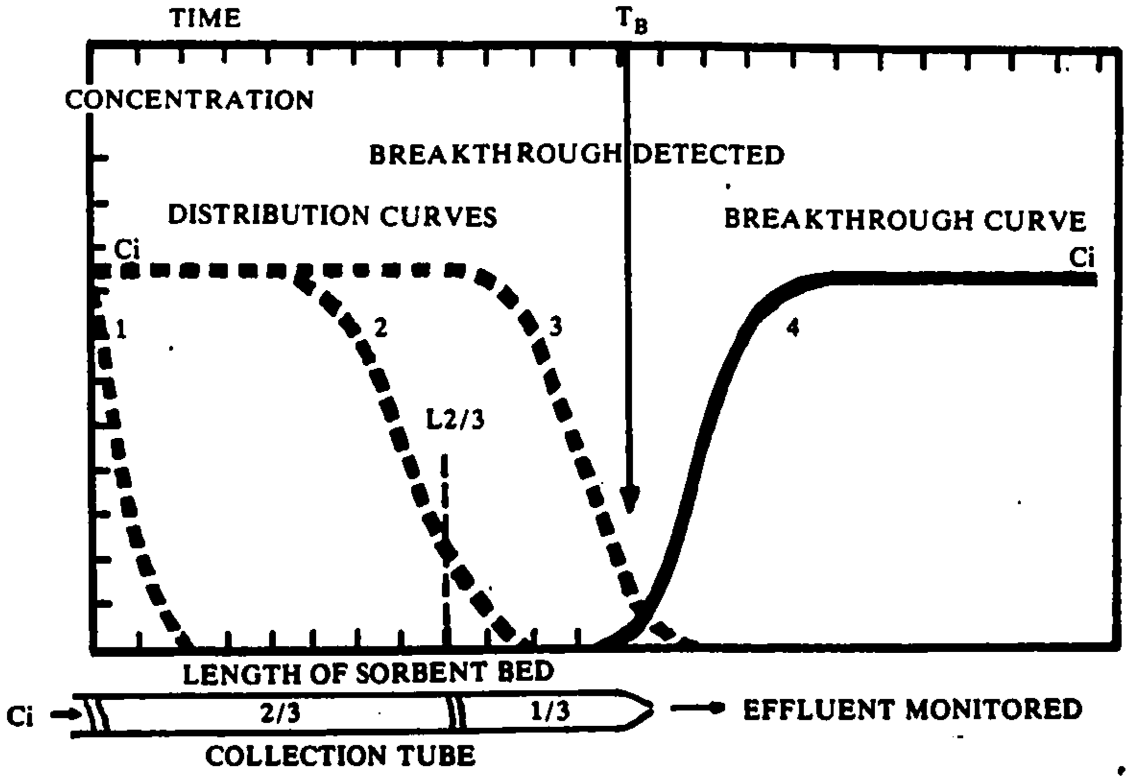

Fig.1 Diagram of a theoretical breakthrough test of a chemical in an adsorbent tube, showing three distribution curves (#s 1, 2, 3) for different lengths of adsorbent bed, together with breakthrough point and time (T_B) and the breakthrough curve (#4). (Melcher et. al, 1978)

Muller, 1984).

ADSORBENTS AND THEIR PROPERTIES

Solid adsorbents have been used extensively as sample collector for industrial atmosphere and ambient air. An ideal adsorbent should have the following characteristics:

(1) trap and retain very low concentrations of contaminants until the analysis can be made

(2) have a capacity large enough to retain all of the collected contaminants

(3) allow storage for prolonged intervals without causing any chemical changes to the contaminants

(4) efficient desorption of the contaminants.

The use of the adsorbent tube has many advantages. The technique can be applied to a wide range of substances and it is simple and cheap and can be used once and discarded to avoid cross-contamination between samples. The method is powerful for measuring the concentration of trace contaminants.

The solid adsorbents which have been widely used to adsorb organic vapours may be grouped as follows:

1. Silica gel

The suitable grade of silica gel for air sampling has a range of pore diameters from 0.3 to 2 nm and specific surface area from 200 to 100 m^2/g (Crisp, 1980). Silica gel is a very useful adsorbent for polar compounds such as alcohols, phenols, aldehyde, ester and ketone (Guenier et al., 1986).

The polarity of silica gel arises from silanol (i.e. Si-OH) groups which attract polar compounds strongly and polarizable compounds to a lesser degree. The disadvantage of silica gel is that it adsorbs water more strongly than most organic compounds. This not only reduces the effective length of the silica gel tube but also results in the displacement of compounds already adsorbed (Crisp, 1980).

2. Porous polymer

Porous polymers are used as widely as charcoal. Synder (1976) has reviewed the use and efficacy of porous polymers for air sampling applications. A number of problems associated with porous polymers have been summarized as follows (cited by Crisp, 1980):

(i) displacement of less volatile compounds, especially by carbon dioxide;

(ii) irreversible adsorption of some compounds. e.g. amines, glycol;

(iii) oxidative, hydrolytic and polymerizing reactions of the sample;

(iv) chemical changes of the contaminants due to the presence of reactive gases and vapours, e.g. oxides of nitrogen and sulphur, inorganic acids;

(v) artifacts arising from reactions and thermal desorption;

(vi) limited adsorption capacity;

(vii) thermal instability;

(viii) limitations of sampling volume, flow and time.

The variety of these materials presents a large degree of selectivity for particular applications. The porous polymer group comprises Tenax GC, the Porapaks, the Chromosorbs and the XAD resins. The properties of porous polymers including surface areas, pore diameters and monomer compositions are summarized in Table 9.

a. Tenax GC Tenax is a polymer of 2,6 diphenyl-p-phenylene oxide. It has a surface area of 18.6 m^2/g (Table 9). Tenax is preferred by many investigators because of its upper thermal limit of about 350 °C which facilitates thermal desorption (Brown and Purnell, 1979; Arnts, 1985; Wallace et. al., 1989; Michael et. al., 1990). Tenax can be used to collect organic bases (ethylamine and aniline), neutral compounds (butyl acetate and isobutanol) and high boiling point compounds (n-tridecane and 2-methylnaphthalene). Lower boiling point compounds which may also be trapped on Tenax include methanol, acetonitrile, ethylmethylketone, benzene, styrene, etc. There are a number of problems associated with the use of Tenax-GC and Tenax-TA, the latter being a special form of poly 2,6-diphenyl-p-phenylene oxide, prepared from purified precursors to minimize contamination (Hutte et.al.,1984). Neher and Jones (1977) have reported that contact with acid, especially sulfur dioxide and sulfuric acid, can result in cleavage of Tenax-GC to 2,6-diphenylhydroquinone, which is further oxidized in air to 2,6-diphenyl-

Table 9 Properties of Porous Polymers

Sorbent	Surface area (m^2/g)	Pore dia. (nm)	Temp. limit (°C)	Monomer composition
Tenax GC	18.6	720	350	Diphenyl-phenylene oxide
Porapak P	110	15	250	Sty/Dvb
Porapak Q	840	7.5	250	Sty/Dvb
Porapak R	780	7.6	250	Vinylpyrollidone
Porapak S	670	7.6	250	Vinyl pyridine
Porapak N	437	-	190	Vinylpyrollidone
Porapak T	450	9.1	190	Ethylene glycol/ dimethyl acrylate
Chromosorb 101	30-40	300-400	275	Sty/Dvb
Chromosorb 102	300-400	8.5	250	Sty/Dvb
Chromosorb 103	15-25	300-400	275	Cross-linked polystyrene
Chromosorb 104	100-200	60-80	250	Acn/Dvb
Chromosorb 105	600-800	40-60	250	Polyaromatic
Chromosorb 106	-	-	250	Cross-linked polystyrene
Chromosorb 107	-	-	250	Cross-linked acrylic esters
Chromosorb 108	-	-	250	Cross-linked acrylic esters
XAD-1	100	20	200-250	Sty/Dvb
XAD-2	300	9	200-250	Sty/Dvb
XAD-4	849	5	200-250	Sty/Dvb
XAD-7	450	9	200-250	Acrylic esters
XAD-8	212	16	200-250	Acrylic esters
XAD-9	70	37	-	Sulphoxide
XAD-11	69	35	200-250	Amide
XAD-12	20	130	-	Very polar N, O group

Abbreviations: Sty, Styrene; Dvb, Divinylbenzene;
Acn, Acrylonitrile.
Data from Sydor and Pietrzyk (1978).

benzoquinone. Gordon (1988) reported that Tenax itself reacted with strong oxidizing agent such as Cl_2/O_3, NO_x, SO_2/SO_3 to yield benzaldehyde, acetophenone and phenol. Degradation products of Tenax-GC that have been identified include acetophenone, benzaldehyde, benzoic acid, ethylene oxide, α-hydroxyacetophenone, and phenol (Pellizzari, 1984; Gordon, 1988). This led to the conclusion that the analysis for air-borne contaminants with this adsorbent requires taking certain precautions to avoid degradation of the adsorbent.

b. The Porapaks. The Porapaks comprise a group of porous polymers with a wide range of polarity. The least polar member, Porapak P, has chromatographic properties which facilitate the separation of compounds such as ketones, aldehydes, alcohols and glycols. The most polar member, Porapak T, is sufficiently polar for fractionating water from formaldehyde. The Porapaks offer a range of adsorbents, but the most polar members have disadvantages arising from strong water retention and greater energy required to remove chemicals for analysis (Crisp, 1980).

c. The Chromosorbs. Similar comments apply to this group of porous polymers as with the Porapaks. Chromosorb 101 is the least polar member and Chromosorb 104, the most polar, which is noted for its water retaining properties. Chromosorb 102 is particularly useful as an adsorbent for air contaminants because of its large specific surface area (Crisp, 1980).

d. The XAD resins These porous polymers include a number of different polymeric forms (Table 9). It should be noted that XAD-2 is the same composition as Chromosorb 102. Most applications of these materials as adsorbents have involved XAD-2. Sydor and Pietrzyk (1978) compared the XAD resins and other adsorbents such as Tenax GC, Porapak P and Q for sampling a wide range of organic solvents. They found that XAD resin performed better than other sorbents owing to the greater surface area and smaller pore size. XAD-7,8,9 and 12 were more suitable for polar compounds and XAD-1,2 and 4 for non polar compounds. The capacity of various adsorbents was found to follow the following sequence; XAD-4 > XAD-7 > Porapak Q > XAD-2 >> Porapak P > XAD-1 ≈ TENAX-GC.

3. Activated carbon and charcoal

Charcoal can be obtained from a variety of materials including coconut shells, coal, wood and petroleum. Each form has its own characteristic properties and uses. For air sampling, the main types of charcoal used are derived from either coconut shells or petroleum. The pore structure of charcoal is generated by the exposure of charcoal to steam or compressed air under high temperature and pressure. The micro-structure of charcoal is very important because it differentiates the properties of charcoal. The International Union of Pure and Applied Chemistry (IUPAC) definition of pore sizes is as follows: macropores, r> 25 nm; mesopores, 25 nm>r>1 nm; micropores 1 nm>r>0.4 nm; sub-micropore 0.4 nm>r (r is the pore radius) (Crisp, 1980).

Coconut charcoal is the adsorbent recommended by the NIOSH because it has a dense porous structure which produces a high adsorption capacity. An alternative to coconut charcoal is the Pittsburgh activated carbon (PAC). The PAC has specific surface area of 1000 m^2/g and 70-75% of surface comprises pores of diameter less than 2 nm. Yasuda and Loughran (1977) claimed that PAC is cheaper and has less batch variation than coconut charcoal. Saalwaechter (1977) made a study of several types of coconut and petroleum charcoals and found no significant differences in performance between the two types. Commercial activated carbons typically have total surface areas in the range from 450-1500 m^2/g as measured by the nitrogen adsorption method.

Another form of carbon, used especially for large volume samples of ambient air, is **graphitized carbon black**. There are several materials available such as Carbotrap and the Carbopacks. Their surface areas ranged from 7 to 90 m^2/g. Their surfaces are non-polar and non-selective. They contain no sites of irreversible adsorption and do not retain low molecular weight compounds such as water, carbon dioxide, carbon monoxide and methane. Adsorption of water is observed only when condensation occurs at 90% relative humidity. Furthermore, they can be desorbed thermally at 400 °C and are stable up to 3100 °C (cited by Crisp, 1980). With Carbotrap, after 30 repetitive uses of the trap, no changes in its adsorbent properties have been observed (Fabbri et. al., 1987).

Carbon molecular sieves are formed by the thermal degradation of organic polymers. The surface area of carbon molecular sieve (carbosieves) varies from 400 to more than 1000 m^2/g. The surface properties, sieve particle size and shape and sieve pore structure are a function of starting materials and manufacturing process. These adsorbents have been evaluated for the collection of volatile airborne contaminants (Betz et. al., 1989). Examples of carbosieves are Ambersorb^R XE-340, Ambersorb^R XE-347, Carboxen^{TM} 563, Carbosieve^{TM} S-III, etc.

Charcoal Cloth and Its Applications

Activated charcoal cloth (ACC) was developed during the late 1960's at the Chemical Defence Establishment (CDE) of the British Government, Porton Down, England, as a highly efficient adsorbent material for chemical defence application, particularly as filter material in facial masks and clothing to protect against highly toxic chemical warfare agents. The synthesis of charcoal cloth, described in a British patent, consisted of passing an undyed, non-finished viscose rayon cloth (having 13 threads per centimeter) into a bath containing 6% zinc chloride, 4% calcium chloride and 2% ammonium chloride. The dried impregnated cloth was carbonized at 830 °C in an atmosphere of nitrogen and then carbon dioxide (cited by Farant and Pant, 1985). The activation rate used had an effect on pore development of the final product. This yielded a tough, porous, flexible material composed of 100% fibrous charcoal. Each thread is made up of many filaments of small diameter (d = 16 um). The properties of activated charcoal cloth (ACC) are shown in Table 10. Canisters using ACC filter provide relatively low breathing resistance and light weight. The development of protective clothing from ACC increased the level of protection.

In medicine, ACC could be used as a special filter layer in surgical masks to protect nursing and theatre staff against anesthetic gases. A prototype filter, 10 cm diameter, 10 cm long, was constructed and filled with charcoal cloth. Hospital trials of this filter showed that it was effective in practice as a Halothane™ adsorber (Maggs and Smith, 1976).

In addition, ACC has special properties to adsorb bacteria. The test bacteria were Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, Proteus vulgaris, Staphylococus aureus and Staphylococcus epidermis. The result showed that the number of bacteria reduced (a 3 to 5 log reduction) when treated with ACC, compared with uncarbonized cloth (less than 1 log reduction). George and Davies (1988a) studied the adsorption of Escherichia coli (E. coli) and Saccharomyces cerevisiae to ACC. Two characteristic adsorption trends have been found depending on the system used to investigate adsorption. With universal tubes and E.

Table 10 Physical Properties of Charcoal cloth.

Physical properties	Value
Weight	120 gm m^2
Pore diameter	0.4-2 nm
Breaking strength	2.5-3.5 kg/cm width
Tensile strength	6.3-8.8x10^5 gm m^2
Nitrogen surface area	>1300 m^2 gm^{-1}
Thickness	0.4-0.5 mm
Electrical resistance	0.4-1.2 ohm cm^{-3}
Air flow resistance	0.1 mm per cm^{-1} per layer of cloth

Data from Maggs et al., 1977

coli, Langmuir-type adsorption was produced. The Langmuir model is predicated on the assumptions that adsorption energy is constant and independent of surface coverage; that adsorption occurs on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate (Weber, 1985). The observed capacity of about $4x10^{10}$ bacteria/g ACC was quite consistent with monolayer formation. However, in stirred vessels containing activated charcoal cloth and microorganisms, multilayer isotherms were obtained (George and Davies, 1988b). The differences may be due to hydrodynamic variability in the systems. The investigator suggested that the adsorption between ACC and bacterial cells involved hydrophobic interaction and electrostatic forces. Experimental observations indicated that polyvalent cations (Al^{+3} , Zn^{+2}) present as impurities in the cloth, may have been involved in ionic bridging of the cells to the ACC surface. The adsorption isotherm obtained suggested that ACC was a suitable material for bacterial removal in medical applications. Johnson & Johnson Ltd. have made ACTISORB™, a flexible fabric wound dressing, from ACC. It was extensively used for granulating wounds such as venous ulcers. Ninety-seven patients who were treated with ACTISORB™ demonstrated significant improvements in the condition of their ulcers: increased epithelialization and reduced levels of exudate, odour and oedema (Mulligan et al., 1986).

The physical adsorption of organic and inorganic vapours by activated charcoal generally decreases with decreasing boiling point. If ACC is to be used for air filtration purposes, it is usually necessary to incorporate additives to enhance its retentivity for low boiling point atmospheric pollutants by chemisorption. Capon et. al. (1981) impregnated copper and sodium dichromate (oxidizing agent) to ACC. They found that the adsorptivity of charcoal cloth for nitrogen dioxide, hydrogen sulfide, sulfur dioxide and hydrogen cyanide increased and the results were additive. Brown et al. (1987) impregnated ACC with copper and found that the impregnated ACC had excellent hydrogen cyanide (HCN) adsorption properties but an amount of $(CN)_2$ was produced. The $(CN)_2$ could be removed by further impregnation of the ACC with alkaline dichromate which would also enhance the effectiveness of HCN chemisorption. For cyanyl chloride (CNCl), impregnation with copper, sodium dichromate and 3% of triethylenediamine, increased the cyanyl chloride uptake/ area of cloth 25 fold from that of non-impregnated ACC (Capon et.al., 1981). The adsorption characteristics of triethyl phosphate (TEP), dimethyl phosphate (DMP) and orthophosphate (OP) from aqueous solution on to ACC was studied. The isotherms obtained were of a Langmuir type and, at neutral pH and 293 °K, the equilibrium adsorption capacities were 2,430, 107 and 44.6 umole/g for TEP, DMP and OP respectively (Jayson et al., 1981).

Several investigators have used ACC as a medium to develop air sampling devices. Bailey and Hollingdale-Smith (1977) developed the Porton diffusion sampler (PDS) consisting of a holder containing a single disc of ACC (30 mm diameter and 130 mg) and a similar disc of membrane material. The basis of the sampling method was the transfer of a gas or vapour across a diffusion barrier onto the charcoal cloth medium. The PDS could adsorb carbon tetrachloride, Freon-12 and styrene with the sensitivity of 1, 10 and 100 $ppm.min^{-1}$ respectively. The authors also claimed good results for toluene, trichloroethylene, methylethylketone, dichloromethane, halothane and tri-n-butyl phosphate. Evan et al.(1977) compared the PDS with conventional personal samplers in a survey where workers were exposed to methylethylketone and styrene. The conventional active sampler used was a standard 37 mm open sampling head containing a disc of the same charcoal cloth. The PDS produced similar results to conventional samplers. The authors also stated that the PDS approached the ideal sampling device in terms of size, simplicity, cost and ease of wearing. Purnell et al. (1981) compared the PDS with conventional nutshell charcoal tubes by sampling 8 organic solvents, styrene, halothane, acrylonitrile, benzene, carbon tetrachloride, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene. The "safe sampling volume" of PDS was investigated under given vapour concentrations and ambient humidity. The rate of diffusional uptake was also evaluated and compared with theoretical calculations. The diffusional uptake of the sampler was affected only by ambient air velocities below about 0.1 ms^{-1} and by the capacity of the charcoal cloth medium. Field trials confirmed that , under appropriate conditions, the PDS gave valid results (Purnell et. al., 1981). Charcoal cloth was also used as an adsorbing medium in the TK-200 passive dosimeter developed by Italian researchers. The performance of the TK-200 passive dosimeters and the activated charcoal tubes was compared in the sampling of nine solvents (styrene, toluene, n-hexane, 2-methylpentane, 3-methylpentane, methylcyclopentane, cyclohexane, acetone and ethylacetate) (Bartolucci et al., 1986). Significant correlations were found between the data obtained with the two sampling systems (Bartolucci et al., 1986).

Cohen and Popendorf (1989) developed a charcoal cloth dosimeter for direct monitoring of the dermal exposure to chemicals. Depending on the exposure characteristics, the dosimeter could be used for quantitative evaluation of volatile liquid deposits, qualitative indicators of chemical contact with the skin, or as a means for in situ testing of the effectiveness of protective clothing. The dosimeter could retain over 60% of the volatile deposits such as toluene or dichloropropene droplets over an 8-hr workday. The study showed that evaporation from liquid deposited was inversely proportional to the log of the deposited size (volume), vapour pressure and the air humidity (Cohen and Popendorf, 1989). Vapour adsorption was proportional to the vapour concentration, exposure duration and the log of air velocity.

Glaser and Arnold (1989) evaluated charcoal cloth as a sorbent for sampling solvents present in expired breath. A stainless steel device for integrated sampling of solvents from expired breath under simulated physiological conditions was established. The results indicated that a 3-wafer or a 10-wafer charcoal cloth could be used to sample m-xylene or 1,1,1-trichloroethane, respectively, in 10 to 50 L of exhaled breath. The concentrations sampled ranged from 2.2 to 190 mg/m^3 for 1,1,1-trichloroethane and from 0.44 to 35.6 mg/m^3 for m-xylene. At least, 80% recovery was obtained for m-xylene or 1,1,1-trichlorothane samples stored from 1 to 14 days. The recovery of other solvents such as hexane, 1-hexene, ethyl acetate, methylene chloride and methyl isobutyl ketone from the charcoal cloth was from 78 to 103%.

VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds (VOCs) are composed of a large group of low boiling point organic substances that vaporize into the atmosphere at room temperature. The commonly detected VOCs can be divided into four categories (Bayer and Black, 1987). The largest class is the <u>aliphatic hydrocarbons</u>, the compounds in this class being derived from petroleum distillate-type solvents. It includes the straightchain hydrocarbons and cyclohexane derivatives. The second class is aromatic hydrocarbons, including benzene, toluene, xylene , other alkylated benzenes and methylated napthalenes. Chlorinated hydrocarbons make up the third class, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene being the most common in this group. The other compounds can be consolidated into a miscellaneous class, the majority of which are ketones, aldehydes and alcohols (modified from Bayer and Black, 1987). The physical properties of some VOCs are shown in Table 11.

The vapour pressure, p, of a solvent is the pressure exerted by the vapour when in equilibrium with a liquid or a solid phase (Popendorf, 1984). Of four aliphatic hydrocarbons in Table 11, pentane is the smallest chemical having only 5 carbon atoms in the molecule while decane is the largest. Pentane has the lowest boiling point and highest vapour pressure among the four aliphatic hydrocarbons. The smaller the molecule, the lower the boiling point and the higher is the vapour pressure. In this study, VOCs are defined as organic substances with a vapour pressure greater than or equal to 0.02 psi (pound per square inch) (Harkov et. al., 1987).

Many of the modern industrial and commercial processes involve the use of organic solvents. Through the transport, storage, transfer and use of these solvents, releases into the atmosphere can occur. The use of liquid fuels by motor

Table 11 The Physical Properties of some Volatile Organic Compounds.

VOC	Molecular formular	Molecular weight	Boiling point (°C)	Vapour pressure[+++] (torr)	Density at 25 °C (g/cm^3)
Pentane	C_5H_{12}	72.15	36.07	512.5	0.6214
Hexane	C_6H_{14}	86.18	68.74	151.3	0.6548
Octane	C_8H_{18}	114.23	125.67	14.0	0.6985
Decane	$C_{10}H_{22}$	142.29	174.12	1.3	0.7263
Benzene	C_6H_6	78.12	80.10	95.2	0.8737
Toluene	C_7H_8	92.14	110.63	28.5	0.8623
o-Xylene	C_8H_{10}	106.17	144.41	6.6	0.8760
Cl[*]	C_6H_5Cl	112.56	131.69	11.8	1.1063[+]
T3[**]	C_2HCl_3	131.39	87.19	47.3	1.4514[++]
T4[***]	C_2Cl_4	165.83	121.20	18.5	1.6064[++]

[*] Cl = Chlorobenzene
[**] T3 = Trichloroethylene
[***] T4 = Tetrachloroethylene
[+] Density at 20 °C
[++] Density at 30 °C
[+++] Vapour pressure at 25 °C

vehicles can also result in evaporation and losses of organic solvents and combustion products to the environment. The quantity of the organic substances emitted into the atmosphere as solvent or through the use of liquid fuels was classified as VOCs (Harkov et al.,1987). Sources of VOCs are also found in homes and office buildings as products of emissions from building materials (floor coverings, furnishings, paint), consumer products (polishes, cleansers, solvents), combustion (from cigarettes, kerosene heater, wood stove) and other miscellaneous categories (cooking, ambient air contaminants) (Table 1) (Amman et al., 1986).

Shah and Singh (1988) reported the distributions of the median concentrations of the 261 VOCs in outdoor and 66 VOCs in indoor air. The VOCs level for both outdoor and indoor air was very low; nearly 50% of the chemicals presented were in the range of 0.01-1.0 ppbv. The median VOC concentration exceeded 1 ppbv in 10% of the cases for outdoor air and 25% of the cases for indoor air. Several studies have shown that indoor VOCs are frequently higher than outdoor concentrations (Cohen et al., 1989; Mongomery and Kalman, 1989).

Up to 300 VOCs have been detected in homes during the TEAM (Total Exposure Assessment Methodology) study conducted by the U.S.Environmental Protection Agency (EPA) (Amman et al., 1986). VOCs are dissolved readily in lipids; therefore, they are transported across cell membranes and are adsorbed by the lung, skin, and gastrointestinal tract. Many VOCs are irritants, and/or are neurotoxic agents, and/or can act as carcinogens, co-carcinogens, or promoters (Amman et al., 1986). Total concentrations of VOCs in new homes have been reported to be as high as to 19 mg/m^3 (Amman et. al., 1986). These concentrations may be of concern to human health with respect to acute and chronic health effects. Selected VOCs and health effects have been summarized in Table 12 (Turiel, 1985). Presently, indoor air standards for VOCs do not exist for public and private buildings because of inadequate knowledge of low level, dose-effect relationships and the health effects of certain chemicals. Threshold limit values (TLVs) or regulatory permissible exposure level (PELs) have been developed only for industrial environments. However, health complaints have been documented at concentrations far below these limits (Mongomery and Kalman, 1989).

Molhave et al.(1984) has explored health effects for indoor exposure in a controlled chamber. When subjects having experience of sick building syndrome were exposed to a mixture containing 22 organic gases and solvent vapours (Table 13), they experienced the same symptoms as were associated with the sick building syndrome. Molhave observed a clear health effect for concentrations of the VOC mixture in the range of 5 mg/m^3 to 25 mg/m^3. He hypothesized that some of the sick building syndrome symptoms could be explained by a total mixture, rather than exposure to an individual compound.

Table 12 Selected Organic Compounds and Their Health Effects.

Compound	Health effects	Sources and uses
Formaldehyde and other aldehyde	Eye and respiratory irritation; possibly more-serious long-term health effects	Outgassing from building materials(particle board, plywood, and urea-formaldehyde insulation foam); also from cooking and smoking
Benzene	Respiratory irritation; recognized carcinogen	Plastic and rubber solvents; from cigarette smoking; in paints and varnishes,including putty, filler, stains, and finishes
Xylene	Narcotic;irritating; in high concentrations, possibly injurious to heart, liver, nervous system	Solvent or resins,enamels, etc.; in non lead automobile fuels and in manufacture of pesticides, dyes, pharmaceuticals
Toluene	Narcotic; may cause anemia	Solvents; by-product of organic compounds used in household products
Styrene	Narcotic; can cause headache, fatigue, stupor, depression, and incoordination	Widespread in manufacture of plastics, synthetic rubber and resins
Trichloroethylene	Subject of OSHA carcinogenesis inquiry	Aerosol propellant, pesticide, cleaning solvents
Tetrachloroethylene	Animal carcinogen; subject of OSHA carcinogenesis inquiry	Oil and wax solvents, cleaning compounds, vapour degreasing products dry cleaning operations; also as an anesthetic
Ethyl benzene	Severe irritation to eyes and respiratory system	Solvents; in styrene-related products
Chlorobenzene	Strong narcotics; possible lung,liver, and kidney damage	In production of paint, varnish, pesticides and various organic solvents
Polychlorinated biphenyls (PCB's)	Suspected carcinogens	In various electrical components; in waste oil suppliers and in plastic and paper products

Data from Turiel, 1985

Table 13 List of 22 organic gases and solvent vapours

n-Hexane
1-Octene
3-Xylene
n-Propylbenzene
n-Hexanal
2-Butanol
n-Butylacetate
n-Decane
n-Nonane
1-Decene
Ethylbenzene
α-Pinene
Isopropanol
3-Methyl-3-Butanone
Ethoxyethylacetate
n-Undecane
Cyclohexane
1,2,4-Trimethylbenzene
n-Pentanal
n-Butanol
4-methyl-2-Pentanone
1,2-Dichloroethane

Data from Molhave et. al., 1984

Molhave et al. (1991) studied human subjective reactions to a mixture of those 22 VOCs in a controlled chamber. The perceived odour intensity of 25 subjects were found at 3 mg/m^3. Irritation of eye and nose showed significant effect at 8 mg/m^3 and significant reduced well being was reported at 25 mg/m^3. Kjergaard et al.(1991) compared human reactions to a mixture of those 22 VOCs using 21 healthy subjects and 14 subjects suffering from the sick building syndrome in a double blind study. Both groups reacted to the air, reporting worse odour, worse indoor air quality (25 mg/m^3) and more irritated mucous membranes in eye, nose and throat than in the clean environment (5 mg/m^3).

Amman et. al.(1986) have suggested that pollutants of immediate concern for indoor environments be evaluated in terms of the following characteristics: known or suspected carcinogens to either humans or animals; present in residences or expected to be present from knowledge of emission sources, such as tobacco smoking and solvents; and identifiable and quantifiable using reliable techniques. The chemicals that have these characteristics are shown in Table 14.

Personal activities have influence on exposure to VOCs. Major exposures were associated with the use of deodorizers (p-dichlorobenzene); washing cloths and dishes (chloroform); visiting dry cleaners (1,1,1-trichloroethane, tetrachloroethylene); smoking (benzene, styrene); cleaning a car engine (xylenes, ethylbenzene, tetrachloroethylene);

Table 14 List of Pollutants of Immediate Concern for Indoor Environments

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Vinyl chloride
Chloroform
Benzene
o-Xylene
m,p-Xylene
m,p-Dichlorobenzene
Ethylbenzene
Styrene
Decane
Chlorobenzene
Ethylphenol
Acrolein
Toluene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2-trichloethanedecane
1,2-dichloroethane
Hexachloroethane
Methylene chloride
Carbon tetrachloride
1,1,1-Trichloroethane
Trichloroethylene
Tetrachloroethylene
Vinylidene chloride

Data from Amman et. al., 1986

painting and using paint remover (n-decane, n-undecane); and working in a scientific laboratory (many VOCs) (Wallace et al.,1989). Common materials found in nearly every home and place of business could also cause elevated exposure to VOCs (Wallace et al., 1987)

OBJECTIVES

The main objective of this study is the development and evaluation of a simple and effective sampling device using charcoal cloth as an adsorbing medium for the monitoring of volatile organic compounds (VOCs) in indoor air. A tube or cassette container for the charcoal cloth will be constructed for use with different amounts of the adsorbing medium and to interface with commercially available sampling pumps. The efficacy of charcoal cloth will be assessed by determining:

(1) the adsorption capacity for a number of VOCs;

(2) the desorption efficiency using extraction by solvent(s), supercritical fluids and thermal desorption;

(3) the stability of the medium when reactivated by heat to permit repeated use; and

(4) the reliability (reproducibility, accuracy) of the sampling device operated under both laboratory and field conditions.

MATERIALS AND METHODS

The research experiment was divided into six sections as follows:

1. APPARATUS FOR SAMPLING

Two types of sampling devices were constructed and studied, one being a 5 mm diameter (i.d.) stainless steel tube and the other a 25 mm diameter (i.d.) stainless steel cassette. The tube was 9 cm long containing packed discs (5 mm diameter) of charcoal cloth or rolled tightly charcoal cloth. The charcoal cassette was designed to hold one or more layers of charcoal cloth of 2.5 cm diameter (Fig.2). In the cassette, two fine stainless steel screens were used; one was placed approximately one inch above the charcoal cloth to distribute the inlet air in the cassette and the other was placed at the bottom of the cassette to support the cloth. Three Teflon washers were used to hold the cloth in position in the cassette; one being beneath the charcoal cloth and the other two washers above the charcoal cloth. The average surface area of the charcoal cloth in the cassette exposed to influent air was 3.80 cm^2.

Initial experiments with the charcoal cassette showed the difficulty in placing the charcoal cloth in position in the cassette. This required a re-designing of the cassette to improve the positioning of the cloth in the holder (Fig.3). The two layers of cloth were placed between two stainless steel washers. The washers were held in place in the cassette

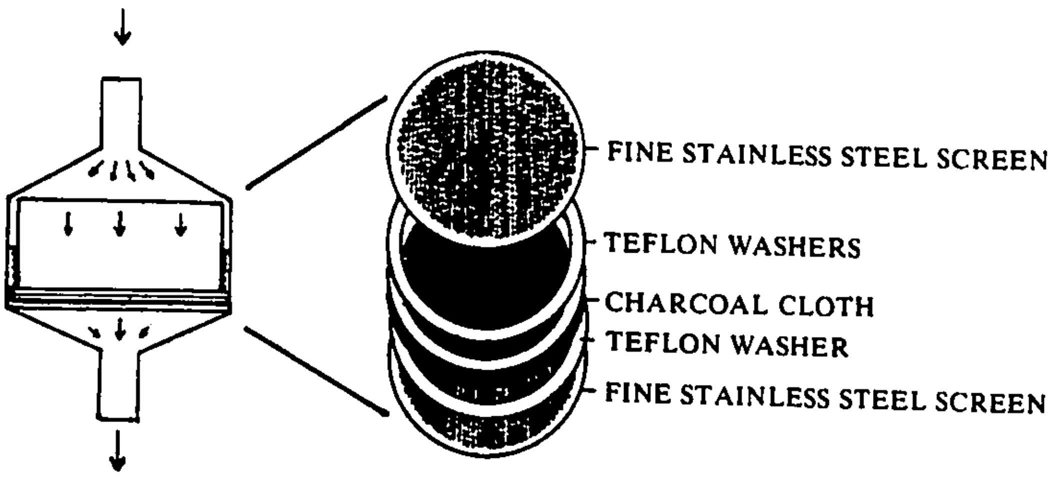


Fig.2 Diagram of the first design of a stainless steel cassette, showing exploded view of the placement of screens, charcoal cloth and retaining washers.

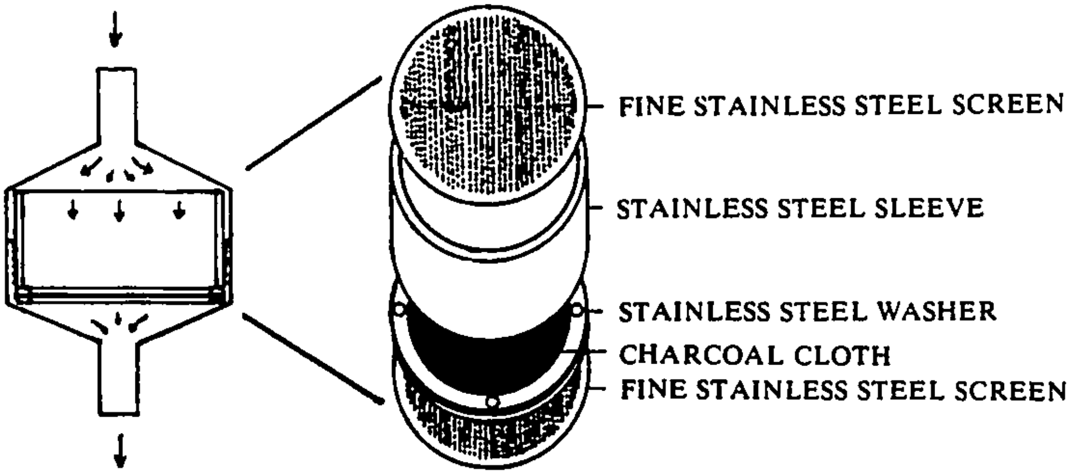


Fig.3 Diagram of re-designed stainless steel cassette, showing exploded view of the placement of screens, sleeve, washers and charcoal cloth.

by a circular stainless steel sleeve. This new cassette could be heated to high temperatures because the Teflon washers were eliminated. The surface area of the 2-layer charcoal cloth exposed to influent air was reduced from 3.80 cm^2 (91.0 mg of charcoal cloth layers) to 2.84 cm^2 (67.8 mg of charcoal cloth layers) because of the greater width of the stainless steel washers.

2. CHARCOAL CLOTH

A charcoal cloth, namely CDE Charcoal Cloth, manufactured by the Charcoal Cloth Limited, Maidenshead, Berkshire, England, was selected to use as an adsorbent for this study. The physical properties of this charcoal cloth are summarized in Table 10 (Maggs et. al., 1977).

2.1 Preparation of Charcoal Cloth

Two types of packings of charcoal cloth were used in the stainless steel tube: a tightly rolled cloth and packed flat layers of cloth discs (0.5 mm diameter). The weights of charcoal cloth tested in the tube were 50, 100 and 150 mg. For use in the cassette, charcoal cloth was cut into 2.5 cm diameter discs (4.91 cm^2). The average weight for 1, 2 and 3 layers of charcoal cloth discs in the initial cassette was 45.5, 91.0 and 136.5 mg respectively. For the redesigned cassette, two layers of charcoal cloth (67.8 mg) were placed between two stainless steel washers (Fig.3). The charcoal cloth packed tubes and cassettes were activated by purging with nitrogen gas for 4 hrs at a temperature of 300 °C. The purpose of the activation process was to remove any residual VOCs and water from the cloth.

2.2 Comparison of Charcoal Cloth with Nutshell Charcoal

The nutshell charcoal tubes used were SKC (SKC INC., 334 Valley View Road, Eighty Four, Pensylvania 15330, U.S.A.) type 226-01 from Lot 120. There were two sections of activated nutshell charcoal, a front section containing 100 mg of nutshell charcoal and a back 50 mg section to indicate breakthrough. The weight of nutshell charcoal used for comparison with charcoal cloth were 50, 100 and 150 mg. The 50 mg and 100 mg of nutshell charcoal was obtained by separating the front section from the back section of standard nutshell charcoal tubes. The 150 mg of nutshell charcoal was used as such.

3. VOC GENERATION

VOCs were generated with a Vici Metronics (2991 Corvin Drive, Santa Clara, CA 95051, U.S.A.) model 340 Dynacalibrator in an air-tight glass sampling chamber controlled at a temperature of 20-23 °C and at selected relative humidities using a Haake (HAAKE Mess-Technik GmbH u. Co., DieselstraBe 4, D-7500 Karlsruhe 41, Federal Republic of Germany) model D8-GH heating, refrigerating bath and circulator and a Solomat (65

Rowayton Avenue, Rowayton, CT 06853, U.S.A.) MPM 2000 humidity and temperature probe respectively. The diagram of the apparatus used for VOC generation is shown in Fig.4.

4. GLC ANALYSIS OF VOCs

Analysis of volatile organic compounds (VOCs) was performed using a Varian (Varian Associates, Inc., 611 Hansen Way, Palo Alto, California 94303, U.S.A.) model 3700 gas chromatograph (GC) equipped with an HNU (HNU Systems Canada Ltd, 2 Robert Speck Parkway, Mississauga, Ontario, L2H 1H8, Canada) photoionization detector (PID) and a 10.2 eV lamp and a Asea Brown Boveri model SE 120 recorder (ABB GOERZ Aktiengesellschaft, Sonnleithnergasse 5, Postfach 204, A-1101 Vienna, Austria). A VOCOL wide-bore fused silica capillary column (30 m x 0.53 mm id, 3.0 um film thickness) obtained from Supelco Canada Ltd.(46-220 Wyecroft road, Oakville, Ontario, L6K 3V1, Canada) was used to separate the VOC mixture. The optimal operating conditions for the GC, chosen for the best separation of the tested VOCs were: nitrogen carrier gas flow of 10 ml/min, injector,oven and detector temperatures of 190°C, 70°C and 200°C, respectively. Solvents used for the analysis by GLC such as hexane, pentane, cyclohexane and decane were distilled in glass provided by Caledon Laboratories Ltd. (40 Armstrong Avenue, Georgetown, Ontario, L7G 4R9, Canada).

Six VOCs (benzene, toluene, tetrachloroethylene,

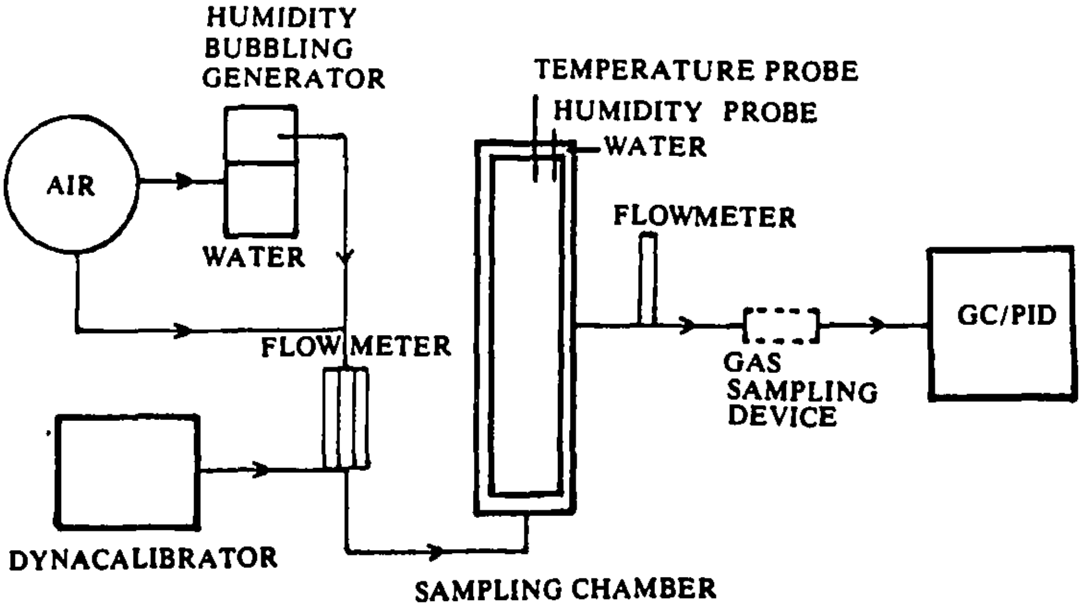


Fig.4 A schematic diagram of the instrumentation required for VOC generation, capture and analysis. The solvent mixture was placed in a diffusion tube in the chamber of the Dynacalibrator which was heated to 30 °C. Dilution of the solvent concentration(s) was controlled by the flow rate determined by the Dynacalibrator pump.

chlorobenzene, trichloroethylene and o-xylene) were selected for study. All of these have extensive industrial use. They are commonly found in indoor air in buildings and they have been shown to elicit adverse health effects. These VOCs were analyzed by GLC, optimizing the method and obtaining standard curves for a mixture of these chemicals. The standard curves were prepared by adding 50 ul of 200 ppmv 1-chloro-2-fluorobenzene (internal standard) in hexane into 350 ul of various concentrations of the mixture of VOCs (200 ppmv of each six VOCs stock solution in hexane), ranging from 2.2 to 18.31 ng/ul. One ul of the solution was injected into the GLC. See chromatogram in Fig.12. The calculated peak height ratio (peak height of VOCs/ peak height of internal standard) was plotted against VOC concentrations of at least three replicate determinations.

5. EXPERIMENTAL DETAILS

5.1 Adsorption Capacity

The adsorption capacity was investigated by measuring the time(s) taken for different concentrations of the VOC to break through the adsorbent material, the presence of the VOC being measured in the effluent air under controlled flow rates and relative humidities. A representative experiment is shown in Fig.5. When the tube or the cassette containing charcoal cloth was placed in line between the sampling chamber and the GLC at time 0, the known concentration of VOC (C 100%) in the

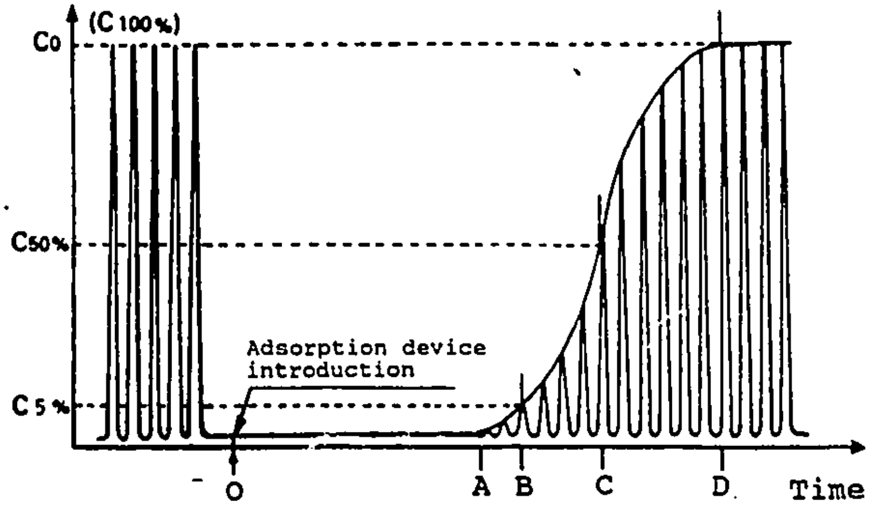


Fig.5 Diagram of a theoretical breakthrough test showing a chromatogram of a chemical, adsorbent device introduction, breakthrough time and breakthrough curve. At A, the chemical is beginning to elute from the adsorbent while B represents 5.0% breakthrough. Modified from Guenier and Muller (1984).

influent air stream would be adsorbed onto the charcoal cloth. In the time interval of 0 to "A", all of the VOC in the flow air stream would be adsorbed by the charcoal cloth. The point at which the charcoal would be saturated with VOC, point "B", was considered to be the breakthrough point, e.g. when 5.0% of the VOC concentration was measured in the effluent air from the tube or the cassette outlet. The time taken from 0 to the breakthrough point B was called the **breakthrough time**. The **breakthrough volume** was the product of the breakthrough time and flow rate. The **breakthrough capacity** (weight of trapped VOC) was the result of the breakthrough volume and VOC concentration. The **adsorption capacity** was the ratio of weight of trapped VOC and the weight of charcoal cloth used in that experiment (examples of calculation are shown in Appendix I).

To select the optimal type of charcoal cloth holder (a cassette or a tube) and the weight of charcoal cloth required for air sampling, breakthrough tests of different weights of charcoal cloth were performed according to the diagram in Fig. 4 using a single VOC, toluene. A small diffusion tube with approximately 300 ul of toluene was put into the chamber of a Dynacalibrator at a controlled temperature of 30 °C. Toluene vapour generated from the Dynacalibrator was mixed with air from a storage purified air tank and water vapour from the humidity bubbling generator in a sampling chamber. The temperature in the sampling chamber was maintained by the circulating water bath at controlled temperatures from the heating/refrigerating circulator. The temperature and humidity of the sampling chamber were monitored with a temperature and humidity probe. All flow rates to the GLC were controlled with flowmeters. Effluent air from the adsorbent outlet was monitored with an air bubble flowmeter. The toluene concentrations in the sampling chamber were monitored by GLC. A gas sampling valve (VICI Valco Instrument Co. Inc. (Chromatographic Specialties Inc., 300 Laurier Blvd., Brockville, Ontario, K6V 5W1, Canada) was used to introduce 100 ul of toluene vapour into the GC. The drop in air pressure across the devices was also measured during the breakthrough test with a MK4 Bench Mounted Test Set (an instrument designed to indicate differential pressures) from Airflow Developments (Canada) Ltd., (1281 Matheson Blvd., Mississauga, Ontario L4W 1R1, Canada).

The breakthrough experiments of various weights of charcoal cloth in tubes and cassettes were conducted at a flow rate of 200 ml/min with a certain volatilized toluene concentration (210-240 mg/m^3). The breakthrough time, volume and capacity of trapped toluene in the charcoal cloth was investigated using various weights of charcoal (approximately 50, 100 and 150 mg) in two air sampling devices, (a cassette and a tube) and a NIOSH-recommended nutshell charcoal tube was used as a comparison tube. Three replicate determinations were carried out with each device. The charcoal cloth holder selected for subsequent experiments was the device that gave the highest adsorption capacity and lowest pressure drop.

To determine the optimal flow rate for the cassette containing two layers of charcoal cloth, experiments were carried out similarly to the breakthrough test. The toluene concentration used was relatively low, approximately 20 mg/m^3, representing total VOCs found in new homes (Amman et al., 1986). The flow rate was varied from 0.2 to 1.5 L/min. The breakthrough time, volume and adsorption capacity were plotted against the flow rate. Operating conditions were optimized using these parameters with a suitable amount of charcoal cloth, a flow rate being selected for the remainder of the experiments.

The effect of relative humidity on the adsorption capacity of the (redesigned) charcoal cloth was investigated using toluene as a representative solvent. A toluene concentration of 128-150 mg/m^3 was generated and passed in the chamber at 200 ml/min at relative humidities of 0, 45 and 80%. The breakthrough test was carried out for these three levels of relative humidity. The effect at different toluene concentrations (32-36, 130-134 and 963-977 mg/m^3) on the adsorption capacity of the (redesigned) charcoal cassette were also investigated at 0 and 40% of relative humidity.

Since there may be a complex mixture of VOCs in a given environment, the adsorption capacity of charcoal cloth for VOC mixtures will be evaluated. The utility of this adsorption capacity experiment for the medium chosen is limited to the first chemical that breaks through.

From the preceding sets of experiments, the optimal conditions selected for sampling were applied to a study of the breakthrough point of a standard weight of charcoal cloth for a mixture of six VOCs. A mixture of benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene was generated at three different concentrations (Table 15) by varying the volume of the stock solution of VOC mixture (55 ul of benzene, 100 ul of trichloroethylene, 250 ul of toluene, 500 ul of tetrachloroethylene and chlorobenzene and 1000 ul of o-xylene) in a few small diffusion tubes in the chamber of the dynacalibrator at 30°C . The length (duration) of sampling time depended entirely on when the first VOC broke through the adsorbent material. For comparison, the breakthrough test for a NIOSH-recommended tube containing 100 mg of nutshell charcoal was evaluated for the highest levels of the VOC mixture, in the range of 52 to 240 mg/m^3 (Table 16).

5.2 VOC Recovery From Cloth

Three methods of quantitatively removing adsorbed VOCs from charcoal cloth were tested and compared. They were solvent desorption, supercritical fluid extraction (SFE) and thermal desorption.

Table 15 Average VOC Concentrations for the Breakthrough Test of 2-layer Charcoal Cassette

VOCs	Low Conc*. mg/m^3	Medium Conc*. mg/m^3	High Conc*. mg/m^3
Benzene	2.8 ± 0.3	7.4 ± 1.2	38.5 ± 5.5
Trichloroethylene	6.0 ± 0.4	17.7 ± 1.2	97.3 ± 8.0
Toluene	4.8 ± 0.1	14.9 ± 0.3	82.0 ± 2.0
Tetrachloroethylene	13.1 ± 0.3	39.8 ± 0.5	212.0 ± 1.0
Chlorobenzene	5.3 ± 0.3	17.0 ± 0.3	83.0 ± 4.6
o-Xylene	5.1 ± 0.4	15.2 ± 0.5	70.7 ± 5.5

* = $\bar{X}$ ± SD , N = 3

Table 16 Average VOC Concentrations for the Breakthrough Test of 100-mg nutshell Charcoal Tube

VOCs	Concentration, N = 3 $\bar{X}$ ± SD (mg/m^3)
Benzene	52.3 ± 7.5
Trichloroethylene	113.8 ± 9.7
Toluene	96.7 ± 3.1
Tetrachloroethylene	239.7 ± 4.7
Chlorobenzene	112.0 ± 4.3
o-Xylene	102.7 ± 5.3

5.2.1 Solvent Desorption

The **desorption efficiency** for the extraction of the VOCs is defined as the ratio of the quantity of chemical(s) removed from the charcoal cloth to the amount of chemical applied to the cloth. The solvent that gave highest desorption efficiency of VOCs was selected to standardize the method for subsequent experiments where desorption techniques would be compared.

The 2-layer charcoal cloth disc was spiked with 0.2, 2 and 10 mg of individual chemical or 0.02, 0.2 and 2 mg of each chemical in a mixture. n-Hexane, n-pentane and cyclopentane were tested as solvents to extract the adsorbed VOCs from the charcoal cloth. Usually, carbon disulfide is used for extraction of VOCs from the adsorbent but it gave a broad peak with PID detection. Carbon disulfide is an extremely flammable liquid and volatile (difficult to handle). It is also toxic to the nervous system, heart and circulatory system (Canadian Centre for Occupational Health and Safety, 1987). The solvent extraction was performed in a screw-cap tube containing the charcoal cloth and 2 ml of solvent. After mixing throughly for two min, the solvent was separated from the charcoal cloth. A second extraction with the same amount of solvent was used to improve the extraction of the VOCs from the charcoal cloth. Equal aliquots (100 ul) of the first and the second solvent extracts were removed and mixed together with an internal standard, the solvent extracts being analyzed by GLC/PID. Experiments on solvent desorption were divided into: (a) method reliability and (b) storage stability.

A. Method Reliability

A known concentration of VOC mixture was generated in the sampling chamber at 20-23 °C, with a 40% relative humidity. The cassette, containing two layers of charcoal cloth, was used to collect the VOC mixture over a period of 1, 2 and 4 hrs at a flow rate of 200 ml/min. The cloth-adsorbed chemicals were kept in screw-cap tubes and were stored in a refrigerator until extracted by either n-hexane or n-pentane and analyzed by GLC/PID The accuracy and precision of the method was calculated in terms of percent recovery and percent coefficient of variation respectively from five individual experiments. The accuracy and precision were also expressed in terms of the overall system accuracy (O.S.A.) and overall precision ($\overline{CV}_T$) (examples of calculation are shown in Appendix II). If the O.S.A. is less than ±25%, the NIOSH accuracy criterion is satisfied (Kring et.al., 1984).

B. Storage Stability

Crucial to any sampling device is the time-related stability of the adsorbed chemicals. The stability of known concentrations of mixed VOCs adsorbed on charcoal cloth was evaluated, the 2-layer charcoal cloth being treated with 12.5 ul of VOC mixture (150 ug of benzene, 300 ug of trichloroethylene, 250 ug of toluene, 750 ug of tetrachloroethylene, 350 ug of chlorobenzene and 350 ug of o-xylene) placed in screw-cap tubes and extracted by solvents and analyzed by GLC/PID after 1, 2, 4, 8, 16 and 32 days of storage at room and refrigerated (4 °C) temperatures, the VOC recovery being quantitated by GLC-PID analysis.

5.2.2 Supercritical Fluid Extraction

A Dionex (Dionex Canada Ltd., Mississauga, Ontario, Canada) Model 703 supercritical fluid extraction (SFE) instrument was used to desorb VOCs from charcoal cloth. The schematic diagram of supercritical fluid extraction is shown in Fig. 6. The carbon dioxide flows from the storage tank through the pumps, manifold and then to the extraction cells containing the charcoal cloth at controlled temperature, pressure and flow rate. The flow rates of the supercritical fluid depend on the pressure and temperature of the oven and restrictor used. During extraction, the cloth-adsorbed chemicals are removed by the supercritical fluid and transported through restrictors into the collection vials to be trapped in an appropriate solvent at low temperature (5 °C). The carbon dioxide was released through the vent lines. The use of mixture of carbon dioxide with other volatile chemical (methanol) has been described recently in literature for SFE but this technique was not operational in our laboratory.

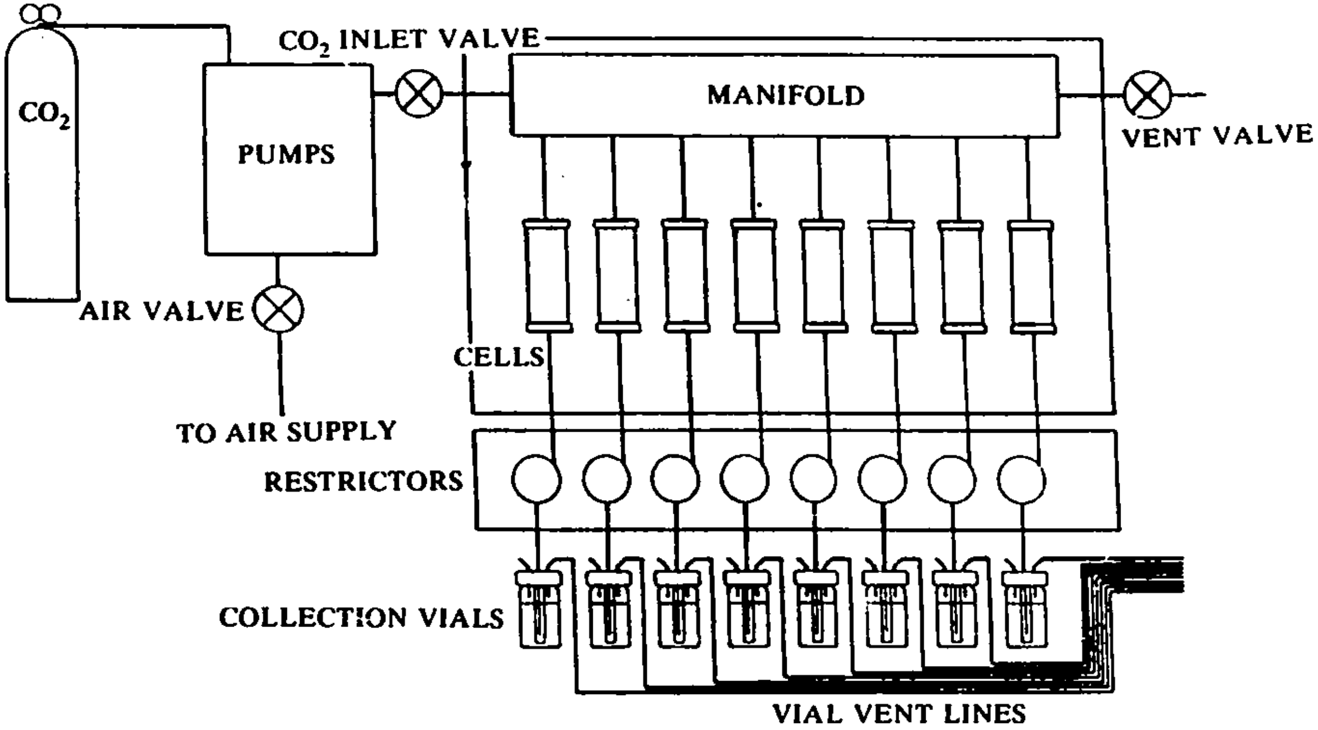


Fig.6 Diagram of a Dionex model 703 supercritical fluid extraction. Modified from the operation manual of Dionex Canada Ltd., Mississauga, Ontario, Canada.

Experiments on SFE were divided into three parts as follows:

A. SFE of VOCs on charcoal cloth

B. Solvent extraction of any residual VOCs from the charcoal cloth

C. Loss of VOCs through the vent lines during SFE

A. SFE of VOCs on Charcoal Cloth

Two discs of charcoal cloth were spiked with 10 ul of the VOC mixture in hexane (120 ug of benzene, 240 ug of trichloroethylene, 200 ug of toluene, 480 ug of tetrachloroethylene, 280 ug of chlorobenzene and 280 ug of o-xylene). The spiked charcoal cloth was inserted into the extraction cells and glass beads were placed on top to fill the space in the cell. The extractions were carried out for 45 min at various temperatures, pressures and flow rates, the optimal conditions being selected from the extraction that gave the highest desorption efficiency. Three different solvents were tested for their efficacy in trapping the VOCs in the collection vials: 10 ml volumes of n-pentane, n-hexane or n-decane being used. After extraction, a known internal standard (1-chloro-2-fluorobenzene) was added to the collection solvents. One microlitre of the collection solvent was injected into the gas chromatograph equipped with PID. The desorption efficiencies of SFE for each chemical in the mixture were reported.

B. Solvent Extraction of any Residual VOCs from the Charcoal Cloth

To determine the efficiency of SFE, the supercritical fluid-extracted charcoal cloth was subsequently removed from the extraction cells, placed in a screw-cap tube with 2 ml of n-hexane and any remaining VOCs were extracted as described above for solvent extraction.

C. Loss of VOCs through the Vent Lines during SFE

There was a possibility of losing the VOCs from the collection vials through the vent lines due to volatilization of the cooled collecting solvent and the trapped VOCs. The loss of VOCs would depend on the volatility of VOCs of interest, the volatility of the collecting solvents and the pressure (flow rate) applied to the cells. The untreated two layers of charcoal cloth were put into the extraction cells as described above. The 10-ul VOC mixture was added to 10 ml of those three solvents in the collecting vials and supercritical fluid extraction was carried out at 100, 200 and 300 ATM for 45 min. The temperature of the extraction cells and the restrictors was set at 150 °C and 150 or 200 °C respectively. After extraction, the internal standard was added to the collection vials and the collecting solvents analyzed by GLC/PID.

5.2.3 Thermal Desorption

There is no commercial instrument available or adaptable to thermally remove adsorbed VOCs from the 2-layer charcoal cloth disc developed for air quality analysis. Most thermal desorbers are designed for desorbing chemicals from adsorbents packed in tubes. The ideal instrument should provide sufficient heat to the cloth, be resistant to high temperature, be leakproof and not outgas or adsorb any chemicals. The instrument can be made of glass or stainless steel. If the instrument is made of glass, the heating tape can be wrapped around the instrument to provide heat to the charcoal cloth inside. If it is made of stainless steel, the heating element should be placed inside the instrument to distribute the heat evenly over the surface of the cloth.

The first design of the instrument was similar to the earlier cassette designed, being composed of a top and a bottom portion of a cassette separated by an asbestos gasket connected together with screws (Fig.7, Model 1). The bottom half contained a small heating element consisting of a mesh support (boron nitride) and nichrome wire. The temperature of the heating element was monitored by a temperature probe externalized to a temperature controller. The top part of the cassette had a port where the cloth was inserted and removed from the instrument. The cloth was placed on the support approximately 6.0 mm above the heating element. The port was opened or closed by a circular gasket and a circular stainless

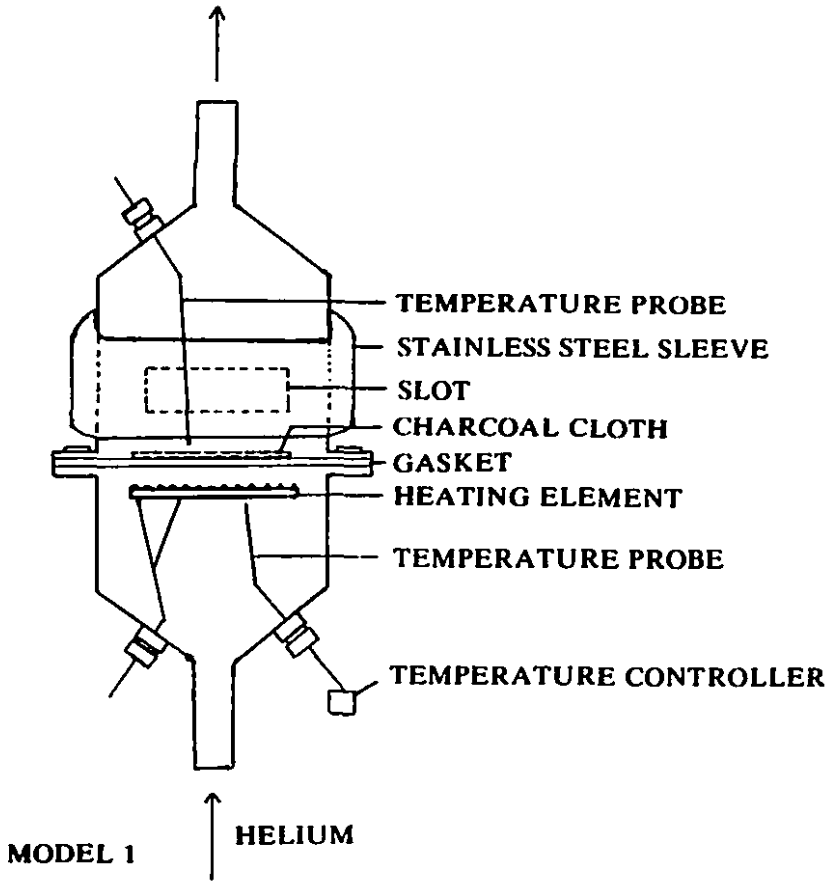


Fig.7 Diagram of stainless steel cassette desorber (model 1), showing the exploded view of the placement of a heating element, temperature probe, temperature controller, gasket and charcoal cloth.

steel sleeve. An asbestos gasket was tried initially since it would serve to seal the opening and insulate the instrument at the same time. The top of the cassette also had a temperature probe to monitor the temperature of the cloth during heating. Preliminary experiments showed that the asbestos gasket outgassed chemicals into the system and could not be sealed tightly enough at high temperature. The asbestos gasket was replaced by a Teflon gasket but the leakage still occurred at the port. To reduce the probability of loss of desorbed VOCs, the port of the instrument was sealed and the upper temperature probe was removed. The top part of the instrument was shortened to reduce the space inside the instrument (Fig.8, Model 2). With this model, leakage still occurred at the gasket seal between the top and the bottom portions of the cassette. Several types of gasket materials have been tried, including asbestos, Viton, silicone and Teflon. All of them changed their properties and offgassed chemicals after heating at 300°C, because the maximum allowable temperature for these materials was less than 300°C. What was required was some sort of material that could be used at high temperature without chemical offgassing.

The third model of the thermal desorber was built and the gasket was placed outside the instrument far from the heating element (Fig.8, Model 3). The screw connecting the top and the bottom of the cassette was changed to threading. Teflon material was used to make a gasket and Teflon tape was used

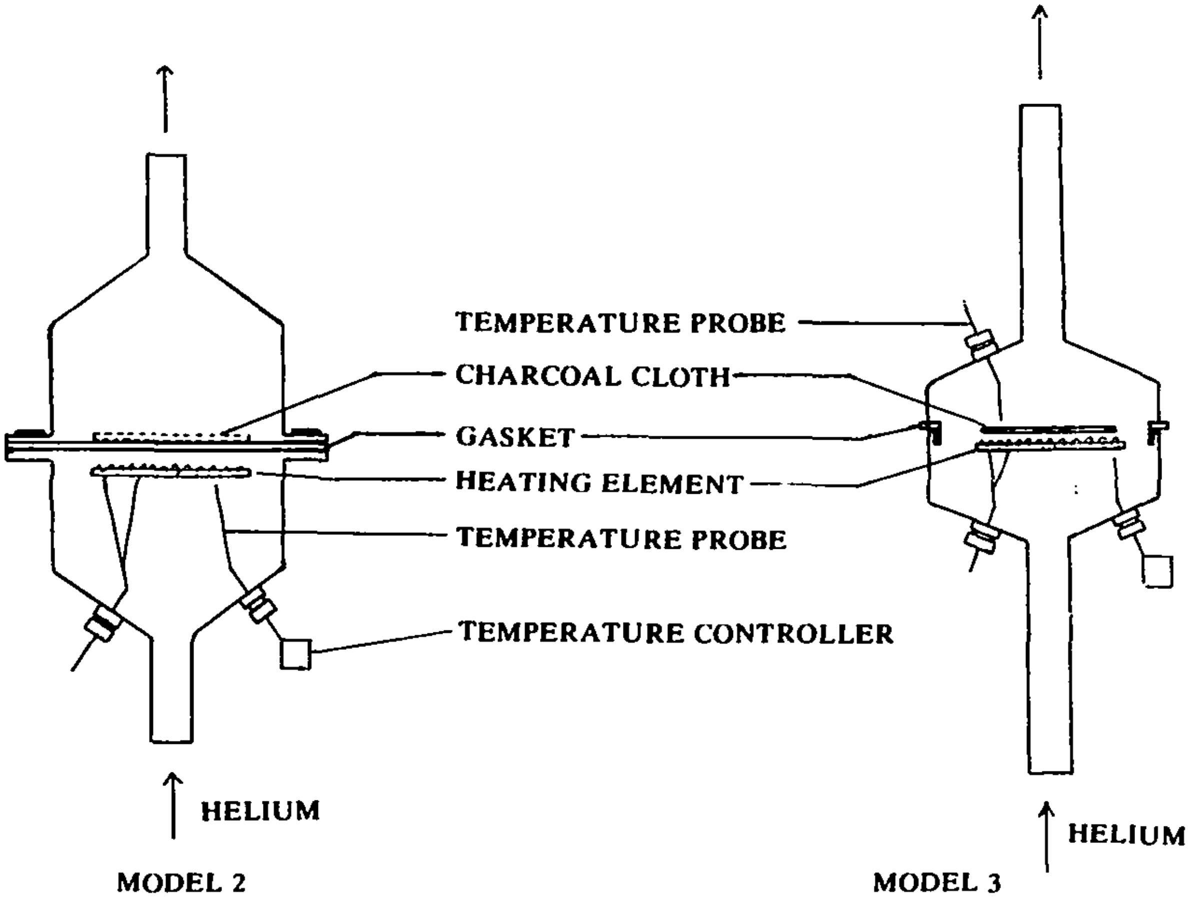


Fig.8 Diagram of stainless steel cassette desorbers (models 2 and 3), showing the exploded view of the placement of heating elements, temperature probes, temperature controllers, gaskets and charcoal cloth.

for additional sealant. The distance between the cloth and the heating element was reduced from 6.0 mm to 3.0 mm. A temperature probe was placed on the top part of the cassette to monitor the temperature at the surface of the cloth and a heating element and accompanying temperature probe were built into the base portion of the cassette. The photograph showing the vertical and horizontal view of the model 3 cassette desorber is shown in Fig.9. The cassette was connected to a Tekmar LSC 2000 automatic concentrator system and a Varian model 3700 gas chromatograph. Helium gas was used as a carrier gas and for the detection of leaks at all connections using a gas leak detector (Model 21-250, Gow Mac Instrument Co., Bridgewater, N.J., U.S.A.). Under optimized operating conditions, the temperature at the cloth face was approximately 300°C. Such experiments demonstrated that this final design of a thermal desorbing cassette (model 3) was adequate for the purposes required.

A. Using the cassette as a thermal desorber

The model 3 desorber was connected to a Tekmar LSC 2000 automatic concentrator system , a capillary interface and a Varian model 3700 gas chromatograph (Fig.10). The Tekmar LSC 2000 automatic concentrator system was used to control a temperature programme of the capillary interface. Appropriate temperatures had to be determined both for cooling and trapping VOCs in the capillary interface and heating it

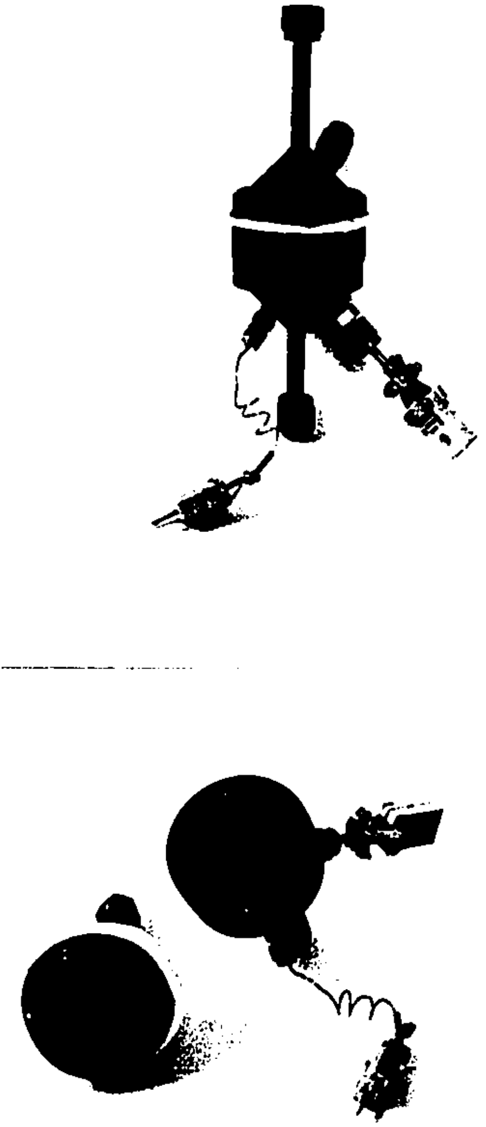


Fig.9 The photograph of the model 3 cassette desorber showing the vertical and horizontal view and the placement of charcoal cloth disc.

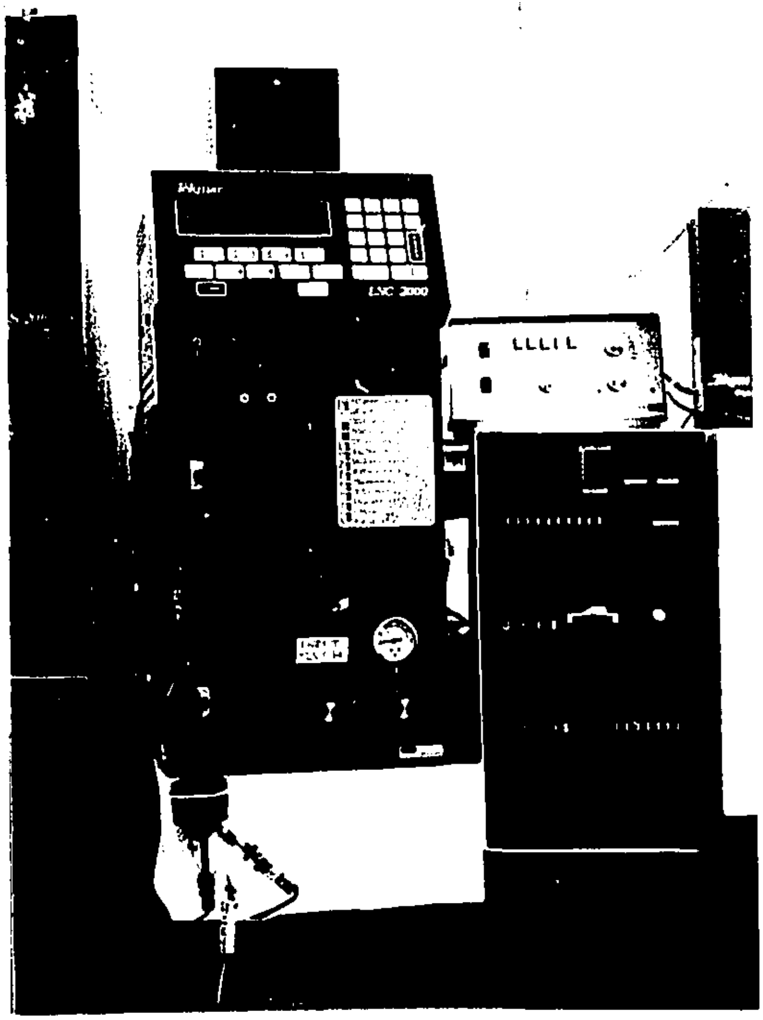


Fig.10 The photograph of thermal desorption system consisting of the model 3 cassette desorber, trap, Tekmar LSC 2000 automatic concentrator system, capillary interface and gas-liquid chromatograph.

quickly to volatilize the VOCs for transferring to the GC. Following thermal desorption from the charcoal cloth, the VOCs were trapped in the capillary interface cooled to -120 °C by liquid nitrogen. Subsequently, in the injection mode, the capillary interface was rapidly heated to 250 °C to vaporize the VOCs.

B. Using the cassette as a purge unit

Using the newly designed cassette (model 3) as a thermal desorber, it was found that it took 60 min to remove the VOCs from the charcoal cloth, a procedure that would be much too slow to be of practical use. This cassette might also function as a purge unit to transfer the VOCs from the charcoal cloth to another trapping medium in the Tekmar LSC 2000 automatic concentrator system and subsequently desorbing the VOCs from this trap into a capillary interface and into the GC. The commercially available trap consisted of 200 mg of Carbopack B (7.5 cm) and 50 mg of Carbosieve S-III (1.3 cm) packed in a 0.3 cm diameter and 25 cm long column (Supelco, Inc., Supelco park, Bellefonte, PA 16823-0048, USA). Another trapping device was prepared by packing Carbopack B (60/80 mesh) in a 0.6 cm diameter and 15.0 cm long column.

C. Recovery of the VOCs

The 2-layer charcoal cloth disk was spiked with 0.5 ul of the mixture of 0.3 ug of benzene, 0.75 ug of trichloroethylene, 0.63 ug of toluene, 1.5 ug of tetrachloroethylene and 0.88 ug of chlorobenzene and o-xylene. The adsorbed VOCs on charcoal cloth were removed by thermal desorption under optimized condition. The recovery of the mixture of VOCs from charcoal cloth was also performed at the standard VOC concentration of 2,4 and 10 times greater than the first concentration studied. The standard curve for percent recovery of VOCs from Carbopack B was prepared from applying the different concentrations of standard VOC mixture directly to the trap and desorbing the VOCs by thermal desorption. The percent recovery of VOCs from Carbopack B was set at 100%. The average percent recovery of each VOCs from the charcoal cloth was calculated.

D. Method Reliability

Preliminary results showed that benzene and o-xylene could not be measured by thermal desorption technique under the conditions used. The known concentrations of a mixture of four VOCs (trichloroethylene, toluene, tetrachloroethylene and chlorobenzene) was generated in the sampling chamber at 20-23 °C and 40% relative humidity. The cassette, containing two layers of charcoal cloth, was used to collect the VOC mixture over a period of 10, 20 and 30 min at a flow of approximately 200 ml/min. The cloth-adsorbed chemicals were kept in screw-cap tube until thermally desorbed and analyzed by GLC/PID no longer than two weeks. The accuracy and precision of the method was calculated in terms of percent recovery, overall system accuracy and percent coefficient of variation, overall precision ($\overline{\overline{CV}}_T$) respectively from four individual experiments.

5.3 Reactivation/Re-use of Charcoal Cloth

With a view to using charcoal cloth discs repeatedly, the adsorption and desorption efficiency of charcoal cloth was investigated to ensure the constancy of the adsorptive properties of the charcoal cloth.

The cassettes containing charcoal cloth were heated at 300 °C with a low flow of nitrogen (10 ml/min) for an hour and cooled down to approximately 60 °C and then reheated again. The charcoal cloth discs were reheated and cooled down for 5, 10 and 20 times and were kept in a desiccator. The process of heating and cooling the charcoal cloth was done to simulate the repetitive use of charcoal cloth by thermal desorption for 5, 10 and 20 times. The adsorption capacity of known concentrations of VOC mixture for "used" charcoal cloth was determined at a flow rate of approximately 200 ml/min and at a relative humidity of 40%. The breakthrough time and volume were plotted against the number of repetitive usages of charcoal cloth.

6 APPLICATION OF THE CHARCOAL CLOTH CASSETTE

Having developed a cassette sampling system for charcoal cloth and having determined the appropriate operational parameters, it was essential to "field-test" the system. The charcoal cloth cassette was used to assess worker exposure to paint vapours in Building no. 3, Canadian Forces Base, Longue Pointe, Montreal, Quebec. The paint Infra Red RAF green acrylic G60351 was used exclusively in two painting operations in this study. During the first painting operation conducted on March 10, 1993, a troop carrier was painted over a 30 minute period and left in the paint room for five hours before removing to the staging area. The operation room was ventilated and the two painters wore appropriate protective equipments. Sampling of paint vapours was initiated 30 min after the end of the paint application because breakthrough was expected. Paint vapours were collected with 3 sets of SKC air pumps equipped with sampling cassette containing two layers of charcoal cloth at a flow rate of 200 ml/min over a period of 15, 30, 45 and 60 min consecutively. Another set of SKC air pump equipped with SKC charcoal tube no.226-01 was also used for comparison. The charcoal tubes were used to sample air at a flow rate of 126 ml/min and changed every 30 min during the sampling period of 2.5 hr. All sampling devices were put side by side on a trolley (site A) near the troop carrier (Fig.11). After sampling, the two layers of charcoal cloth were kept in screw-cap tubes under refrigerated temperature until the samples were analyzed. Two of three sets of charcoal cloth discs with adsorbed paint vapours were extracted by hexane solvent desorption and analyzed by

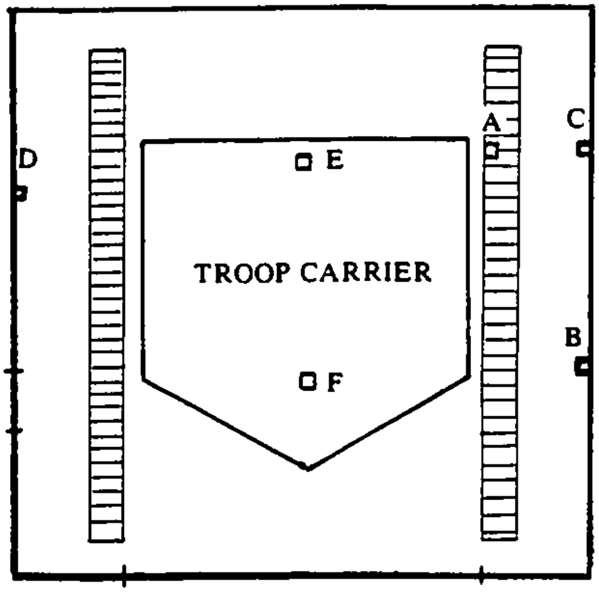


Fig.11 Diagram of a paint room showing the placement of a troop carrier and the cassette air sampling devices at points A, B, C and D and nutshell charcoal tubes at points A, E and F, the latter two being on the vehicle being painted. The hatched rectangles represent the position of a ventilation system in the floor of the room.

GLC/PID. The third set of charcoal cloth samples was thermally desorbed and subsequently analyzed by GLC/PID. The charcoal granules in charcoal tubes were extracted by carbon disulfide and analyzed by GLC/FID (flame ionization detector) (NIOSH method, No.127).

The second painting operation was conducted on March 17, 1993. A troop carrier was painted and remained in the paint room for three hours before removing into the staging area. Paint vapours were sampled during painting for 23-24 min with three sets of SKC air pumps equipped with two layers of charcoal cloth cassette connected to SKC charcoal tubes no. 226-01 to determine breakthrough of paint vapours. The sampling was performed at a flow rate of 200 ml/min in three different locations (site B, C and D) near the troop carrier (Fig.11). As soon as the painting was finished, five sets of air samplings were initiated. Two air samplings were SKC air pumps equipped with SKC charcoal tubes no. 226-01 with a flow rate of 126 ml/min at site E and F (hanging on the troop carrier). Charcoal tubes were changed every half an hour for a period of three hours. The other three sets of air samplings were performed with SKC air pumps connected with charcoal cloth cassette. The charcoal cloth cassette was operated at a flow rate of 200 ml/min for 3 hr at site B,C and D. The charcoal cloth was extracted by hexane solvent desorption and analyzed by GLC/PID. Charcoal granules in charcoal tubes was extracted by carbon disulfide solvent desorption and the VOCs being analyzed by GLC/FID (NIOSH method, No.127).

RESULTS

1. APPARATUS FOR SAMPLING

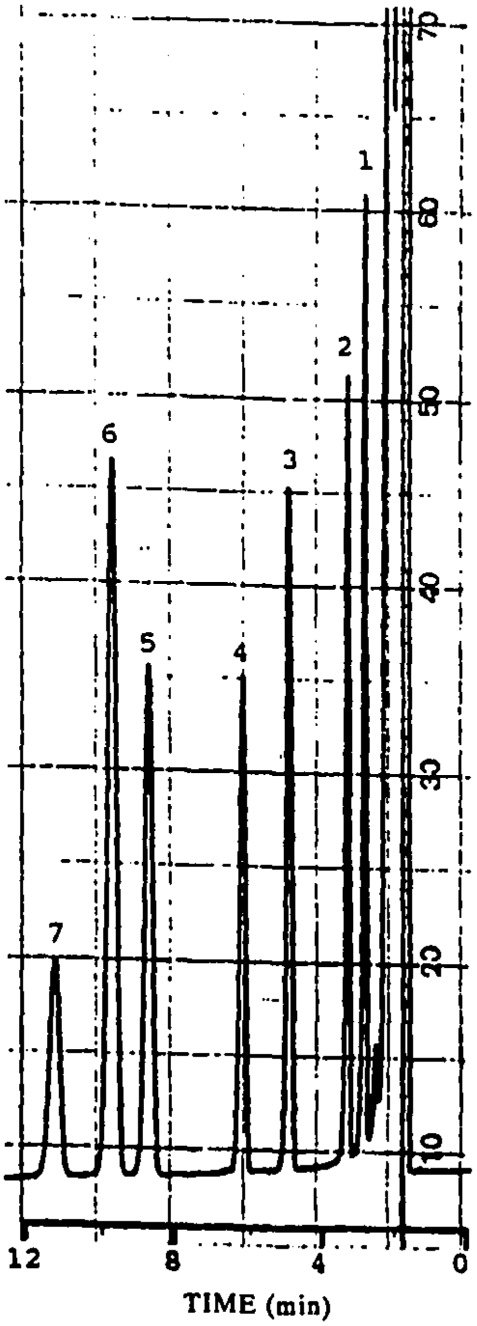
Several parameters should be considered in the development of an effective device for air sampling. They are breakthrough time and volume, adsorption capacity of an adsorbent used, pressure drop across the device, bed geometry (sampling tube dimension), sampling flow rate, pollutant concentration and properties, co-adsorption, humidity and temperature during sampling (modified from Guenier and Muller, 1984). The stability of pollutants on adsorbent, interaction of trapped pollutants and pollutants recovery (desorption efficiency) are also important parameters. In addition, analytical process including sensitivity, specificity, precision and accuracy should be known before the device can be used in the field.

An initial design of the cassette made it difficult to keep charcoal cloth in position in the cassette (Fig.2). The top and the bottom part of the cassette had machined threading. When the parts were fastened together, the charcoal cloth layers inside the cassette were rotated slightly following the direction of the turning top. Consequently, the cloth layers were not always properly positioned in the cassette. This sampling cassette was tested for adsorption capacity. The preliminary results showed that a chemical could break through it immediately if the layer of cloth was not seated properly in the cassette. The redesigned cassette (Fig.3) eliminated the problem of the positioning of the charcoal cloth in the cassette. The two layers of charcoal cloth were placed between two stainless steel washers. The washers were held in place in the cassette by a circular stainless steel sleeve. This cassette could be heated to high temperatures. The surface area of the 2-layer charcoal cloth exposed to VOCs was 2.84 cm^2 and weighed on average 67.8 mg.

2. GLC ANALYSIS OF VOCs

A typical chromatogram of the separation of a standard VOC mixture is shown in Fig.12, along with the optimal operating parameters for the GLC separation. All compounds were resolved as distinct peaks. The retention time of benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene was approximately 2.8, 3.4, 4.9, 6.2, 8.7, 9.7 and 11.2 min respectively and the total retention/ analysis time was approximately 12 minutes. The peak of the internal standard, 1-chloro-2-fluorobenzene, eluted between chlorobenzene and o-xylene. The close proximity of the benzene peak to the solvent (hexane) front was a potential problem. In addition, even the highest purity hexane tested contains a small amount of benzene as a contaminant which must be taken into account during analysis.

Standard curves for each of the components of the VOC mixture are shown in Fig.13. A linear relationship was



PEAK IDENTIFICATION

1 = BENZENE

2 = TRICHLOROETHYLENE

3 = TOLUENE

4 = TETRACHLOROETHYLENE

5 = CHLOROBENZENE

6 = 1-CHLORO-2-FLUOROBENZENE

7 = O-XYLENE

Fig.12 A chromatogram of selected volatile organic compounds analyzed by a gas-liquid chromatograph equipped with photoionization detector (GLC/PID). Operational conditions for the GLC included: injector temperature, 190 °C; oven temperature, 70 °C; detector temperature, 200 °C; flow rate of nitrogen, 10 ml/min.

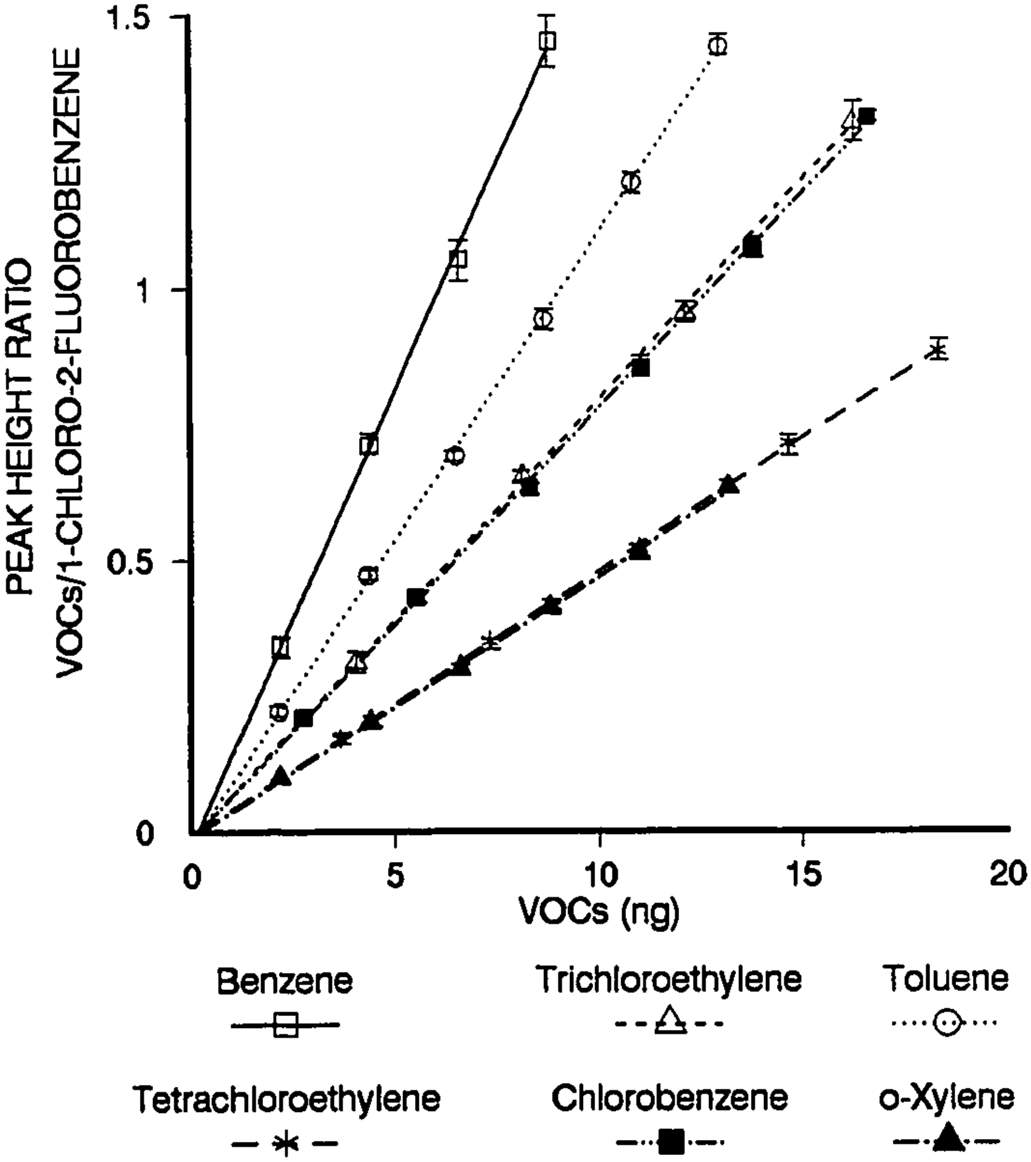


Fig.13 Standard curves of six volatile organic compounds assayed by a gas-liquid chromatograph equipped with photoionization detector (GLC/PID). The concentrations of chemicals (ng) were plotted on the x-axis against the peak height ratio (height of peak of chemical/ height of peak of internal standard, 1-chloro-2-fluorobenzene) on the y-axis.

detected between the calculated peak height ratio (peak height of agent/peak height of internal standard) plotted against concentration (nanograms, ng) over a range of 2.20 to 18.3 ng/ul stock solution. The linear plots represent the mean values ± standard deviation of three replicate determinations. At the concentration of 5 ng of each chemical in the VOC mixture, benzene and toluene had higher response (peak height ratio) than other chemicals for photoionization detection. o-Xylene and tetrachloroethylene had the lowest response (peak height ratio) of the GLC. The sensitivity by weight of these VOCs for GLC detection was found to follow the sequence; benzene > toluene > trichloroethylene = chlorobenzene > tetrachloroethylene = o-xylene. The linear correlation coefficient of standard curves for six VOCs ranged from 0.9995 to 0.9998.

3. EXPERIMENTAL DETAILS

3.1 Adsorption Capacity

A. Comparison of Three Air Sampling Devices

The breakthrough time, volume and capacity of trapped toluene of the charcoal cloth was investigated using various weights of charcoal in three air sampling devices (a cassette, a tube and a standard NIOSH nutshell charcoal tube). The breakthrough time of trapped toluene (210-240 mg/m^3) in the three air sampling devices is shown in Fig.14. The results showed that the charcoal tube with packed discs of cloth and

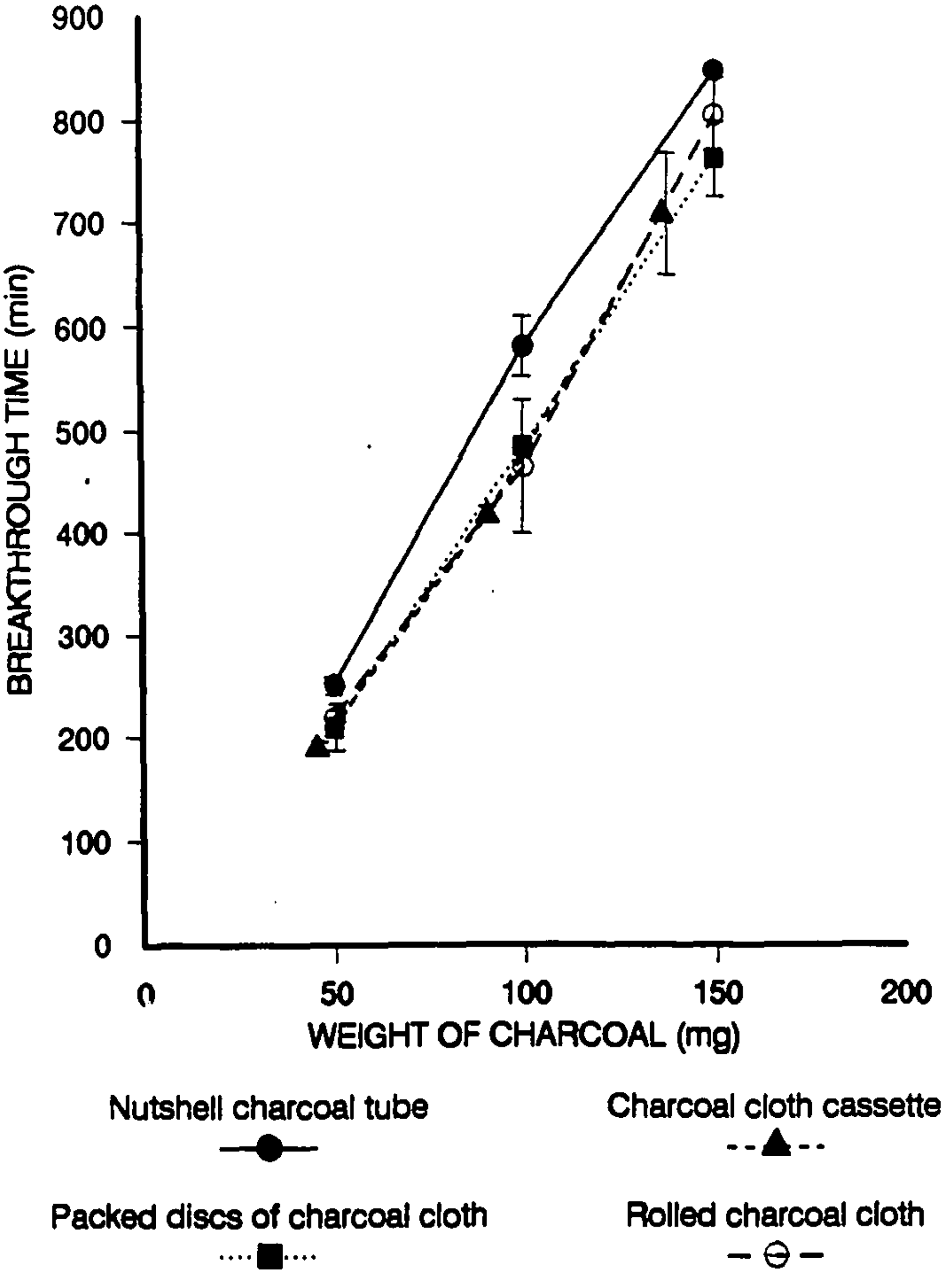


Fig.14 Breakthrough time of trapped toluene vapours with various weights of charcoal in three air sampling devices: commercial nutshell charcoal tube, charcoal cassette containing one to three layers of charcoal cloth and a tube containing either packed discs of charcoal cloth or rolled charcoal cloth. A flow rate of 200 ml/min was used for each adsorbent system.

rolled charcoal cloth had comparable breakthrough times to the charcoal cloth cassette but the values were slightly lower than those of the NIOSH nutshell charcoal tube. The average breakthrough time increased in an almost linear manner with the increased weight of charcoal. The average breakthrough times of trapped toluene for 100 mg of nutshell charcoal, 100 mg of packed discs of charcoal cloth in a tube and 91.0 mg of 2-layer charcoal cloth was approximately 581, 484 and 416 min (9.7, 8.1 and 6.9 hr) respectively. The breakthrough volume and capacity of trapped toluene in the three air sampling devices are shown in Fig.15 and 16 respectively. The nutshell charcoal tube gave the greatest breakthrough volume and capacity for trapping toluene. The charcoal cloth tube and cassette showed comparable breakthrough time and capacity for toluene. The breakthrough volume and capacity of 100 mg of nutshell charcoal, packed discs of charcoal cloth and 91.0 mg of 2-layer charcoal cloth were approximately 123.4, 101.2, 85.2 L and 27.1, 22.3, 19.6 mg respectively. The adsorption capacity (ratio of trapped toluene to the weight of charcoal) of charcoal is shown in Fig.17. The adsorption capacity of NIOSH nutshell charcoal was increased when the weight of charcoal increased from 50 to 100 mg and it was relatively constant from 100 to 150 mg of charcoal. Both the tube and the cassette, containing charcoal cloth showed an increase of adsorption capacity for each of the weights tested. The adsorption capacity of nutshell charcoal for toluene was

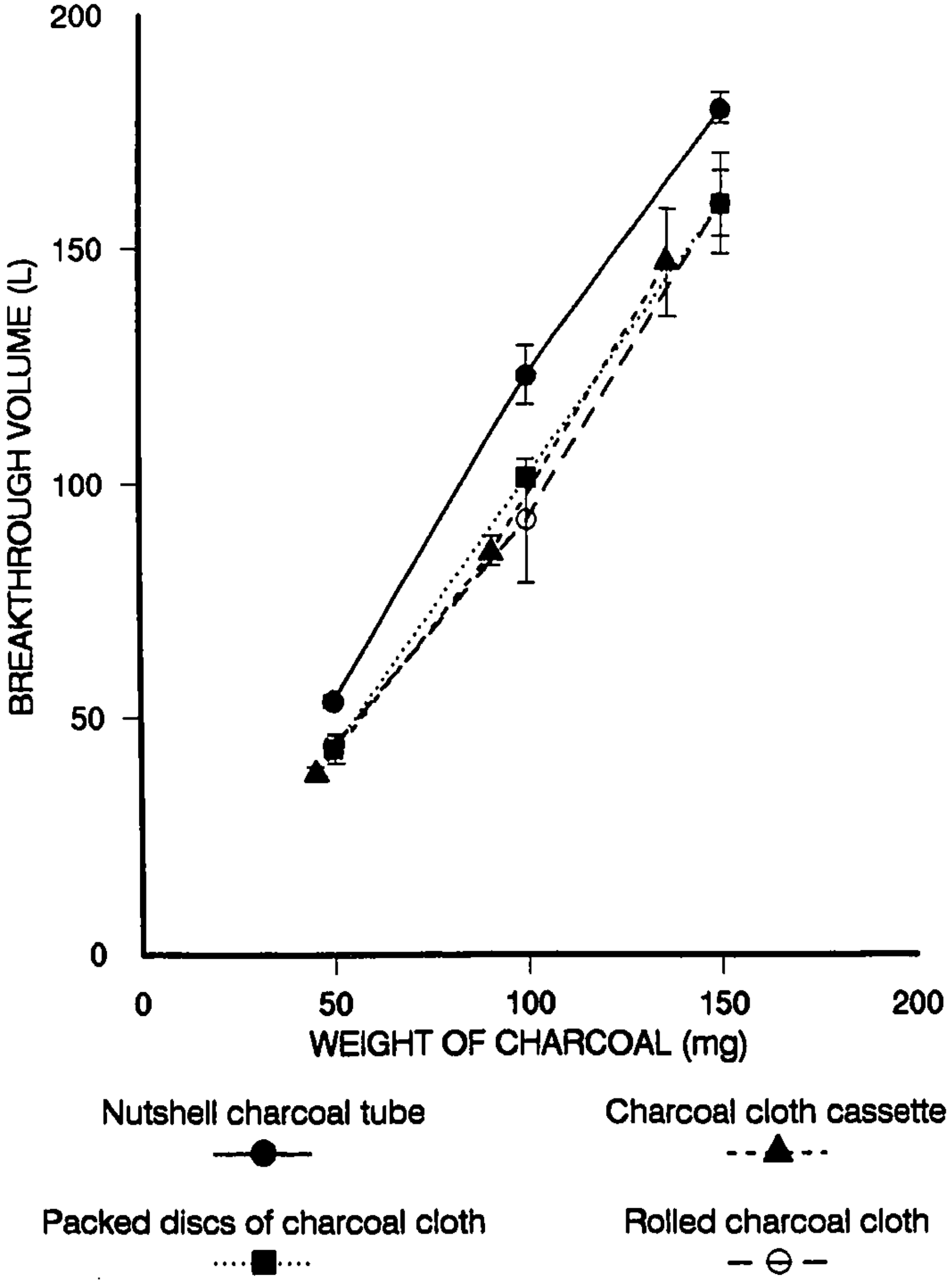


Fig.15 Breakthrough volume of trapped toluene vapours with various weights of charcoal in three air sampling devices: commercial nutshell charcoal tube, charcoal cassette containing one to three layers of charcoal cloth and a tube containing either packed discs of charcoal cloth or rolled charcoal cloth.

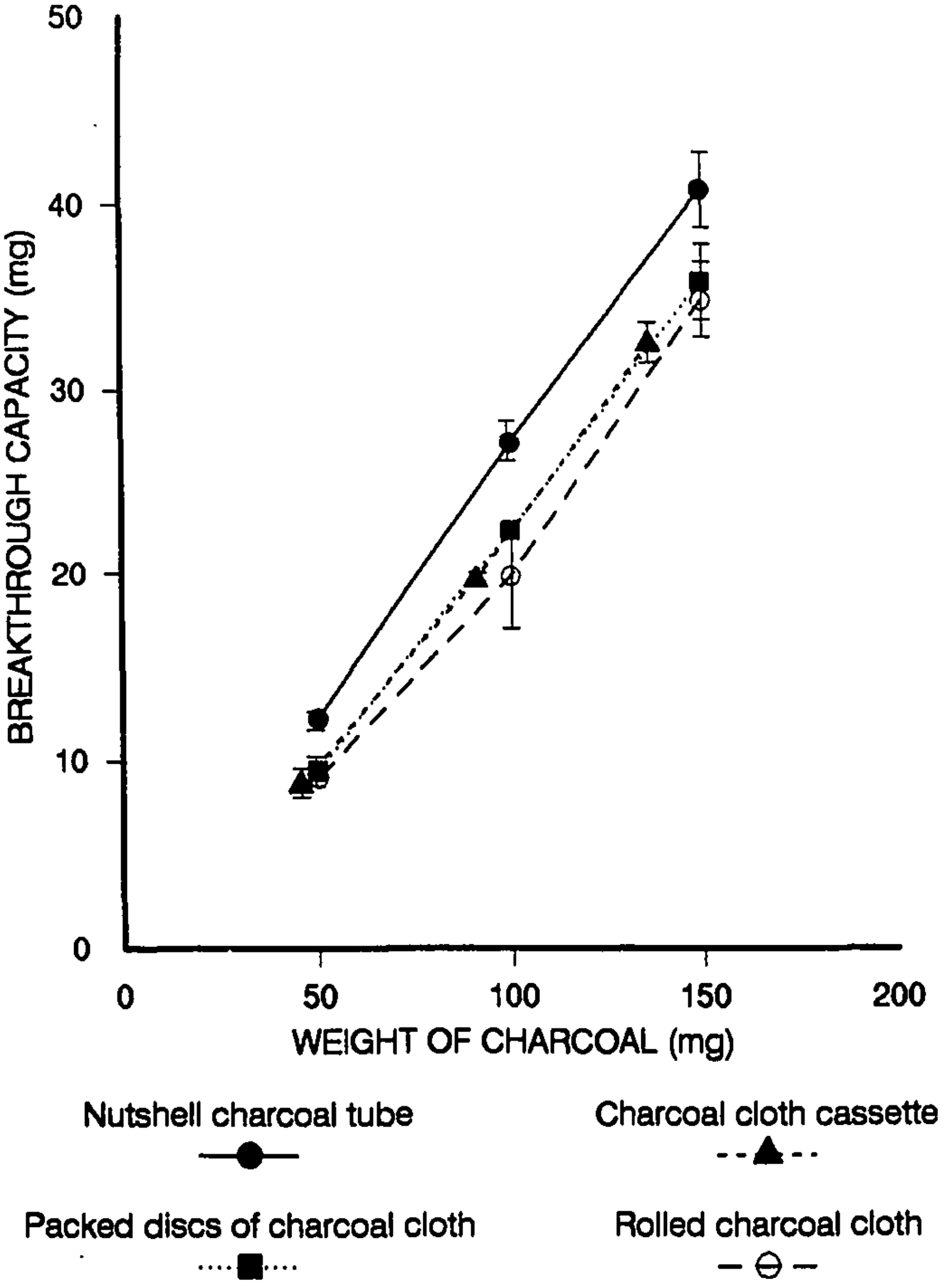


Fig.16 Breakthrough capacity of trapped toluene vapours with various weights of charcoal in three air sampling devices: commercial nutshell charcoal tube, charcoal cassette containing one to three layers of charcoal cloth and a tube containing either packed discs of charcoal cloth or rolled charcoal cloth.

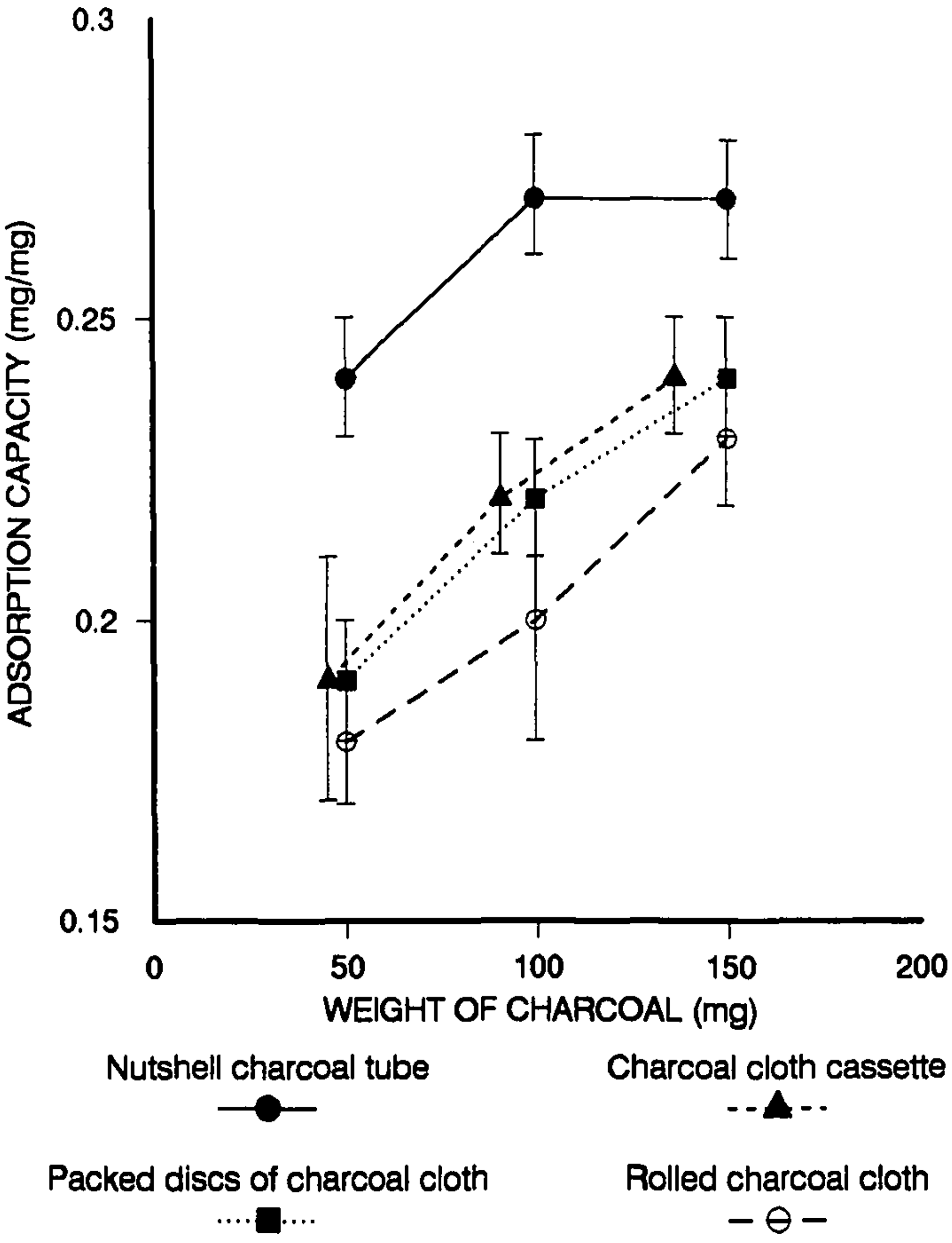


Fig.17 Adsorption capacity (mg of trapped toluene/mg of charcoal) of trapped toluene vapours with various weights of charcoal in three air sampling devices: commercial nutshell charcoal tube, charcoal cassette containing one to three layers of charcoal cloth and a tube containing either packed discs of charcoal cloth or rolled charcoal cloth.

higher than that of charcoal cloth. The rolled charcoal cloth in a tube gave slightly lower adsorption capacity than packed discs of cloth in a tube and charcoal cloth discs layered in a cassette.

Experiments conducted with different weights of charcoal and breakthrough times determined for toluene (Figs.15-17) provided the kinetic adsorption capacity for these two types of charcoal using the modified Wheeler equation as shown in Appendix III.

The relationship between the breakthrough times and the weights of charcoal for both charcoal cloth and nutshell charcoal resulted in two parallel straight lines (Appendix III. Fig.46). From the slope (W_e/C_0Q), C_0 and Q, the kinetic adsorption capacity for these two types of charcoal were determined. The results showed that the kinetic adsorption capacities of nutshell charcoal ($W_e = 0.299$) and charcoal cloth ($W_e = 0.262$) for a single chemical, such as toluene, were comparable.

B. <u>Pressure Drop Across the Devices</u>

Different amounts of charcoal (weights or layers of cloth) might influence the free flow of air through the collecting device. The pressure drop across the device was determined at a flow rate of approximately 200 ml/min. The cassette containing charcoal cloth (2 layers) had the lowest pressure drop among the three devices tested (Fig.18). There was virtually no change in air pressure between 45.5, 91.0 and

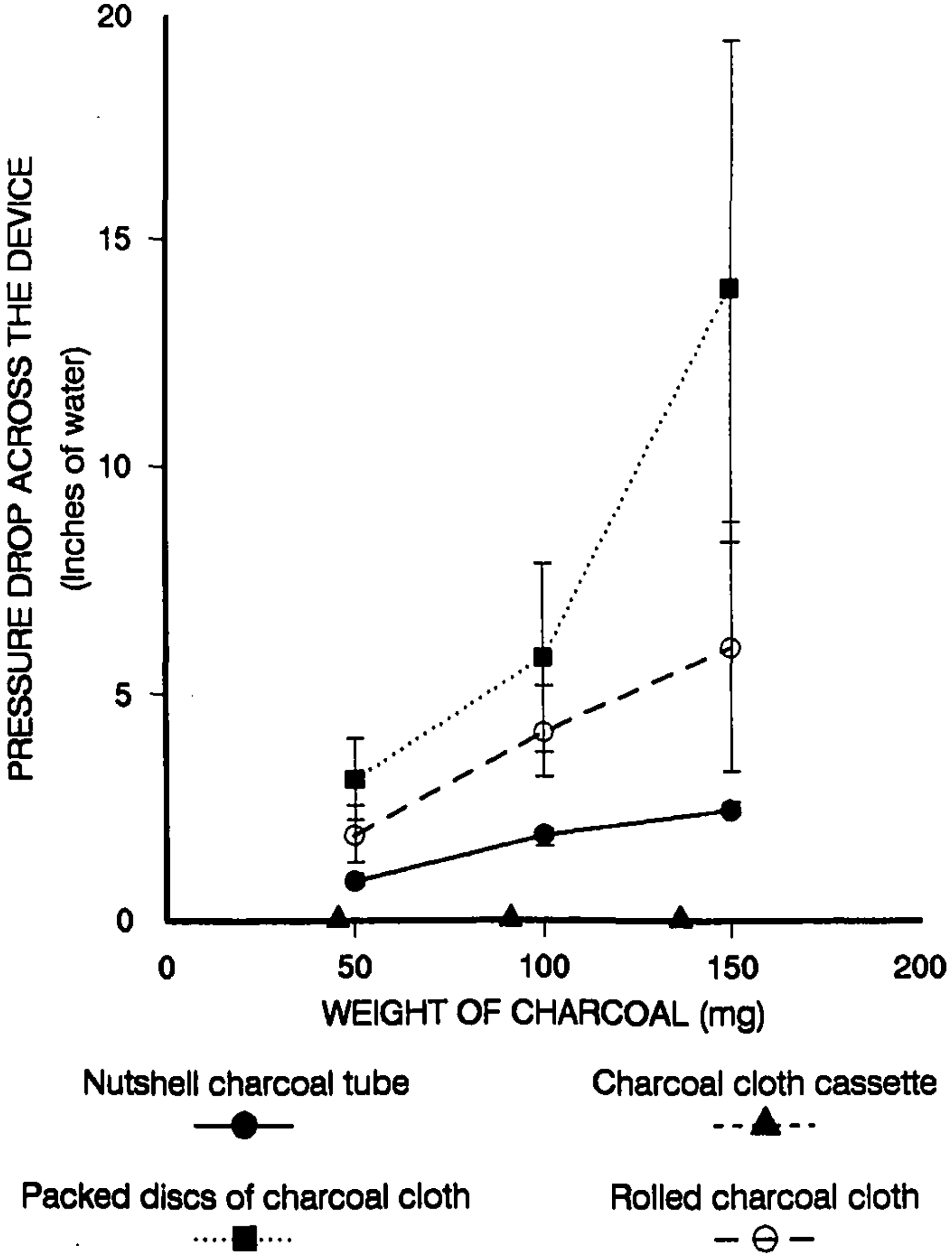


Fig.18 Pressure drop across different weights of adsorbent determined at a flow rate of 200 ml/min in three air sampling devices: nutshell charcoal tube, charcoal cassette containing one to three layers of charcoal cloth and tubing packed with discs of charcoal cloth or rolled charcoal cloth.

136.5 mg charcoal discs (one to three layers) in the cassette. The charcoal tube containing packed discs of cloth discs showed the highest pressure drop due to the thickness of the layers and a large standard deviation, possibly due to uneven packing. The pressure drop across the NIOSH tube was acceptable within NIOSH limits (within 1 inch of Hg at 1 L/min flow rate).

Based on the results of the breakthrough tests of toluene and the pressure drop measured for the three sampling devices tested, the cassette, containing two layers of charcoal cloth, was selected because of its adequate capacity for VOC sampling in indoor air and the low pressure drop across the device. The two layer of charcoal cloth could adsorb toluene vapour at concentrations of 210-240 mg/m^3 containing 85.2 L of air at a flow rate of approximately 200 ml/min. However, VOC concentrations in indoor environments in buildings are much lower than the concentration of toluene tested. The adsorption capacity of 2-layer charcoal cloth (91.0 mg) for toluene was 19 mg, which is much greater than necessary for the VOC analysis by GLC.

C. Selection of Optimal Flow Rate

The breakthrough test of the charcoal cloth cassette was performed with toluene vapour (20 mg/m^3) at flow rates of 0.2, 0.5, 1.0 and 1.5 L/min. At a flow rate 1.5 L/min, the breakthrough time and volume of the charcoal cassette were approximately 6.4 hr and 579.1 L respectively. (Fig.19A and B). When the flow rate was reduced to 1.0 L/min, the breakthrough time and volume increased to 11.5 hrs and 699.2 L respectively. A reduction in flow rate caused a significant increase in both breakthrough time and volume, accompanied by an increase in breakthrough capacity of toluene (Fig.19C). At higher flow rates, toluene would have insufficient contact time to be adsorbed on the surface of charcoal cloth because of the thin (1 mm) depth of the two-layer cloth bed. The breakthrough time of charcoal cassette for toluene at a flow rate of 0.2 L/min was almost three days and the breakthrough volume was 848.3 L. The breakthrough capacity of the charcoal cloth cassette containing two layers of charcoal cloth (91 mg) at flow rates of 0.2, 0.5, 1.0 and 1.5 ml/min was 17.6, 17.3, 14.9 and 11.1 mg respectively (Fig.19C). The adsorption capacity of the charcoal cloth cassette increased when the flow rate was reduced (Fig.19D),rising from 0.12 to 0.19 mg/mg charcoal as the flow rate was reduced from 1.5 to 0.2 ml/min. The flow rate of 0.2 L/min was selected because, under these conditions, charcoal cloth had the highest toluene adsorption capacity (Fig.19D).

D. Effect of Relative Humidity and Toluene Concentration on Adsorption Capacity

Since the adsorption of chemicals on activated charcoal can be influenced by humidity, the adsorption capacity of the

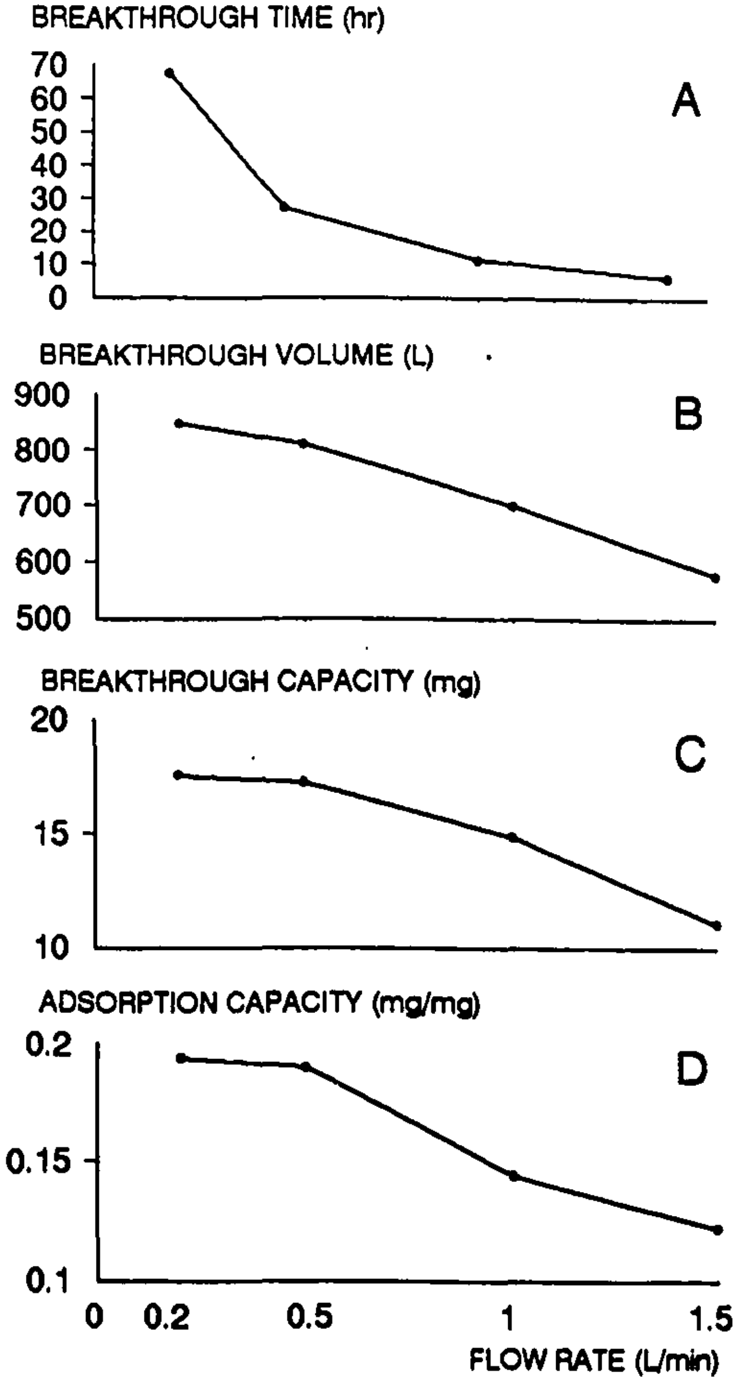


Fig.19 Effects of flow rate (L/min) on breakthrough time (hr), volume (L), capacity (mg) and adsorption capacity (mg/mg charcoal cloth) for trapped toluene vapours in a cassette (first design) containing two layers of charcoal cloth. The challenge concentration of toluene was 20 mg/m^3.

charcoal cloth cassette for toluene (128-150 mg/^{3}) was measured at various relative humidities (0, 45 and 80%). The results showed that the breakthrough time, volume and capacity of charcoal cloth cassette for toluene were reduced with increasing relative humidity (Fig.20A-D), presumably because water vapour occupied the active sites on the charcoal. The breakthrough time and volume decreased from 495 min (8.3 hr) and 117.0 L to 415 min (6.9 hr) and 90.4 L when the relative humidity was changed from 0 to 80% (Fig.20A and B). The breakthrough capacity of the cassette containing two layers of charcoal cloth (67.8 mg) at relative humidities of 0, 45 and 80% was 15.7, 13.6 and 12.7 mg respectively (Fig.20C). The adsorption capacity of charcoal cloth for toluene was reduced from 0.23 to 0.19 mg/mg charcoal when the relative humidity increased from 0 to 80% (Fig.20D).

The breakthrough test of the charcoal cloth cassette for different concentrations of toluene was evaluated at 0% relative humidity, representing the ideal condition (no influence of humidity) and 40% the average humidity of most buildings. The breakthrough time, volume and capacity from three replicate determinations were plotted against the logarithm of toluene concentrations (Fig.21A-D). When the concentration of toluene was increased, the breakthrough capacity and adsorption capacity increased (Fig.21C and D) but the breakthrough time and volume was reduced at both levels of relative humidity (Fig.21A and B). The lower the toluene

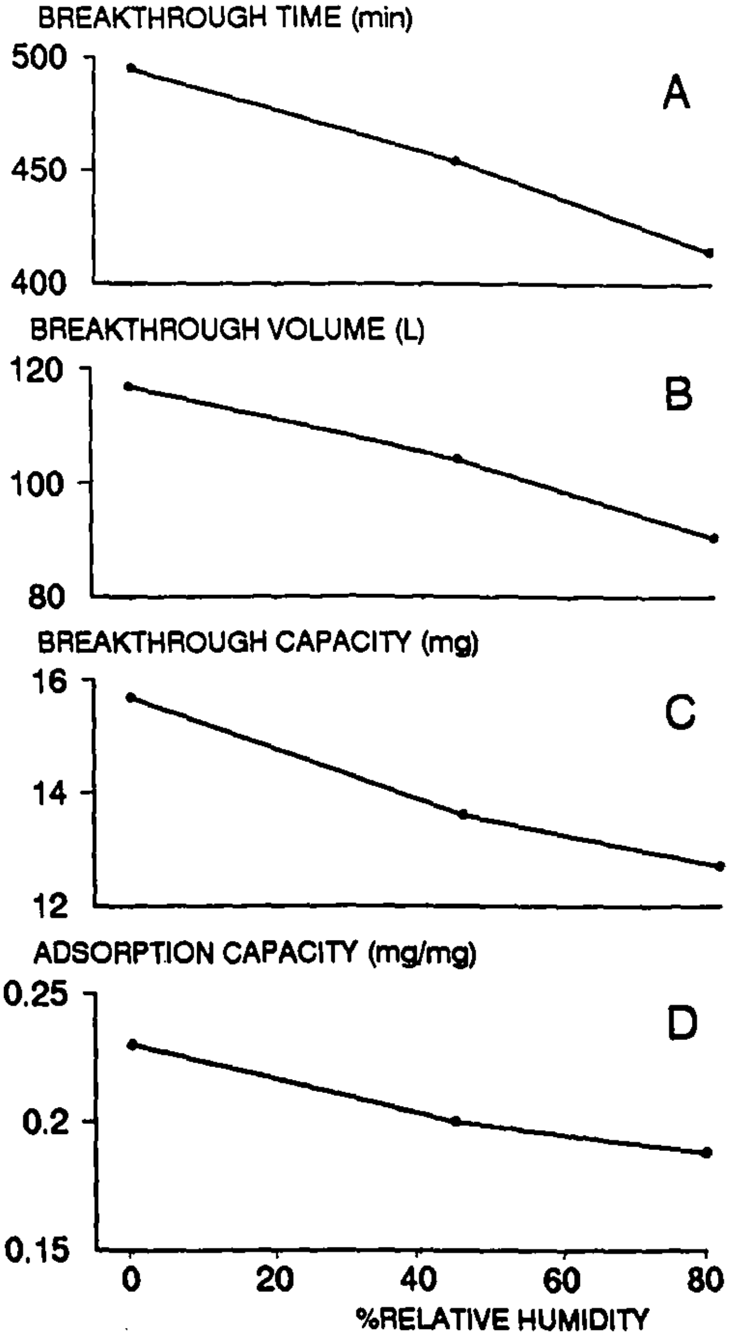


Fig.20 Effect of percent relative humidity on breakthrough time (min), volume (L), capacity (mg) and adsorption capacity (mg/mg charcoal cloth) for trapped toluene vapours in a cassette (re-designed) containing two layers of charcoal cloth.

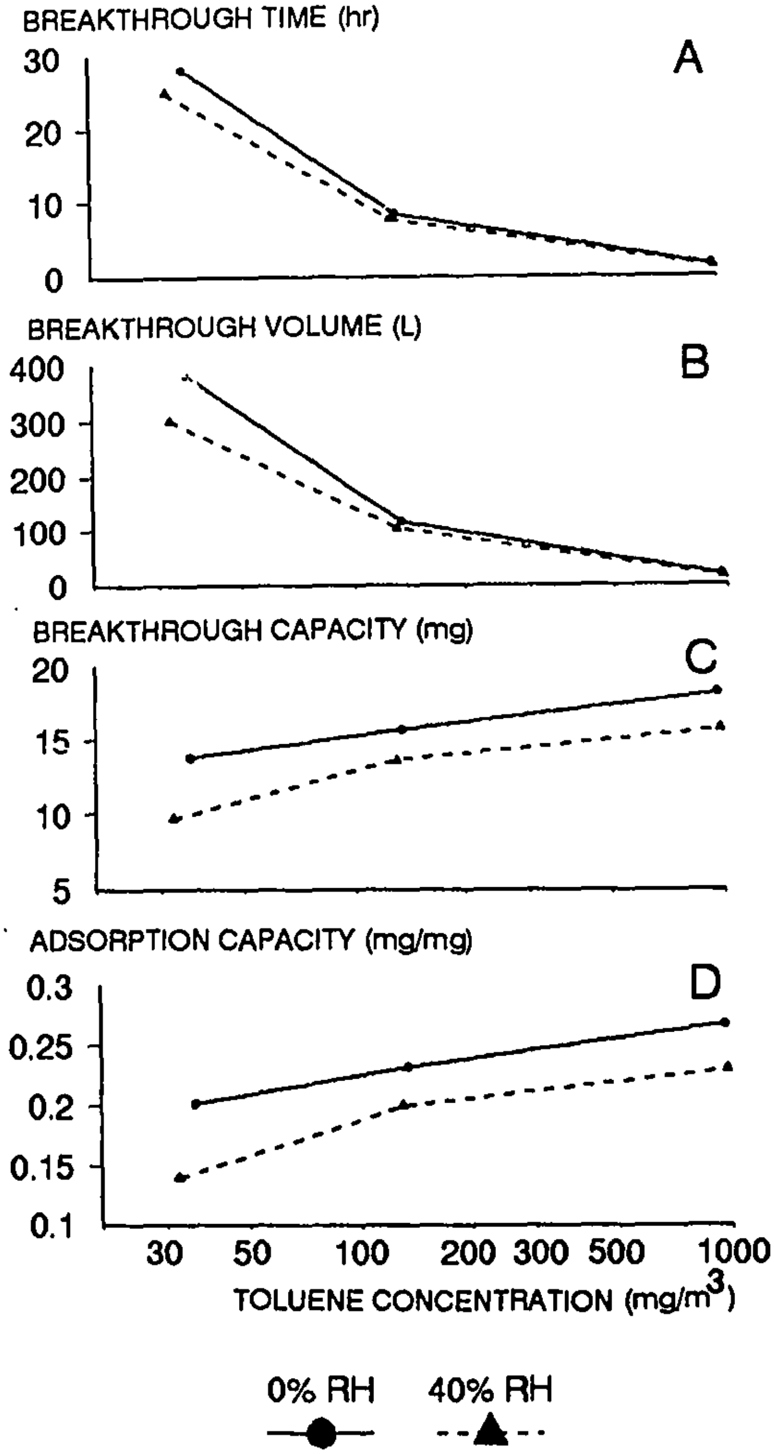


Fig.21 Effect of toluene concentrations and percent relative humidity on breakthrough time (hr), volume (L), capacity (mg) and adsorption capacity (mg/mg charcoal cloth) for trapped toluene vapours in a cassette (re-designed) containing two layers of charcoal cloth.

concentrations, the less toluene was proportionally collected on the 2-layer charcoal cloth. At zero percent relative humidity, the breakthrough time and volume were reduced from 28.1 hr and 382.9 L to 8.3 hr and 117.0 L when the toluene concentration increased from 35.9 to 134.3 mg/m^3 respectively (Fig.21A and B). The breakthrough capacity and adsorption capacity increased to 18.2 mg and 0.27 mg/mg charcoal respectively when the toluene concentration increased to 970 mg/m^3 at zero percent relative humidity. A similar pattern was seen for the breakthrough test of the charcoal cloth cassette for toluene at 40% relative humidity but the relative humidity did not have the same effect on adsorption capacity at each level of toluene concentrations tested. At the lowest toluene concentration, the humidity caused a greater reduction in breakthrough capacity and adsorption capacity than at higher concentration (Fig.21C and D). The adsorption capacity was increased from 0.14 to 0.23 when the toluene concentration increased from 32.3 to 970 mg/m^3.

From the preceding experiments, the optimal conditions for sampling with the cassette were determined to be:

1) two layers of charcoal cloth (67.8 mg),

2) a sampling flow rate of approximately 200 ml/min, the sampling being conducted at a relative humidity of 40% (range 20-60%) found in most buildings.

E. Comparison of the Charcoal Cassette with the Nutshell Charcoal Tube for VOC Mixture Sampling

The breakthrough test of a mixture of six VOCs was compared between the two-layer charcoal cloth cassette and the standard NIOSH nutshell charcoal tube at conditions selected. An example of a chromatogram indicating the breakthrough point of the mixture for charcoal cassette is shown in Fig.22. The chromatogram, composed of six different peaks of VOCs, represented the concentration of each chemical in the standard mixture. The six peaks of VOCs on the right-hand and on the left-hand side showed the VOC concentration in the generated air sample at the beginning and at the end of the breakthrough test. The arrow shows the point at which the 5% breakthrough occurred. Benzene and trichloroethylene were the first chemicals in the mixture to break through the charcoal cloth and to exceed the adsorption capacity, the other components of the mixture did not appear in the eluate in that time period. The length (duration) of sampling is dependent entirely on when the first VOC breaks through the adsorbent material. For the low level VOC mixture concentration (approximately from 2.8 to 13.1 mg/m^3), the average breakthrough time and volume from three replicate tests with the 2-layer charcoal cloth were 1,196 min (19.9 hr) and 243.9 L respectively (Table 17). As the concentrations increased from 7.4 to 39.8 mg/m^3, the breakthrough time was reduced to 608 min (10.1 hr) and 126.3 L respectively. The highest VOC concentrations tested gave

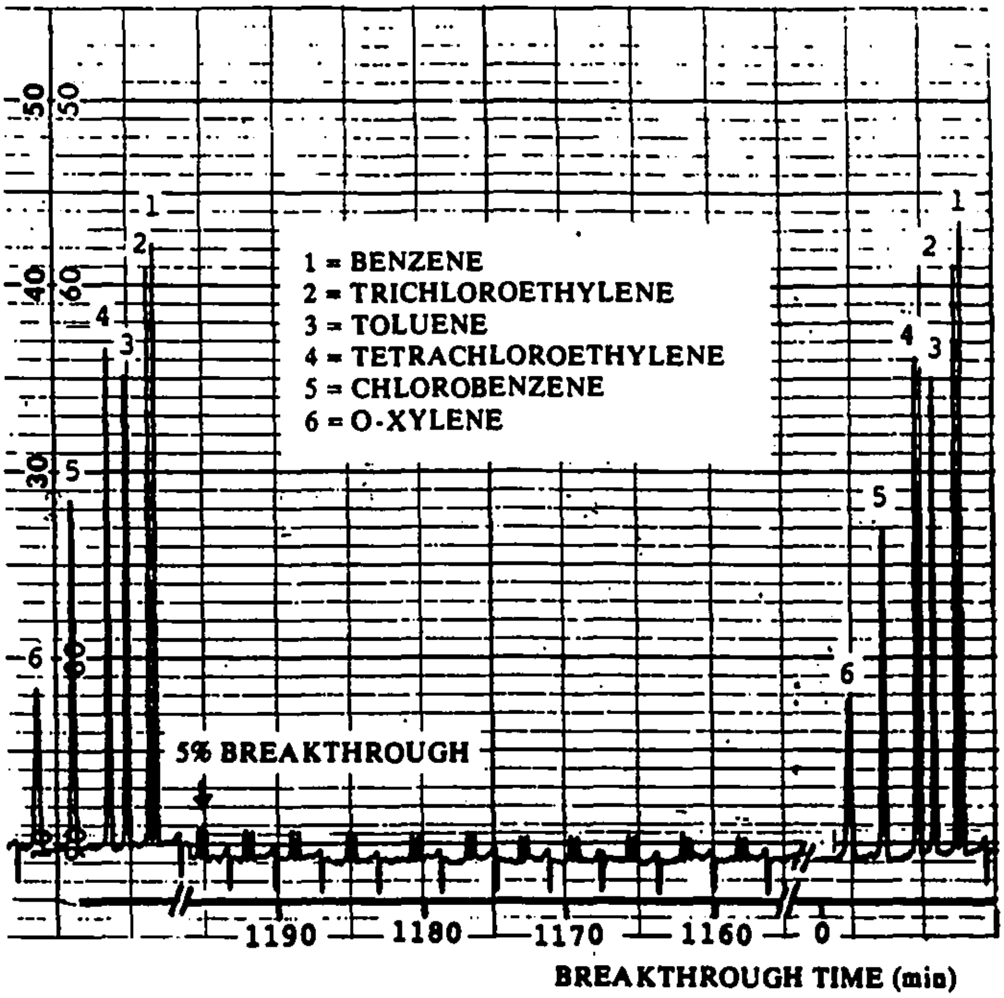


Fig.22 A chromatogram of a breakthrough test of a mixture of volatile organic compounds using two layers of charcoal cloth in the cassette measuring the breakthrough point and the breakthrough time (min). Benzene and trichloroethylene were the first volatile compounds to be eluted from the charcoal cloth, exceeding the 5% breakthrough volume at 1193 min. (Reprint of a continuous recording obtained during the experiment)

Table 17 The Breakthrough Test of 2-Layer Charcoal Cassette.

VOCs	Concentration (mg/m^3) $\bar{X}$ ± SD	Average breakthrough Time (min)	Volume (L)	Capacity (mg)	Adsorption Capacity (mg/mg)
Low concentration					
Benzene	2.8 ± 0.3			0.69	0.010
Trichloro.	6.0 ± 0.4			1.45	0.021
Toluene	4.8 ± 0.1			1.16	0.017
Tetrachlor.	13.1 ± 0.3			3.20	0.047
Chlorobenz.	5.3 ± 0.3			1.30	0.019
o-Xylene	5.1 ± 0.4			1.24	0.018
Total		1,196.3 ± 45.6	243.9 ± 17.7	9.04	0.132
Medium concentration					
Benzene	7.4 ± 1.2			0.93	0.014
Trichloro.	17.7 ± 1.2			2.24	0.033
Toluene	14.9 ± 0.3			1.88	0.028
Tetrachlor.	39.8 ± 0.5			5.03	0.074
Chlorobenz.	17.0 ± 0.3			2.14	0.032
o-Xylene	15.2 ± 0.5			1.92	0.028
Total		607.7 ± 35.9	126.3 ± 7.6	14.14	0.209
High concentration					
Benzene	38.5 ± 5.5			1.16	0.017
Trichloro.	97.3 ± 8.0			2.92	0.043
Toluene	82.0 ± 2.0			2.46	0.036
Tetrachlor.	212.0 ± 1.0			6.36	0.094
Chlorobenz.	83.0 ± 4.6			2.49	0.037
o-Xylene	70.7 ± 5.5			2.12	0.031
Total		146.0 ± 10.5	30.0 ± 1.9	17.51	0.258

n = 3

146-min (2.4-hr) breakthrough time and 30-L breakthrough volume. For the 67.8 mg weight of charcoal cloth (two layers), the total weight of the trapped VOCs were 9.0, 14.1 and 17.5 mg at low, medium and high mixture concentrations respectively (Table 17). The adsorption capacity per mg of charcoal cloth at low, medium and high VOC concentration was 0.13, 0.21 and 0.26 mg respectively. The higher the VOC concentrations, the greater was the adsorption capacity of charcoal cloth.

The breakthrough time and volume of a VOC mixture (concentration range of 52.3-239.7 mg/m^3) for the NIOSH nutshell charcoal tube were 4.2 hr and 53.2 L respectively (Table 18). The total weight of the trapped VOCs was 0.38 mg/mg of nutshell charcoal. The adsorption capacity of nutshell charcoal for the mixture of VOCs was 0.38, considerably greater than that of charcoal cloth. However, the weight of nutshell charcoal and the concentration of VOCs used in this experiment was greater than those used in experiment with charcoal cloth. The greater weight and the higher VOC concentration used would enhance the adsorption capacity of the adsorbing medium. The bed geometry is also different. The bed depth of 2-layer charcoal cloth is 1 mm but it is 250 mm for nutshell charcoal tube. With the nutshell charcoal tube, once again, benzene and trichloroethylene determined the breakthrough point of nutshell charcoal tube, as was noted for charcoal cloth (Fig.23).

Table 18 The Breakthrough Test of 100-mg Nutshell Charcoal Tube.

VOCs	Concentration (mg/m^3) $\bar{X}$ ± SD	Average Breakthrough			Adsorption
		Time (min)	Volume (L)	Capacity (mg)	Capacity (mg/mg)
Benzene	52.3 ± 7.5			2.78	0.028
Trichloro.	113.8 ± 9.7			6.05	0.061
Toluene	96.7 ± 3.1			5.14	0.051
Tetrachlor.	239.7 ± 4.7			12.75	0.128
Chlorobenz.	112.0 ± 4.3			5.96	0.060
o-Xylene	102.7 ± 5.3			5.46	0.055
Total		253 ± 13.8	53.2 ± 4.0	38.14	0.383

n = 3

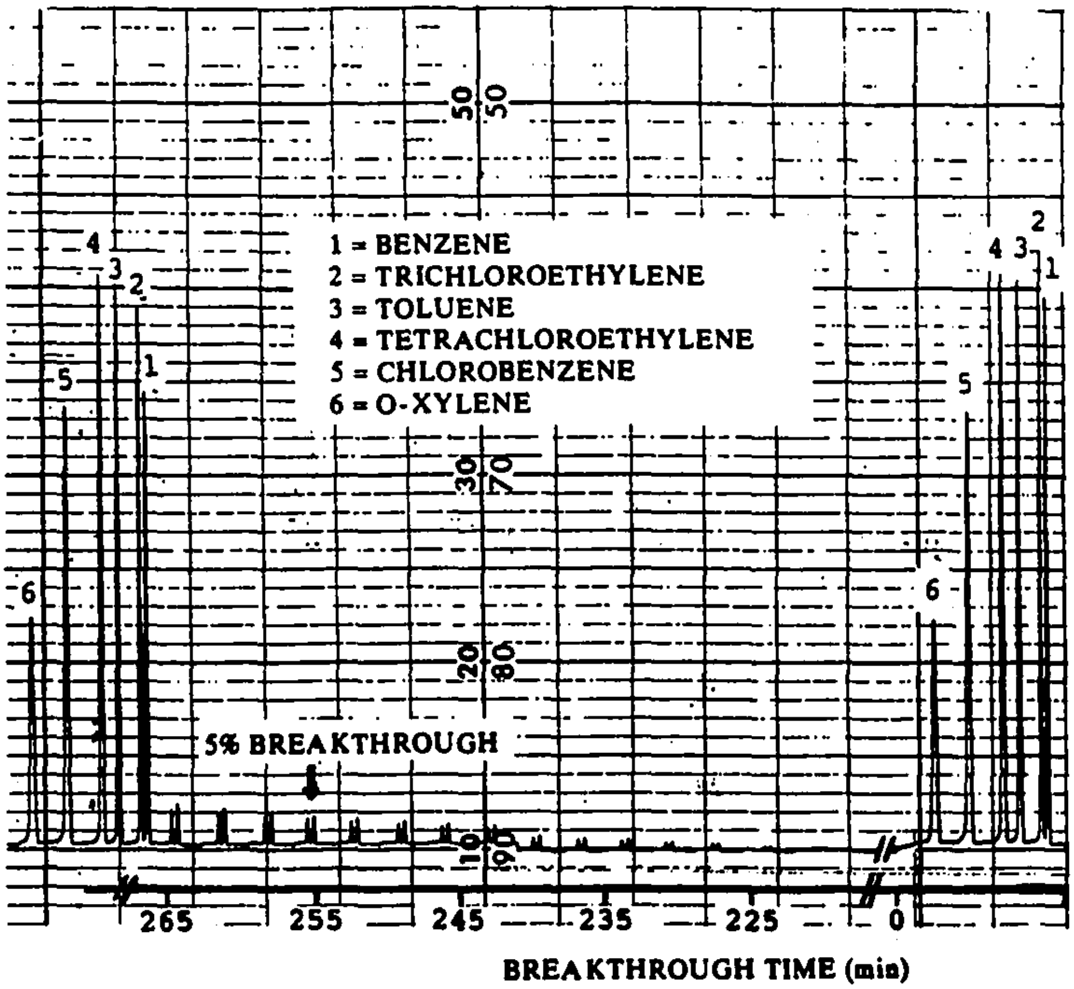


Fig.23 A chromatogram of a breakthrough test of a mixture of volatile organic compounds using a commercial nutshell charcoal tube, measuring the breakthrough point and breakthrough time (min). Benzene and trichloroethylene were the first volatile compounds to be eluted from the nutshell charcoal, exceeding the 5% breakthrough volume at 253 min. (Reprint of a continuous recording obtained during the experiment)

The adsorption isotherm of each VOCs in the mixture on 2-layer charcoal cloth is shown in Fig.24 using data from Table 17. The logarithm of average VOC concentrations in the mixture was plotted against the logarithm of average weight percent VOC adsorbed on 2-layer charcoal cloth. The adsorption isotherm of these VOCs showed similar patterns. When the range of VOC concentration was increased from 2.8-5.1 to 38.5-212.0 mg/m^3, the weight percent of all VOCs adsorbed increased. If the number of charcoal cloth layers had been varied, the results would have shown the adsorption capacity of different weight of charcoal cloth for the mixture of VOCs. The adsorption isotherm of toluene in the mixture was also plotted with the adsorption isotherm of toluene at 0% and 40% relative humidity (RH) on 2-layer charcoal cloth (Fig.25). When the concentration of toluene was increased, the weight percent of toluene adsorbed on 2-layer charcoal cloth increased slightly. Considering the adsorption isotherm of toluene at 0% and 40% RH and toluene (40% RH) in the VOC mixture, the concentration of toluene in the VOC mixture was lower than that of toluene tested at 0 and 40% RH. The weight percent of toluene adsorbed from the mixture of VOCs was considerably lower than that of toluene adsorbed at 0 and 40% RH. In the mixture of six VOCs, the concentration of toluene was much lower (4.8-82.0 mg/m^3) than when it was used alone (32-977 mg/m^3). At lower concentrations of VOCs, the binding capacity was reduced. The presence of other VOCs in a mixture

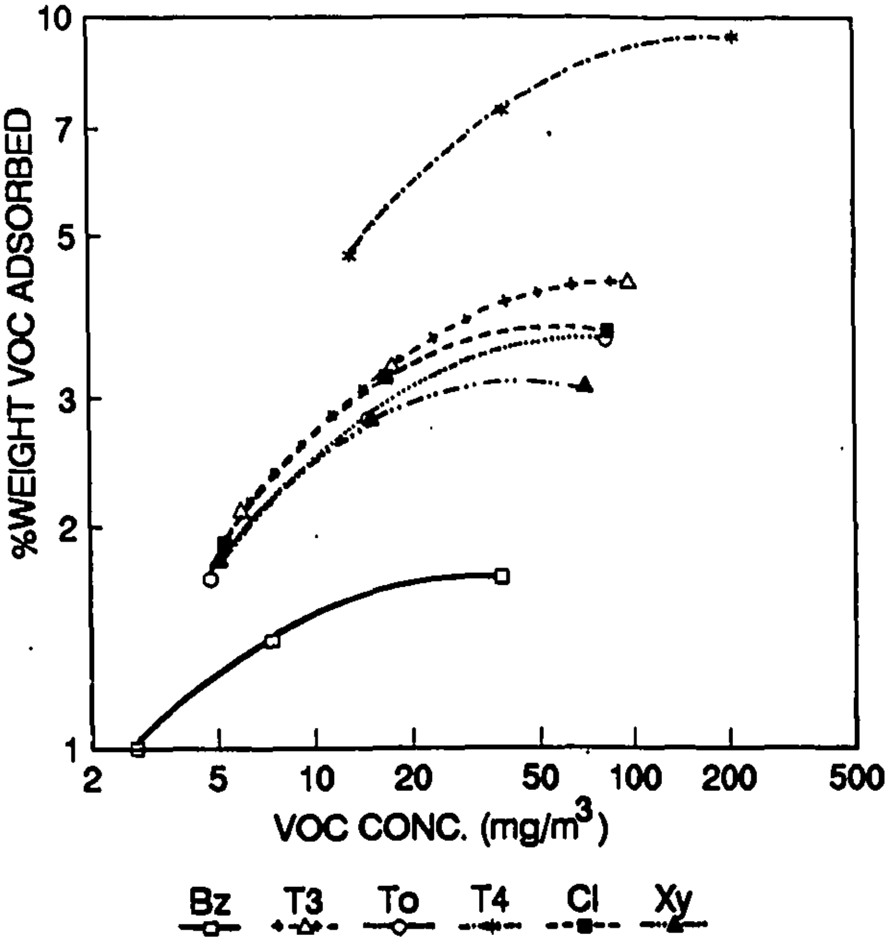


Fig.24 Adsorption isotherms for six volatile organic compounds in a mixture at 40% relative humidity captured on two layers of charcoal cloth. The % weights of chemical adsorbed against chemical concentrations are shown as log-log plots. The chemicals studied include benzene (Bz), trichloroethylene (T3), toluene (To), tetrachloroethylene (T4), chlorobenzene (Cl) and o-xylene (Xy).

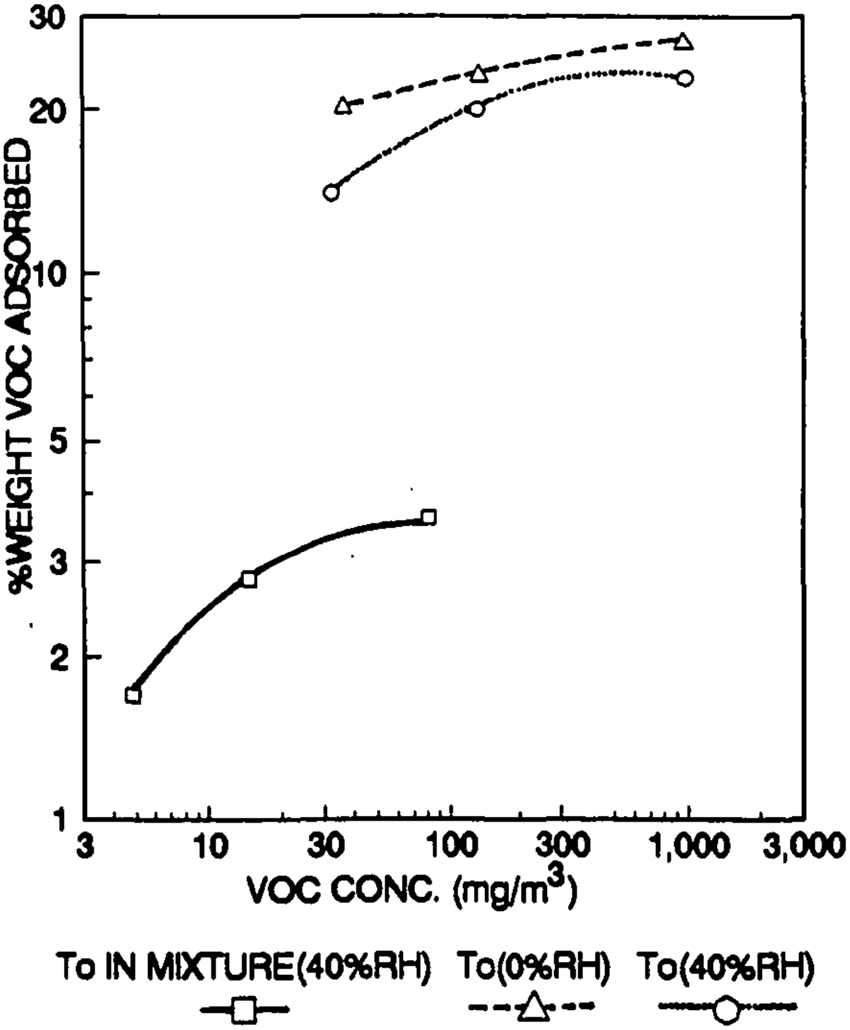


Fig.25 Adsorption isotherms for toluene vapours at 0% and 40% relative humidity captured on two layers of charcoal cloth. This data is shown in relation to the adsorption isotherms plotted in Fig.24.

will also reduce the percent adsorption of toluene on charcoal cloth (Fig.25).

3.2 VOC Recovery from Cloth

3.2.1 Solvent Desorption

The quantitative desorption of individual VOCs from charcoal cloth by pentane, hexane and cyclopentane were plotted as a percent recovered against the logarithm of VOC concentration (Fig.26). Considering the three different solvents tested, pentane and hexane showed higher percent recoveries of individual VOCs from charcoal cloth than cyclopentane. For each individual solvent tested, recovery increased as the VOC concentration increased. Hexane gave the highest percent recoveries for individual VOCs at the concentration of 10 mg. At low VOC concentration, i.e. 0.2 mg, trichloroethylene had the greatest percent recovery and o-xylene and chlorobenzene had the lowest percent recoveries.

The percent recovery of the VOC mixture from charcoal cloth by the three solvents was also reported (Fig.27). The results were similar to those of individual VOCs in that hexane and pentane showed greater percent recovery of the VOC mixture than cyclopentane. At each level of VOC concentrations tested, trichloroethylene and tetrachloroethylene had the greatest percent recoveries among the six chemicals tested for each individual solvents. Chlorobenzene and o-xylene gave the lowest percent recoveries.

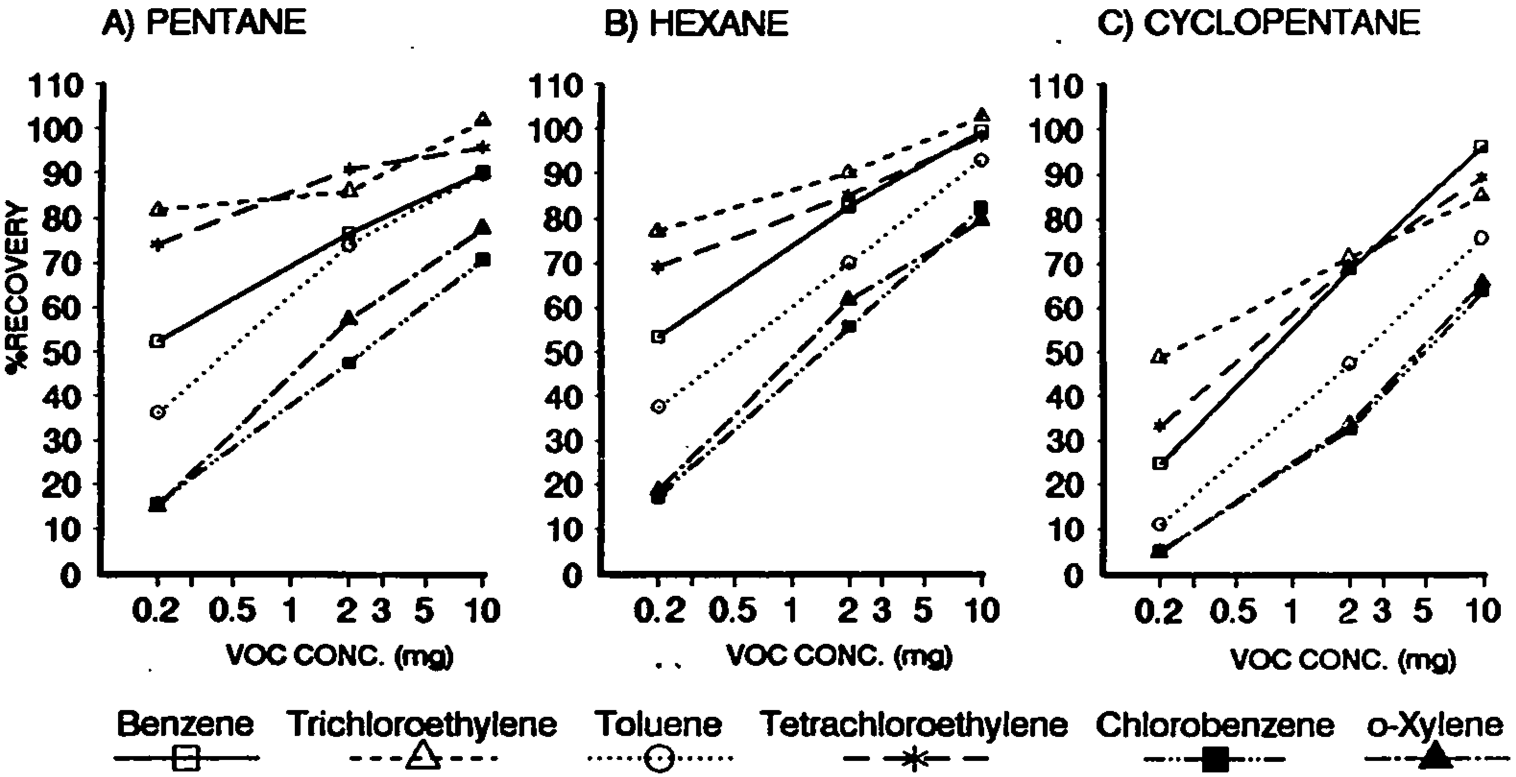


Fig.26 Percent recovery of individual volatile organic compounds by solvent desorption using three different solvents; pentane (A), hexane (B) and cyclopentane (C). The chemicals were applied in different concentrations to two layers of charcoal cloth 30 min prior to extraction.

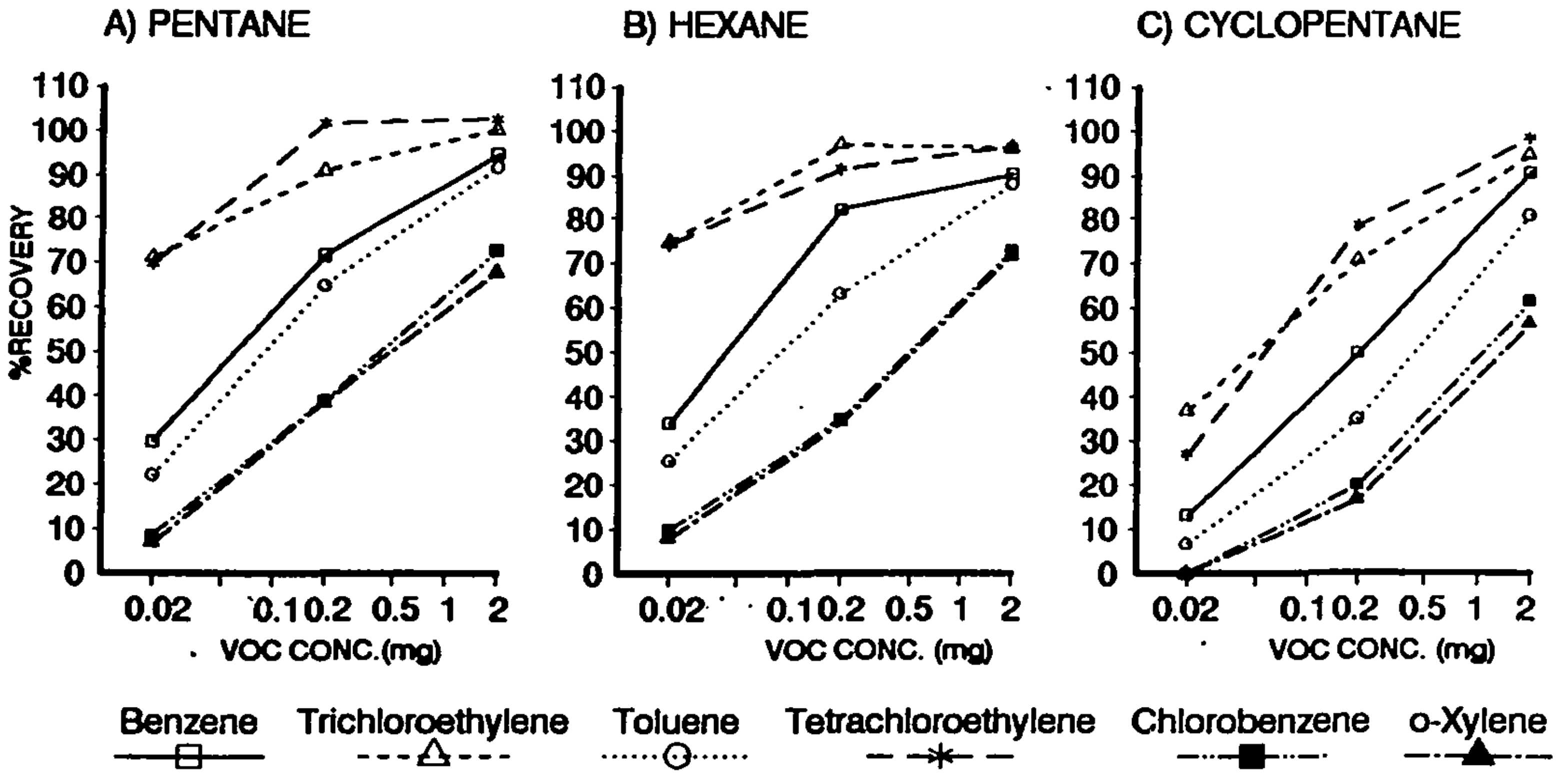


Fig.27 Percent recovery of components of a mixture of volatile organic compounds by solvent desorption using pentane (A), hexane (B) and cyclopentane (C). Various concentrations of the mixture were applied to two layers of charcoal cloth 30 min prior to extraction.

The percent recovery of each VOC in the mixture for three different solvents was found to follow the sequence: tetrachloroethylene ≥ trichloroethylene > benzene > toluene > chlorobenzene ≥ o-xylene.

Considering the extraction of the VOC mixture from charcoal cloth by the solvent pentane and hexane (Fig.27), both trichloroethylene and tetrachloroethylene had the greatest percent recoveries of more than 70% at concentrations of 20 ug of those two chemicals in the mixture. Chlorobenzene and o-xylene gave the lowest percent recoveries (8-10%).

In comparing the percent recoveries of individual VOCs and the VOC mixture from charcoal cloth, the percent recoveries of individual VOCs and the VOC mixture by hexane was comparable to that of pentane, both being considerably greater than cyclopentane (Fig.26 and 27). Considering the desorption of each VOC by hexane, the recovery of 0.2-mg trichloroethylene was 77% (Fig.26) but the recovery of this concentration of trichloroethylene in the mixture was 97% (Fig.27). o-Xylene gave 19% recovery at the concentration of 0.2 mg and this concentration of o-xylene in the mixture resulted in 34% recovery. On an individual VOCs, the recovery of a particular VOC was less than when presented in a mixture. Other chemicals gave the same trend.

A. Method Reliability

The accuracy and precision of solvent extraction was determined in terms of percent recovery and percent coefficient of variation respectively over sampling times of 1,2 and 4 hr and is shown for solvent desorption (hexane) in Table 19. All results were corrected for desorption efficiency of each VOC in the mixture. The recovery of the VOC mixture for 1-hr sampling (concentration range of 126.7-722.8 ug) was in the range of 78.4 to 94.0% and the coefficients of variations were less than 6.7%. For 2-hr sampling (concentration range of 289.5-1,231.7 ug), the recovery was slightly higher than the 1-hr sampling. The recovery ranged from 87.5 to 104.5% and the coefficient of variations were in the range of 3.7 to 7.2%. The high level of VOC mixture (concentration range of 574.1-2,535.3 ug) with 4-hr sampling gave 78.6 to 103.7% recovery and a range of 2.9 to 9.3% coefficient of variation. Benzene and trichloroethylene had the greatest percent recoveries. o-Xylene showed the lowest percent recovery probably due to a a low desorption efficiency of o-xylene with hexane.

The recovery of VOC mixture by pentane desorption is shown in Table 20. For 1-hr sampling, the recovery ranged from 80.8 to 105.5% and the coefficient of variation was less than 7.3%. The recovery of VOC mixture for the 2-hr sampling was in the range of 82.2 to 115.4%, the values for benzene and trichloroethylene being relatively high, possibly due to the high volatility of pentane and these chemicals. The coefficients of variation ranged from 3.2 to 9.9%. The high

Table 19 The Accuracy and Precision of the Method Selected for Sampling a VOC Mixture with a Charcoal Cloth Cassette and Analysis after Hexane Desorption.

VOCs*	ug Expected $\bar{X}$ ± SD	ug Found $\bar{X}$ ± SD	%Recovery $\bar{X}$ ± SD	%CV
<u>1-Hr Sampling</u> (n=5)				
Bz	126.7 ± 0.2	117.2 ± 7.8	92.5 ± 6.2	6.70
T3	281.7 ± 0.6	264.8 ± 10.3	94.0 ± 3.5	3.74
To	270.0 ± 0.9	237.2 ± 6.9	87.8 ± 2.5	2.81
T4	722.8 ± 5.1	592.9 ± 11.6	82.0 ± 1.5	1.86
Cl	330.6 ± 2.7	271.7 ± 9.3	82.2 ± 2.7	3.26
Xy	339.2 ± 5.5	265.9 ± 14.3	78.4 ± 5.2	6.57
<u>2-Hr Sampling</u> (n=5)				
Bz	289.5 ± 7.9	302.3 ± 16.6	104.5 ± 6.9	6.60
T3	569.4 ± 14.1	593.9 ± 32.6	104.4 ± 7.5	7.18
To	479.9 ± 3.0	440.9 ± 16.0	91.9 ± 3.4	3.66
T4	1,231.7 ± 16.6	1,077.5 ± 35.4	87.7 ± 4.1	4.68
Cl	547.3 ± 6.7	505.4 ± 23.1	92.4 ± 4.9	5.34
Xy	530.9 ± 16.1	464.3 ± 9.0	87.5 ± 3.4	3.85
<u>4-Hr Sampling</u> (n=5)				
Bz	574.1 ± 43.7	547.1 ± 70.2	95.0 ± 5.3	5.52
T3	1,158.2 ± 112.5	1,197.0 ± 76.3	103.7 ± 5.5	5.29
To	992.2 ± 51.8	902.0 ± 32.3	91.0 ± 2.2	2.45
T4	2,535.3 ± 155.5	2,194.8 ± 65.8	86.8 ± 4.4	5.04
Cl	1,085.7 ± 144.8	991.1 ± 41.4	92.2 ± 8.6	9.28
Xy	1,122.3 ± 54.9	881.6 ± 17.7	78.6 ± 2.3	2.87

*Bz = Benzene
T3 = Trichloroethylene
To = Toluene
T4 = Tetrachloroethylene
Cl = Chlorobenzene
Xy = o-Xylene

Table 20 The Accuracy and Precision of the Method Selected for Sampling a VOC Mixture with a Charcoal Cloth Cassette and Analysis after Pentane Desorption.

VOCs*	ug Expected $\bar{X}$ ± SD	ug Found $\bar{X}$ ± SD	%Recovery $\bar{X}$ ± SD	%CV
1-Hr Sampling (n=5)				
Bz	126.9 ± 0	131.8 ± 9.6	103.9 ± 7.6	7.27
T3	281.4 ± 0.8	296.9 ± 13.1	105.5 ± 4.4	4.21
To	296.2 ± 0.7	243.8 ± 13.0	90.6 ± 4.7	5.19
T4	712.1 ± 1.4	605.4 ± 15.7	85.0 ± 2.4	2.78
Cl	325.2 ± 0.4	275.1 ± 13.1	84.6 ± 4.1	4.79
Xy	330.4 ± 0.9	267.0 ± 9.5	80.8 ± 2.7	3.38
2-Hr Sampling (n=5)				
Bz	282.5 ± 8.7	312.8 ± 21.8	111.7 ± 6.3	5.60
T3	575.5 ± 18.1	664.4 ± 35.4	115.4 ± 4.3	3.72
To	509.0 ± 18.1	490.2 ± 45.2	96.2 ± 6.3	6.55
T4	1,311.1 ± 50.5	1,255.6 ± 72.2	95.7 ± 3.1	3.21
Cl	598.2 ± 43.8	506.3 ± 50.7	84.8 ± 7.7	9.13
Xy	573.9 ± 52.8	469.1 ± 27.8	82.2 ± 8.1	9.90
4-Hr Sampling (n=5)				
Bz	526.2 ± 14.2	519.6 ± 37.0	98.7 ± 5.4	5.48
T3	1,127.1 ± 35.9	1,068.1 ± 58.9	94.8 ± 5.7	6.03
To	1,021.1 ± 18.5	887.9 ± 26.0	87.0 ± 4.0	4.63
T4	2,651.6 ± 59.9	2,314.5 ± 72.8	87.4 ± 4.5	5.12
Cl	1,241.4 ± 46.7	956.6 ± 11.0	77.3 ± 3.9	5.02
Xy	1,194.4 ± 44.8	917.6 ± 39.3	77.0 ± 5.2	6.73

*Bz = Benzene
T3 = Trichloroethylene
To = Toluene
T4 = Tetrachloroethylene
Cl = Chlorobenzene
Xy = o-Xylene

level of VOC mixture (4-hr sampling) had 77.0 to 98.7% recovery and 4.6 to 6.7% coefficient of variation. Benzene and trichloroethylene had the highest percent recovery and o-xylene the lowest using pentane.

The utility of using either hexane, a neurotoxicant, or pentane a relatively volatile substance as the solvent to extract VOCs from charcoal cloth was compared, the results being shown in Fig.28. The black and the white bars indicate the percent recovery of the test VOCs by hexane and pentane respectively. For the 1-hr sampling period, pentane gave slightly higher percent recovery for benzene and trichloroethylene but comparable results were observed with either solvent for the other VOCs. At the medium VOC concentration (2-hr sampling), pentane desorption gave higher percent recoveries only for trichloroethylene. At the high VOC concentration (4-hr sampling), pentane and hexane desorption showed comparable results except for chlorobenzene.

Summary results of 1,2,4-hr sampling and analysis of VOC mixtures using charcoal cassette at 20-23°C, 40% relative humidity and a flow rate of 200 ml/min are shown in Table. 21 and 22 for hexane and pentane desorption respectively. The concentration ranges tested for each VOC in the mixture by hexane desorption were as follows: benzene (10.1-12.6 mg/m^3), trichloroethylene (19.7-24.6 mg/m^3), toluene (18.5-22.0 mg/m^3), tetrachloroethylene (47.0-59.0 mg/m^3), chlorobenzene (18.5-27.0 mg/m^3), and o-xylene (20.1-27.8 mg/m^3). The overall

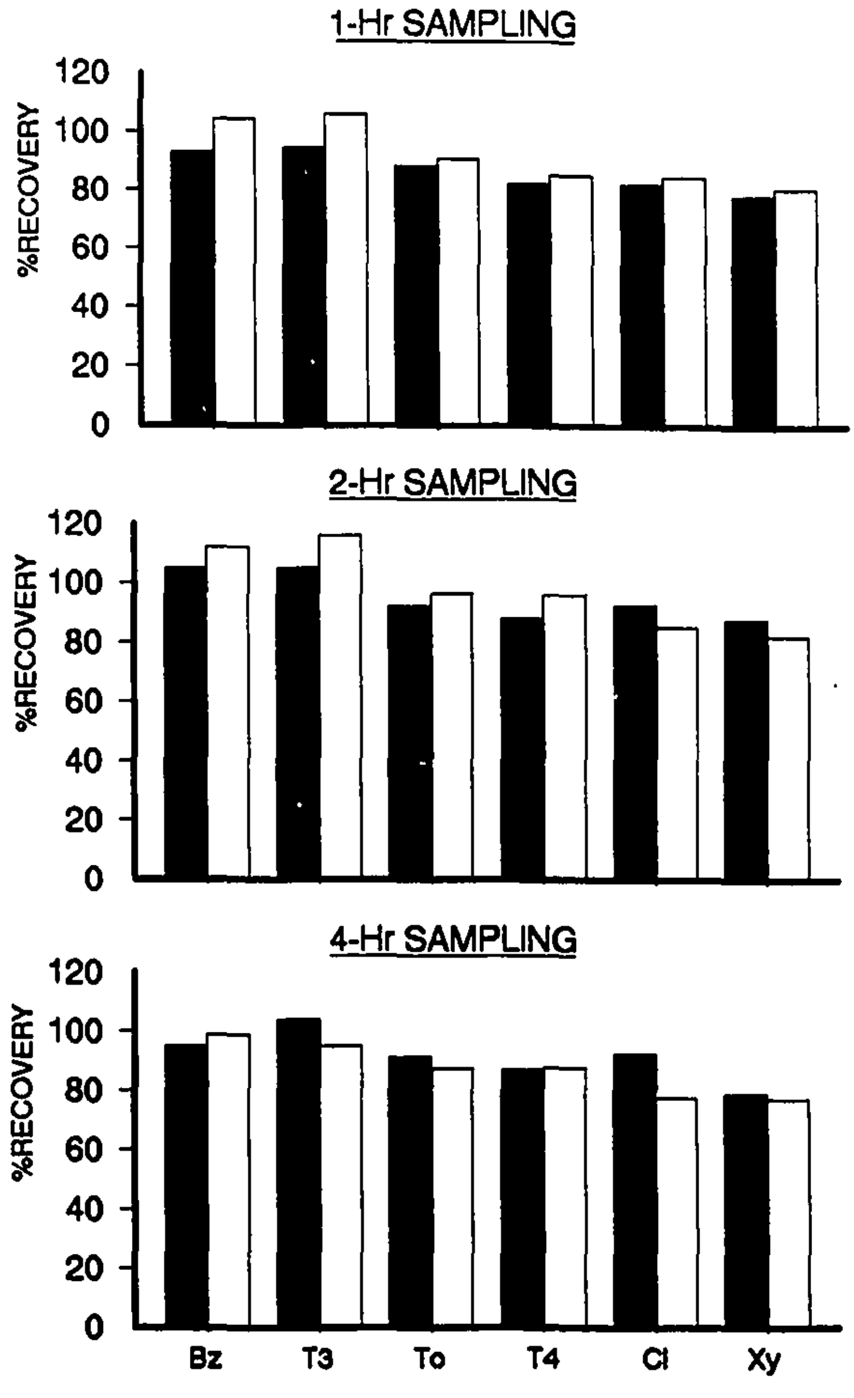


Fig.28 Average percent recovery of the components of a mixture of volatile organic compounds following 1-, 2- and 4-hr sampling by charcoal cloth cassette and desorption of the trapped compounds with hexane (solid bars) and pentane (open bars). Abbreviations include benzene (Bz), trichloroethylene (T3), toluene (To), tetrachloroethylene (T4), chlorobenzene (Cl) and o-xylene (Xy).

Table 21 1,2 and 4-Hr Sampling, Average Precision and Accuracy of Hexane Desorption and Analysis of VOC Mixtures Using the Charcoal Cloth Cassette.*

VOCs**	Concentration tested(mg/m^3)	Range tested(ug)	%$\hat{B}$***	Precision %$\overline{\overline{CV}}_T$+	Accuracy %O.S.A++
Bz	10.1-12.6	126.7-547.1	-2.58	6.30	14.93
T3	19.7-24.6	281.7-1,158.2	+0.55	5.58	11.49
To	18.5-22.0	270.0-992.2	-10.15	3.02	16.07
T4	47.0-59.0	592.9-2,194.8	-14.64	3.84	22.17
Cl	18.5-27.0	330.6-1,085.7	-11.38	6.46	24.04
Xy	20.1-27.8	339.2-1,122.3	-18.54	4.70	27.75

* Operating conditions at the temperature of 20-23 °C, 40% relative humidity and a flow rate of 200 ml/min.

** Bz = Benzene
T3 = Trichloroethylene
To = Toluene
T4 = Tetrachloroethylene
Cl = Chlorobenzene
Xy = o-Xylene

*** %$\hat{B}$, Mean bias (error) = $\Sigma n_i B_i / \Sigma n_i$, n = 5

%B_i = 100(Found-Expected)/Expected

\+ %$\overline{\overline{CV}}_T$ = The precision of the sampling and analytical method

%$\overline{\overline{CV}}_T$ = $[\Sigma (CV_i)^2 f_i / \Sigma f_i]^{1/2}$, n = 5 , f = 4

++ O.S.A. = Overall system accuracy

O.S.A = $[1.96(\overline{\overline{CV}}_T)$ + Absolute mean bias, $|\hat{B}|$]

Table 22 1,2 and 4-Hr Sampling, Average Precision and Accuracy of Pentane Desorption and Analysis of VOC Mixtures Using the Charcoal Cloth Cassette.*

VOCs**	Concentration tested(mg/m^3)	Range tested(ug)	$\%\hat{B}$***	Precision $\%\overline{CV}_T$+	Accuracy %O.S.A++
Bz	10.4-11.3	126.9-526.2	+4.44	6.17	16.53
T3	20.7-24.0	281.4-1,127.1	+5.26	4.76	14.59
To	18.6-22.0	296.2-1,021.1	-11.81	5.52	22.63
T4	48.0-58.5	712.1-2,651.6	-10.64	3.84	18.17
Cl	23.0-27.0	325.2-1,241.4	-17.91	6.62	30.62
Xy	21.3-27.0	330.4-1,194.4	-20.21	7.18	34.28

* Operating conditions at the temperature of 20-23 °C, 40% relative humidity and a flow rate of 200 ml/min.

** Bz = Benzene
T3 = Trichloroethylene
To = Toluene
T4 = Tetrachloroethylene
Cl = Chlorobenzene
Xy = o-Xylene

*** $\%\hat{B}$, Mean bias (error) = $\mathcal{E} n_i B_i / \mathcal{E} n_i$, n = 5

$\%B_i$ = 100(Found-Expected)/Expected

\+ $\%\overline{CV}_T$ = The precision of the sampling and analytical method

$\%\overline{CV}_T = [\, \mathcal{E}(CV_i)^2 f_i / \mathcal{E} f_i \,]^{1/2}$, n = 5 , f = 4

++ O.S.A. = Overall system accuracy

O.S.A. = $[1.96(\overline{CV}_T)$ + Absolute mean bias,$|\hat{B}|]$

precision for 1,2,4-hr sampling and analysis of VOC mixture by hexane desorption was less than 6.5% and the overall accuracy was less than 25% except for o-xylene (Table 21). For the pentane desorption, the overall accuracy of chlorobenzene and o-xylene was 30.6 and 34.3% respectively (Table 22) because of the low desorption efficiency of these chemicals from the charcoal. The overall accuracy of benzene, trichloroethylene, toluene and tetrachloroethylene was acceptable within 25%. The overall precision ranged from 3.8 to 7.2%.

B. Storage Stability

Can charcoal-adsorbed VOCs from "environments" be stored for any length of time before analysis? This question was approached by applying the mixture of VOCs on charcoal cloth, storing the charcoal cloth at either refrigerated (4°C) or at room temperature in tightly sealed glass vials for 1, 2, 4, 8, 16, 24 and 32 days prior to extraction of the VOCs with pentane. The results are shown in Fig.29. The average percent recoveries of VOC mixture on charcoal cloth storage in refrigerated temperature were comparable to those storage in room temperature. The recovery (corrected for desorption efficiency) of benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene were in the range of 94.3-105.9, 90.4-103.5, 95.7-105.3, 95.6-102.4, 98.2-109.0 and 99.2-110.9% respectively over 32 days of storage. The average recoveries of chlorobenzene and o-xylene were

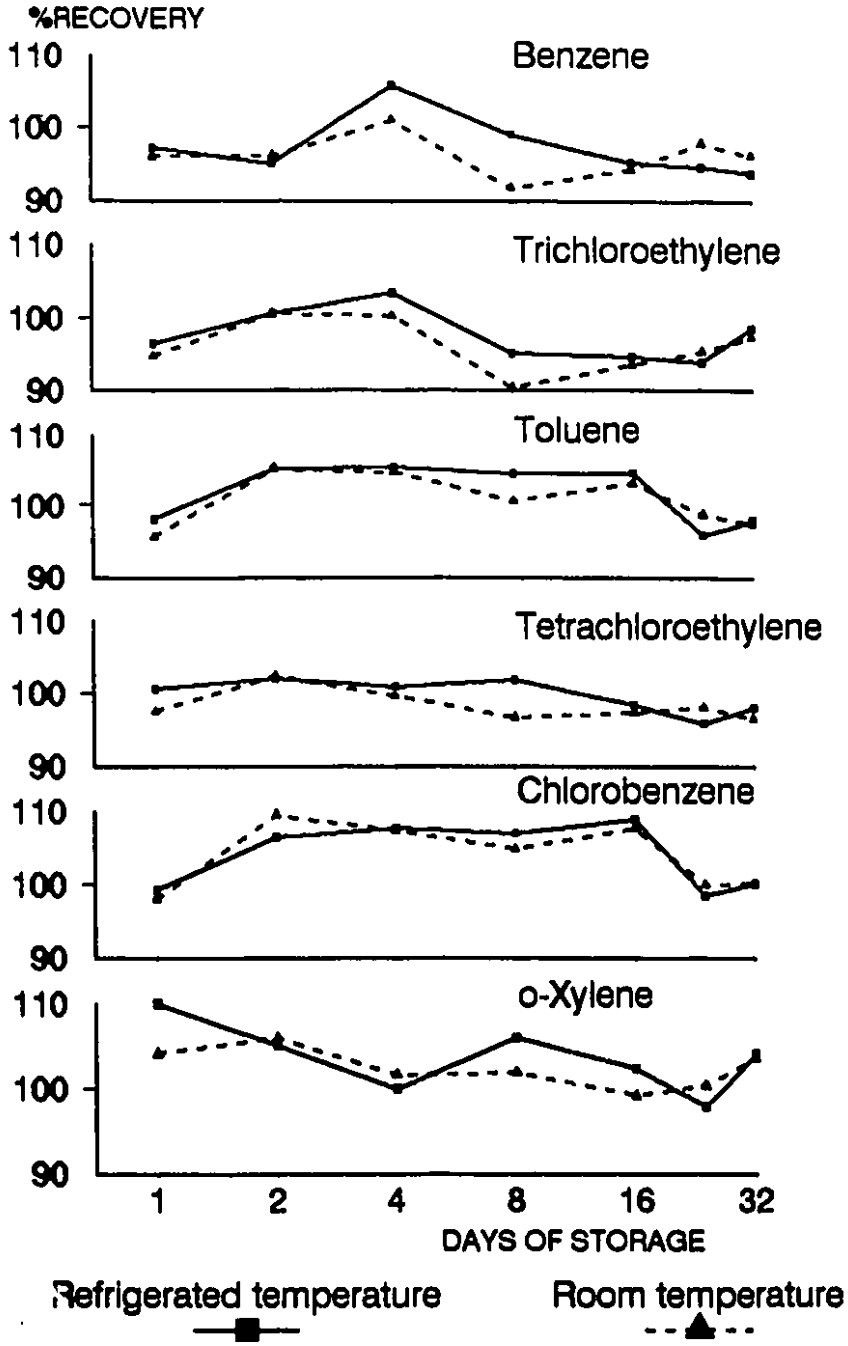


Fig.29 Stability of volatile organic compounds on charcoal cloth over a period of 32 days storage in refrigerated (4 °C) and at room temperature (23 °C) in sealed vials. The VOCs were desorbed from the charcoal cloth with pentane.

slightly over 100%. The storage stability of the VOC mixture on charcoal cloth gave a slightly narrower range of percent recovery following hexane desorption (Fig.30). The range of percent recovery for benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene was 92.5-100.9, 94.3-101.6, 100.3-104.1, 96.1-101.0, 98.1-103.4 and 97.3-103.3 respectively (Fig.30). The results suggested that the variability seen with pentane desorption might be accounted for by evaporation of the extracting solvent. The storage temperature did not have much influence on the loss of VOC mixture from stored charcoal cloth except for benzene and trichloroethylene within experimental error.

3.2.2 Supercritical Fluid Extraction

A. Desorption Efficiency of VOCs by SFE

The optimal conditions for SFE of VOCs on charcoal cloth were determined to be an extraction time of 45 min, a restrictor temperature of 150°C, an oven temperature of 150°C and the temperature of collecting vials at 5°C. This left one parameter, atmospheric pressure (flow rate), to be altered. Using three collecting solvents, pentane, hexane and decane, the desorption efficiencies of spiked charcoal cloth discs placed in extraction cells at different pressures (flow rate) are shown in Fig.31 and 32. Black bars indicate mean desorption efficiencies by SFE while the white bar on top indicates hexane-solvent extraction of residual VOCs

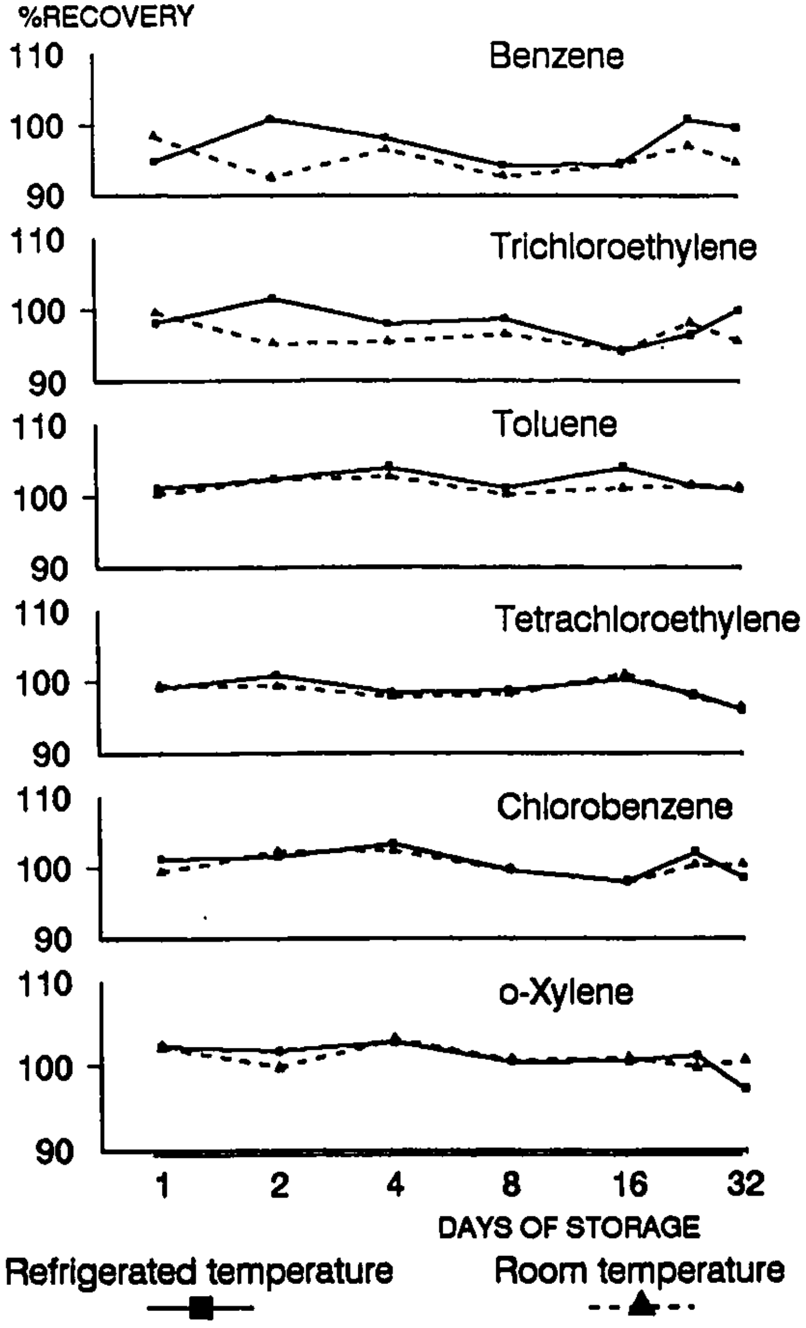


Fig.30 Stability of volatile organic compounds on charcoal cloth over a period of 32 days storage in refrigerated (4 °C) and at room temperature (23 °C) in sealed vials. The VOCs were desorbed from the charcoal cloth with hexane.

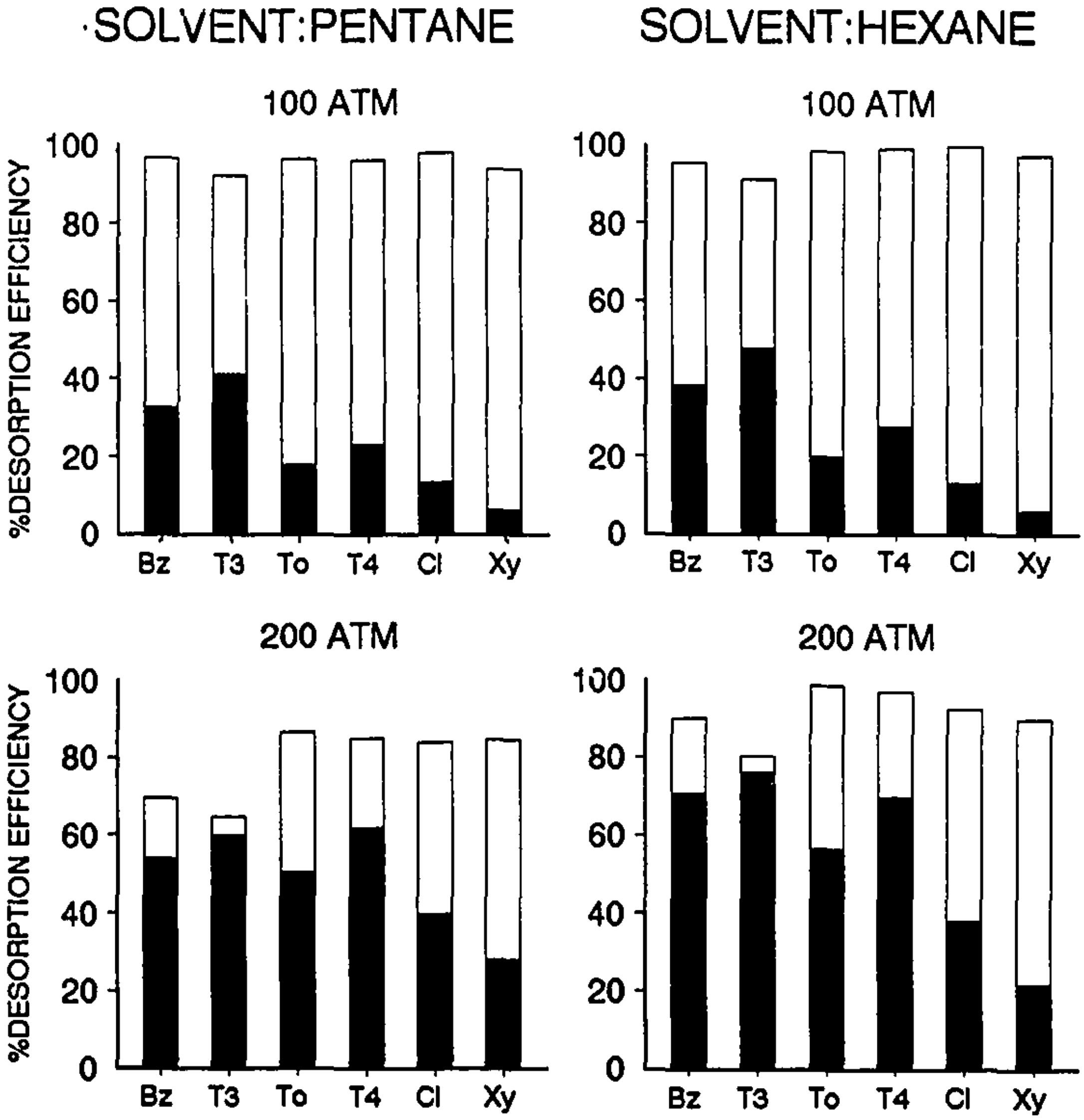


Fig.31 Supercritical fluid extraction (SFE) of charcoal cloth (two layers) pretreated with a mixture of VOCs, using liquid carbon dioxide at 100 or 200 atmospheres (ATM) and either pentane or hexane as the collecting solvent(s). The solid bars represent the average percent desorption by SFE while the open bars represent the average percent solvent desorption (hexane) of residual organics adhering to the cloth. For abbreviations, see Fig.28.

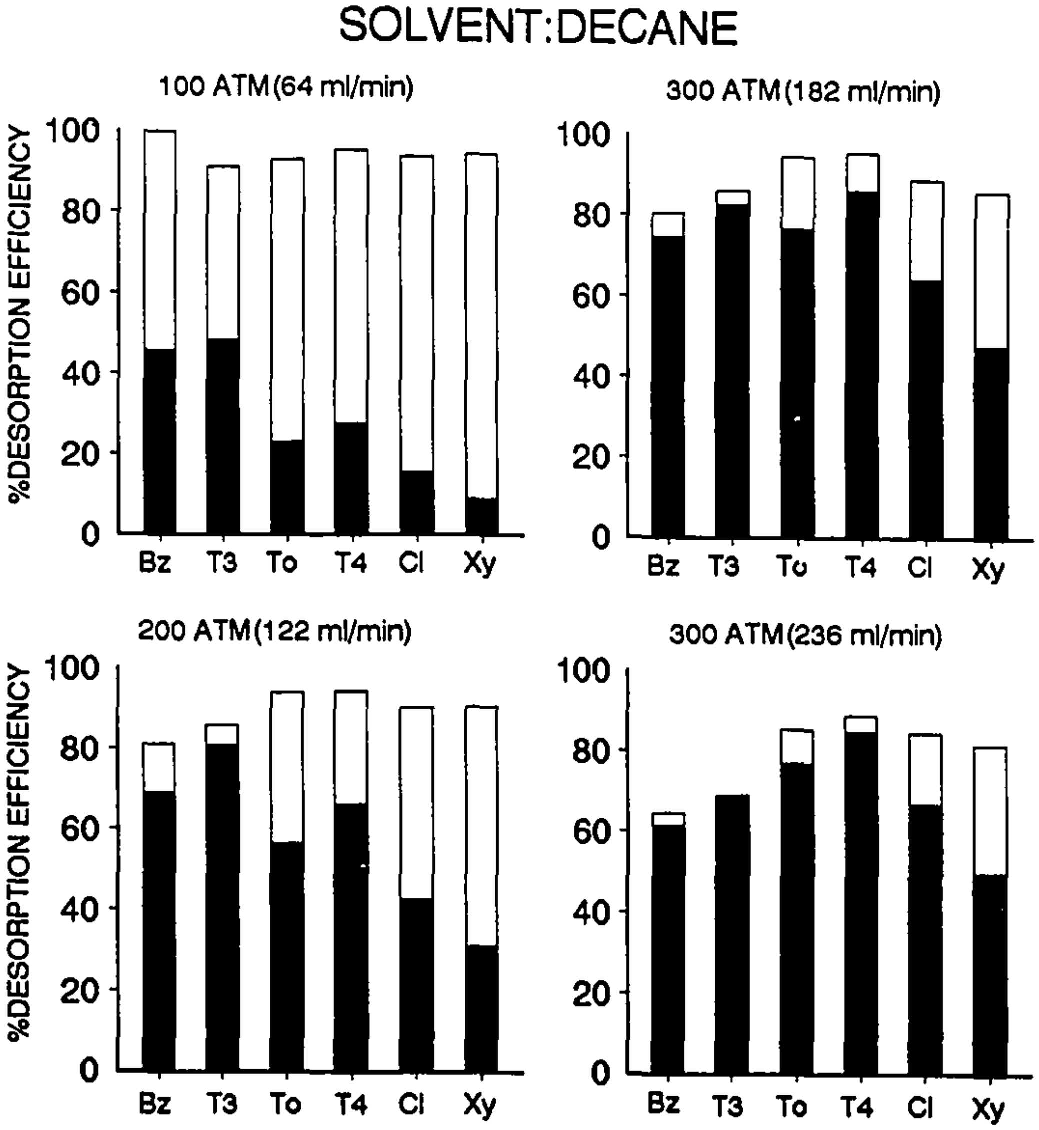


Fig.32 Supercritical fluid extraction (SFE) of charcoal cloth (two layers) pretreated with a mixture of VOCs, using liquid carbon dioxide at 100, 200 and 300 atmospheres (ATM) and decane as the collecting solvent. The solid bars represent the average percent desorption by SFE while the open bars represent the average percent solvent desorption (hexane) of residual organics adhering to the cloth. For abbreviations, see Fig.28.

(corrected for desorption efficiency) not removed from the cloth by SFE. The results were highly variable and the average desorption efficiency from five replications was used (the standard deviations are not shown in the graph). When pentane was used as a collecting solvent at the pressure of 100 ATM, the desorption of VOC mixture on charcoal cloth by SFE ranged from 6 to 41% and trichloroethylene gave the greatest desorption efficiency (Fig.31). The desorption efficiency of SFE was so poor that solvent extraction of residual VOCs (corrected for desorption efficiency) on the charcoal cloth was necessary to determine whether or not residues remained on the cloth. The results showed that the total recovery of the VOC mixture on charcoal cloth for both SFE and hexane-solvent desorption was more than 92%. The loss of VOCs from the collecting vials at 100 ATM was not obvious. At higher pressure (200 ATM) and a higher flow rate, the desorption of VOC mixture on charcoal cloth by SFE was increased from 6-41% to 28-62% but the total recovery of VOCs from charcoal cloth was reduced from 92-99% to 65-87%. Trichloroethylene gave the lowest total recovery. The results suggested that VOCs were lost from the collecting vials and the loss was greater at higher pressure (200 ATM) than at lower pressure (100 ATM) (Fig.31). These results suggested that a less volatile solvent should be placed in the collecting vials. However, similar results were observed with hexane as the collecting solvent. The desorption of the VOC mixture on charcoal cloth by SFE ranged from 6 to 48% and from 22 to 76% at the pressure of 100 and 200 ATM respectively. The total recovery of VOC mixture ranged from 91-100% at the pressure of 100 ATM and it dropped to 81-99% when the pressure inside the extraction cell was 200 ATM. Comparing the two different collecting solvents, pentane and hexane, the desorption efficiency of the VOC mixture spiked on charcoal cloth by SFE was greater with hexane as collecting solvent than with pentane at both pressure levels tested. The total recovery from both SFE and hexane-solvent extraction was also greater with hexane than pentane at the pressure of 200 ATM. A less volatile solvent than pentane and hexane would be more useful, trapping the VOCs rather than allowing them to "blow" through, and less likely to be evaporated during the 45 min extraction time.

Decane was also tried as a collecting solvent for SFE of the spiked VOC mixture on charcoal cloth. The average desorption efficiencies by SFE and hexane-solvent desorption from at least four replicate determinations are shown in Fig.32. As was observed previously, the desorption efficiencies of VOC mixture on charcoal cloth by SFE increased from 9-48% to 31-81% at pressures of 100 and 200 ATM respectively. Trichloroethylene gave the greatest desorption efficiency by SFE but o-xylene had the lowest desorption at both levels of pressure studied. At the lower pressures, considerable residues of all VOCs remained on the charcoal cloth and could be removed by solvent extraction. Among the three collecting solvents tested, there was better extraction as one went from pentane < hexane < decane. It seemed that decane might be an appropriate solvent for trapping VOCs in the collecting vials but decane gave a broad solvent peak at the retention time of 16 min. While it did not interfere with the VOC mixture resolution, it increased the analysis time of GLC for one sample from 12 min to 25 min (Fig.33).

It was noted that, during repeated use of the SFE restrictors, flow rates decreased, this observation suggesting that there was partial obstruction of the restrictors. At the pressure of 300 ATM, old and new restrictors gave flow rates of 182 and 236 ml/min respectively at optimal conditions (oven temperature of 150°C and restrictor temperature of 200°C). The old restrictor with a flow rate of 182 ml/min showed higher desorption efficiencies of most of the VOCs (benzene and trichloroethylene in particular) than the new restrictor with higher flow rate of 236 ml/min (Fig.32). The total recovery of VOC mixture from both SFE and hexane-solvent desorption was greater at lower flow rate than at higher flow rate. However, the best results were obtained even with decane at optimal conditions (oven temperature of 150°C and at pressure of 300 ATM) SFE did not exceed 80%. Tetrachloroethylene showed the greatest desorption efficiency by SFE. For trichloroethylene, recovery by solvent extraction revealed no residues on the cloth at higher flow rate,

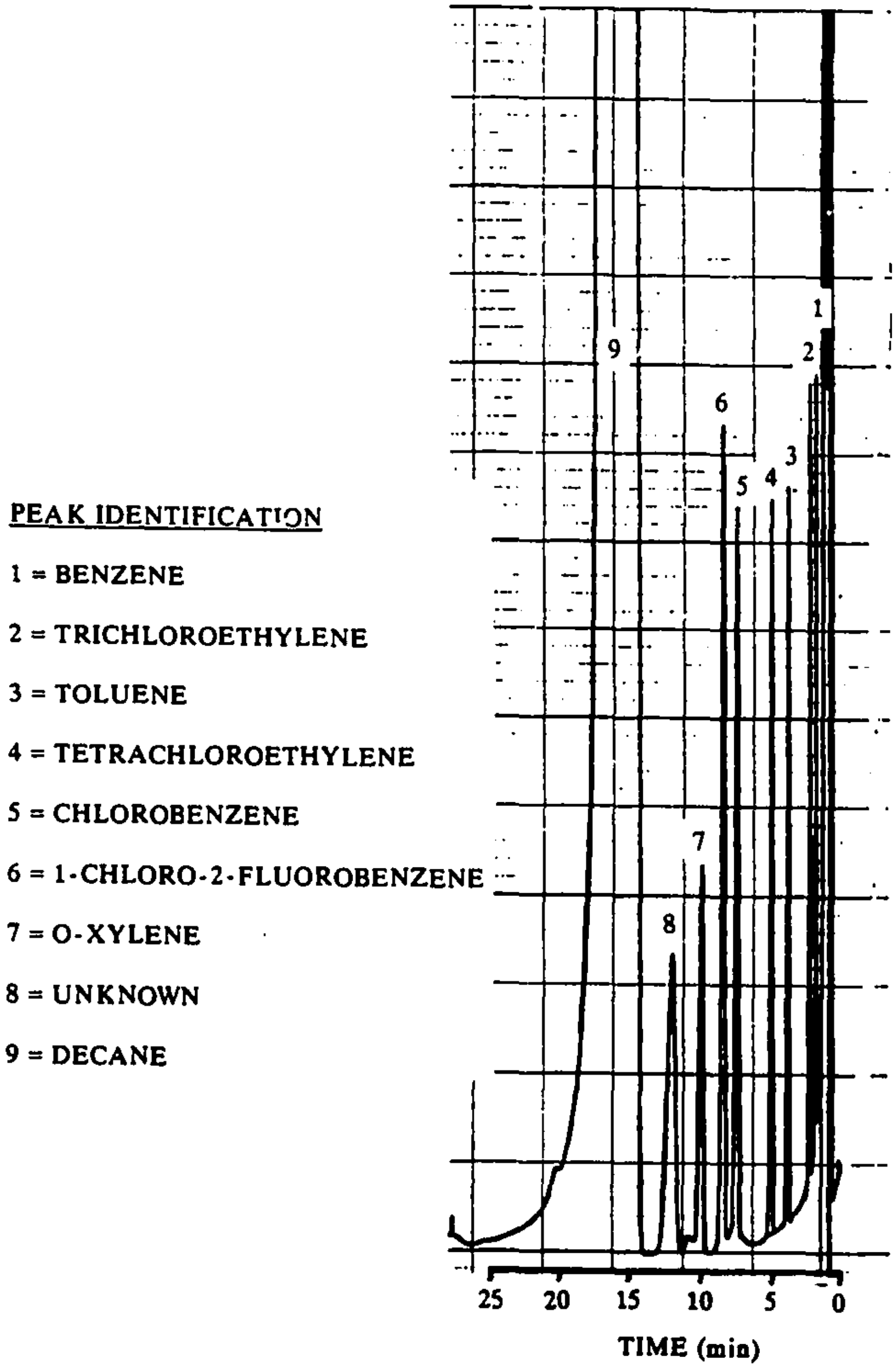


Fig.33 A chromatogram of the mixture of VOCs in decane measured by GLC/PID following supercritical fluid extraction from charcoal cloth (two layers) pretreated with VOCs 30 min prior to extraction. For operating conditions of GLC/PID, see Fig.12.

indicative of loss of the most volatile compounds from collecting vials.

B. Loss of VOCs through the vent lines during SFE

The previous experiments, apparently indicated that the VOCs were evaporating from the collecting vials. The loss was greater at higher pressure (flow rate) than at lower pressure (flow rate). The loss of VOCs might be caused by volatility of the collecting solvents and the VOCs, this being related to the pressure and flow rates used during SFE. This hypothesis was explored by placing known volumes (10 ml) of either pentane, hexane or decane and a known amount of the VOC mixture in the collecting vials and, with charcoal cloth in the extraction chambers, running the SFE under optimal conditions (extraction time of 45 min, oven temperature of 150 °C, restrictor temperature of 150 °C and the temperature of collecting vials at 5°C). The possibility of losing VOCs from the collecting vials was only through the vent lines during SFE, a feature that was confirmed by the results in Fig.34 showing the average percent loss of VOCs. When pentane was used to collect VOCs at 100 ATM (flow rate of 67 ml/min) and 200 ATM (flow rate of 205 ml/min), only 5-6 ml and 2-3 ml of pentane were left at these two pressures, respectively in the collecting vials after extraction. The loss of each VOC in the mixture was considerably greater at higher pressure (200 ATM) than at lower pressure (100 ATM). Benzene, the most

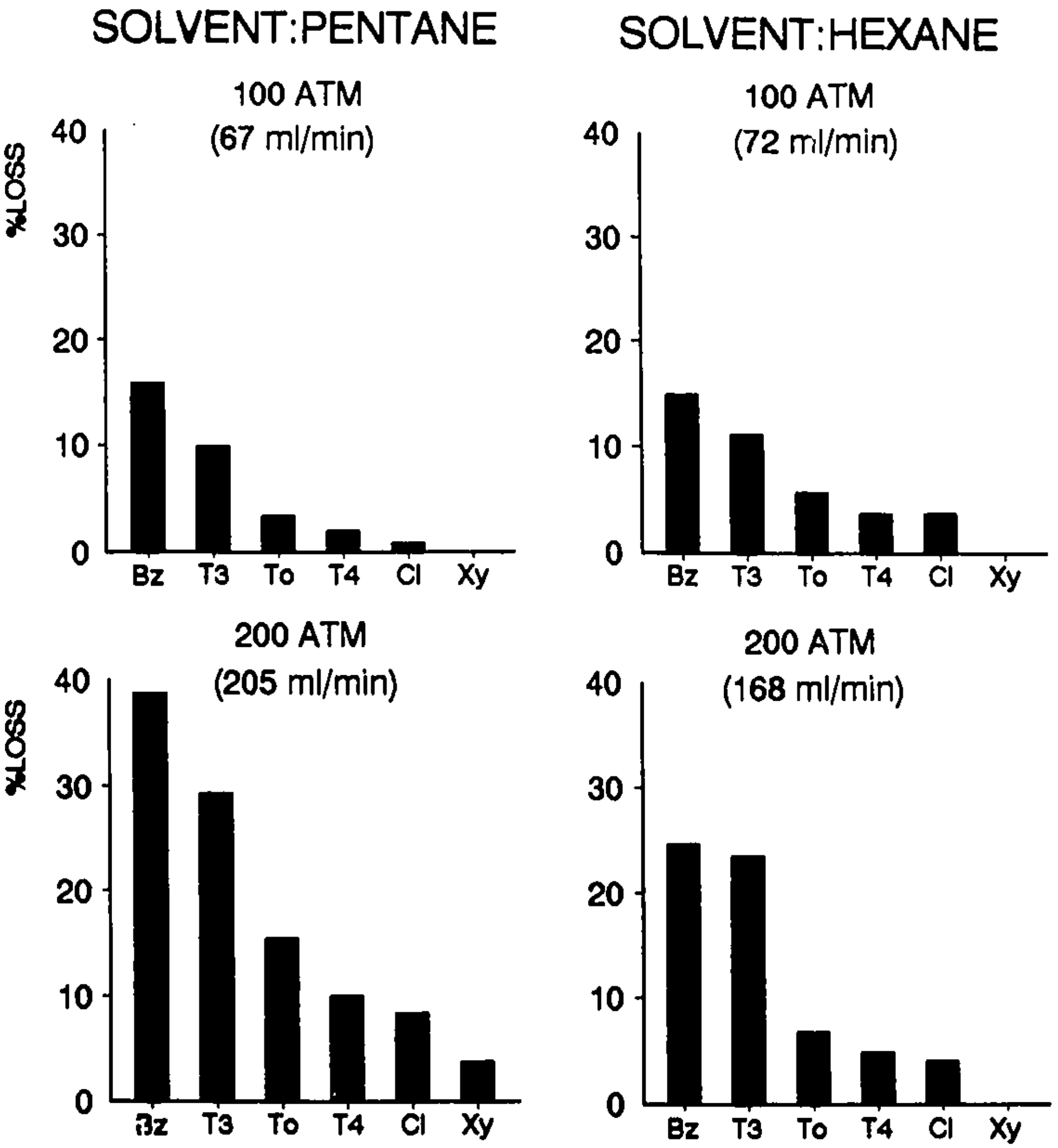


Fig.34 Average percent loss of VOCs through the vent lines during supercritical fluid extraction, the mixture of VOCs being added to the collecting solvents, pentane or hexane and liquid carbon dioxide being used at pressures of 100 or 200 atmospheres (ATM). For abbreviations, see Fig.28.

volatile chemical among the six VOCs tested, showed the greatest loss at both 100 and 200 ATM and o-xylene gave the least loss. The collecting solvent hexane showed the same trend. With a 10 ml volume of hexane, only 7-8 ml of hexane remained in the collecting vials after extraction at 200 ATM while there appeared to be no loss of collecting solvent at 100 ATM. The loss of VOCs with the collecting solvent hexane was less than that of VOCs with pentane at high pressure (200 ATM).

Under similar experimental conditions with decane as the collecting solvent, there was significantly less loss of the VOCs of interest but, again, at higher flow rate (pressure), loss increased (Fig.35). At the pressure of 300 ATM, the graph shows new vs older flow restrictors having different flow rates, illustrating another problem, partial occlusion of the restrictor. The old restrictor gave low flow rate of 180 ml/min and less loss of VOCs than the new one (flow rate of 240 ml/min). The loss of VOCs through the vent lines was increased as the pressure and flow rate increased and the loss was greater with such highly volatile chemicals, as benzene. The temperature of the collecting vials at 5 °C was not sufficiently low to minimize the evaporation of the collecting solvents and VOCs.

3.2.3 Thermal Desorption

The 2-layer charcoal cloth, spiked with one ul of hexane,

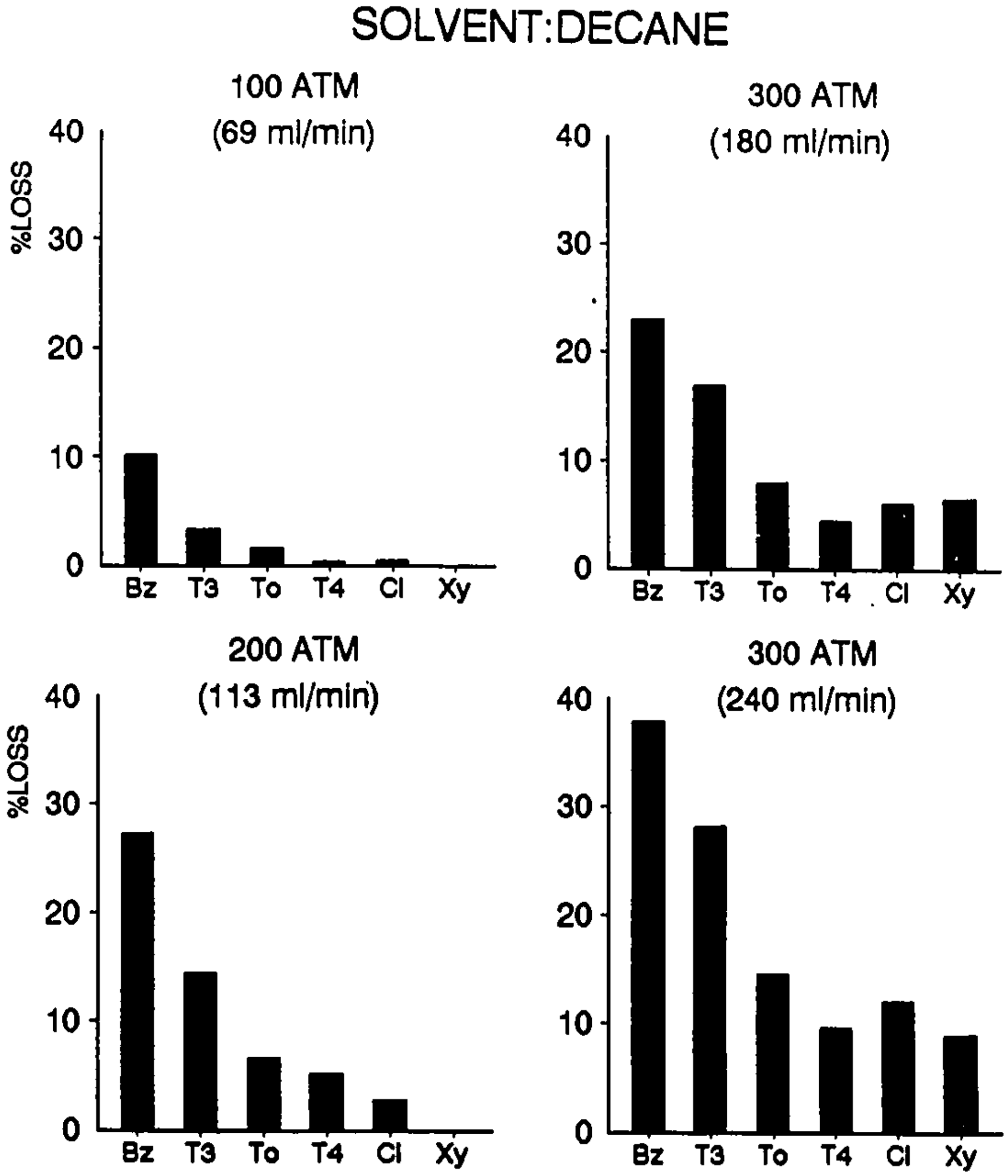


Fig.35 Average percent loss of VOCs through the vent lines during supercritical fluid extraction, the mixture of VOCs being added to the collecting solvent, decane and liquid carbon dioxide being used at pressures of 100, 200 and 300 atmospheres (ATM). For abbreviations, see Fig.28.

was placed in the model 3 cassette (Fig.8) and purged with flow of helium at 300°C (temperature at the surface of the charcoal cloth) for one hour. When the cassette was used as a thermal desorber, temperatures of liquid nitrogen of -30, -70 and -100°C could not condense hexane at the inlet to the GLC column (Fig.36). The broad peak of hexane appeared at the onset of the desorption mode when the temperature of liquid nitrogen was set at -30°C and it reduced with the decrease of the temperature of liquid nitrogen. At a temperature of -100°C for one hr, the hexane peak was smaller and narrower but gas pressure built up in the GLC column. This high pressure buildup in the column for nearly an hour would make it difficult for the gas mixture to pass through the column and it could lead to lower percent recovery. The pressure buildup at the GLC column may have been due to frozen water vapour in the helium carrier gas at the beginning of the liquid nitrogen cooled column. To avoid this difficulty, ultra-high-purity helium carrier gas was used. With this modification, the temperature could be reduced to -120°C to trap the VOCs at the beginning of GLC column without pressure buildup in the column.

Since it took an hour to remove hexane from the charcoal cloth by thermal desorption, it might be advantageous to capture the evaporated hexane in a trapping device which could be thermally desorbed more readily into the capillary interface. The adsorption capacity of two traps was studied

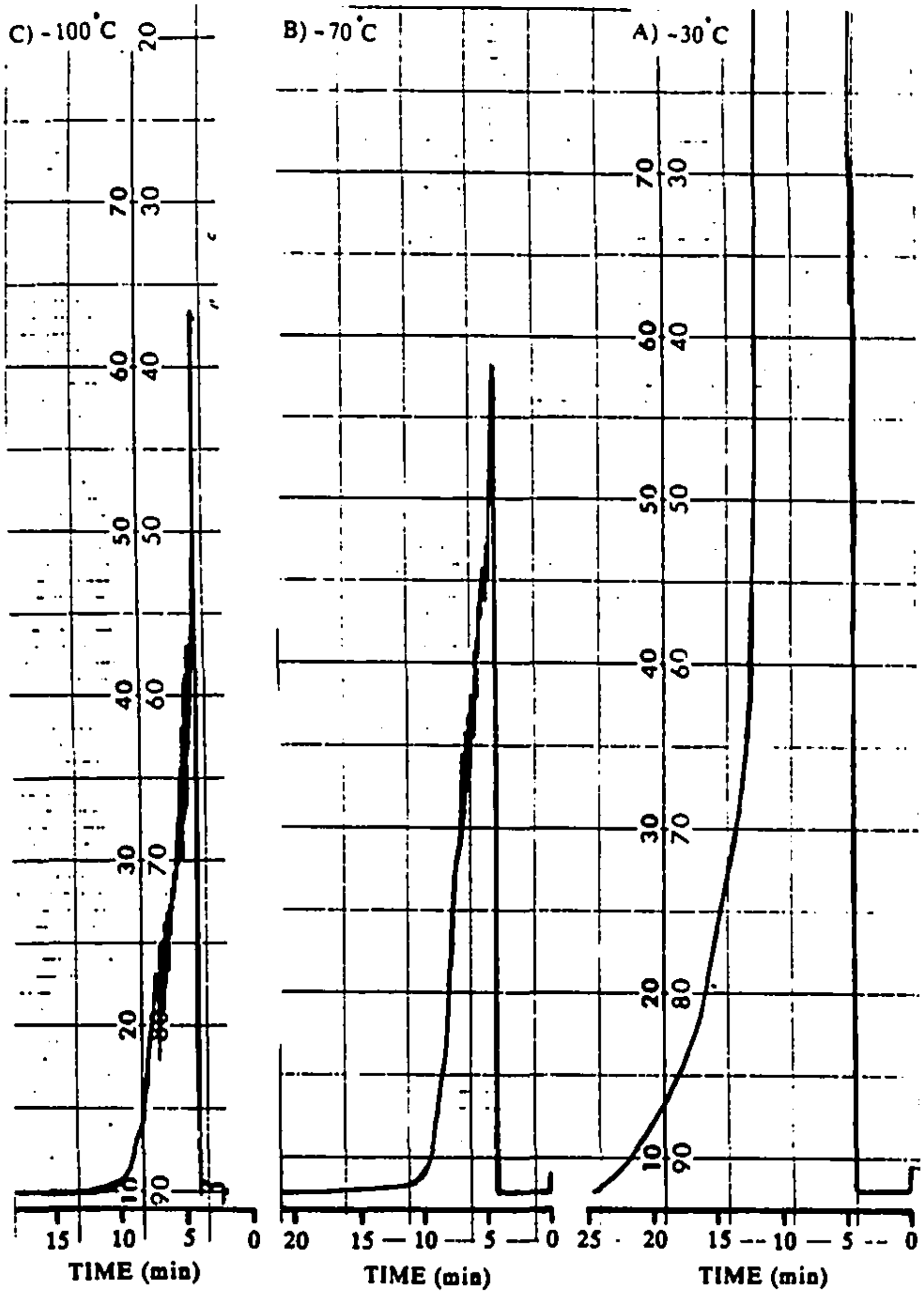


Fig.36 Chromatograms of a thermal desorption experiment from hexane-pretreated charcoal cloth, showing the loss of hexane from the capillary interface cooled by liquid nitrogen to different temperatures (-30 C, -70 C and -100 C). Operational conditions include: cassette temperature, 300 °C; helium carrier gas flow rate, 10 ml/min; GLC column, 65 °C; injector temperature, 190 °C and detector temperature, 200 °C.

by connecting each trap to the purge unit (model 3 cassette desorber) containing 2 layers of charcoal cloth spiked with one ul of hexane. Without liquid nitrogen at the capillary interface, the charcoal cloth was purged with helium gas at a temperature of 300°C for one hr. The mixture of helium and evaporated hexane passed through the trap, hexane being adsorbed onto the trap while the helium carrier gas went through the GLC column. With the trap consisting of Carbopack B (7.3 cm) and Carbosieve S-III (1.3 cm), hexane overloaded the trap and began to break through after 4 min of purging (Fig.37). The trap, containing only Carbopack B (15 cm), showed no breakthrough of hexane and was selected for use for trapping VOCs from thermal desorption.

Optimal operational conditions for thermal desorption of VOCs from 2-layer charcoal cloth were determined to be the following:

1) **The 2-layer charcoal cloth, placed in between two stainless steel washers, was put in model 3 cassette.**
2) **The cassette was purged with helium (10 ml/min) during a 25 min preliminary heating period and an additional 60 min at 300°C during the purge mode and the evaporated VOCs were adsorbed on the Carbopack B trap at room temperature.**
3) **The trap was heated at 280°C with the flow of helium (10 ml/min) for 20 min during the desorb mode and the**

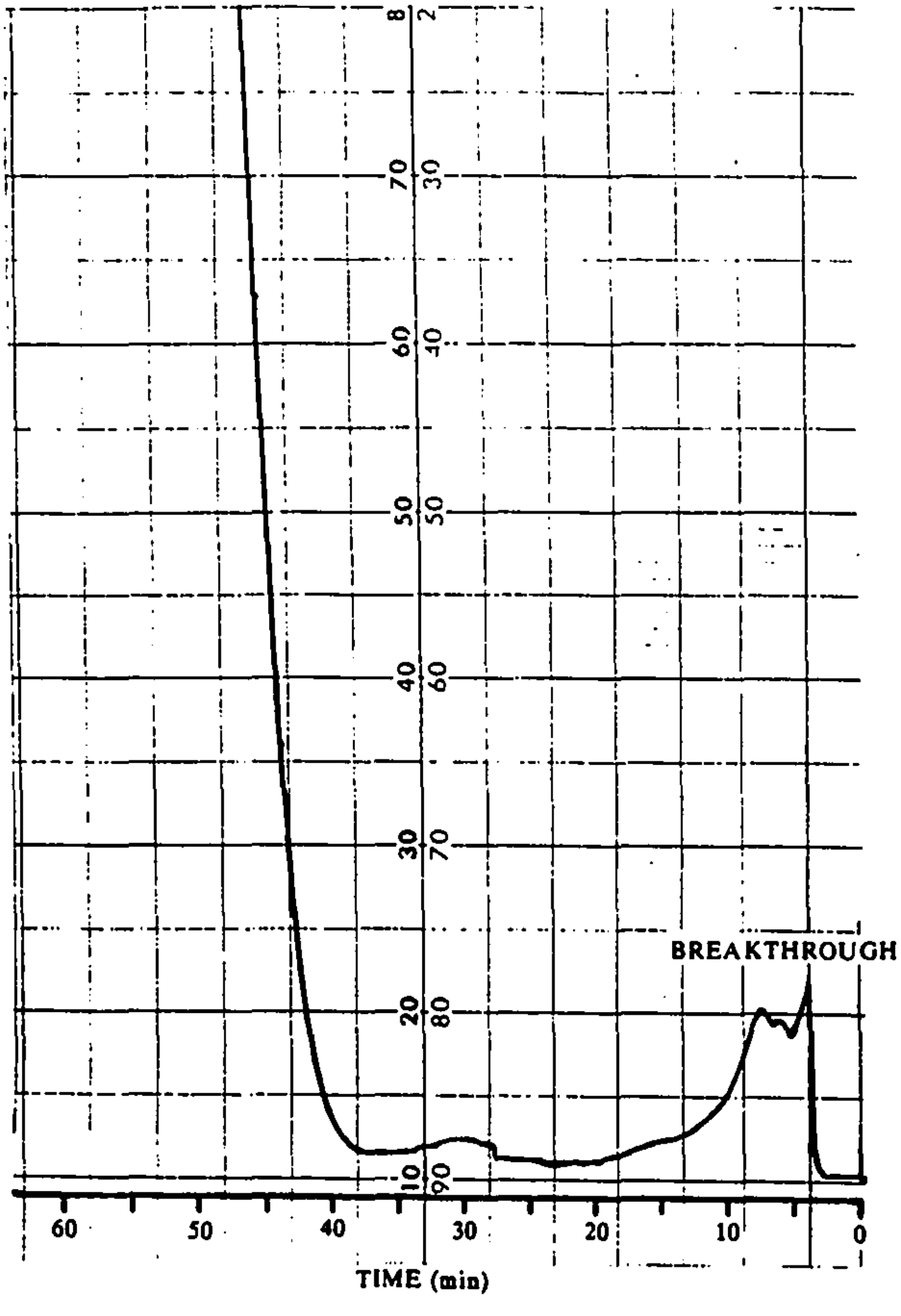


Fig.37 A chromatogram of a thermal desorption experiment from hexane-pretreated charcoal cloth showing the breakthrough of hexane through a "trap" consisting of Carbopack B and Carbosieve S-III. Operating conditions are identical to those described in Fig.36.

volatilized VOCs were concentrated at the capillary interface of the GLC column cooled to -120°C by liquid nitrogen.

4) In the injection mode, the capillary interface was heated rapidly to 250°C within 1.1 min to vaporize the VOCs into the GLC column for analysis.

A. Recovery of the VOCs

When the standard mixture of VOCs was spiked directly on the trap, the VOC mixture was removed completely from the trap at optimized conditions. An example of a chromatogram of the standard VOC mixture thermally desorbed from the trap is shown in Fig.38. This chromatogram was similar to the chromatogram of the standard VOC mixture shown in Fig.12 except that the chromatogram from thermal desorption has a very low response for the solvent peak. All peaks were resolved as distinct peaks and the total analysis time was approximately 12 min. The retention time of benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene, 1-chloro-2-fluorobenzene (internal standard) and o-xylene was 2.7, 3.1, 4.6, 5.8, 8.4, 9.4 and 10.8 min respectively.

The 2-layer charcoal cloth disc was spiked with the standard mixture of VOCs and was thermally desorbed under optimal conditions. Chromatograms of blank charcoal cloth and charcoal cloth spiked with the mixture of standard VOCs after thermal desorption are shown in Fig. 39 and 40 respectively.

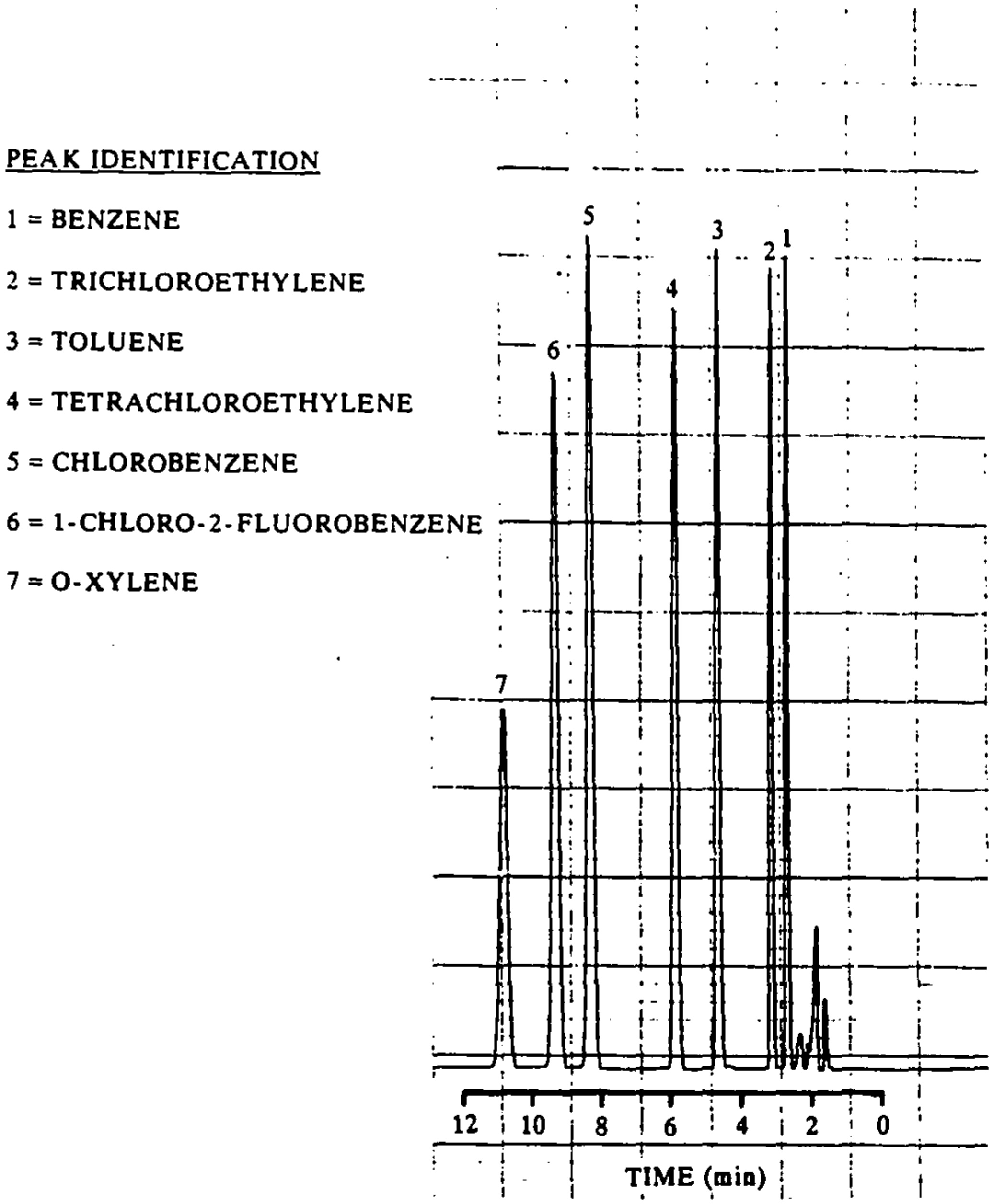


Fig.38 A chromatogram of the thermal desorption (300°C) of a standard mixture of VOCs applied to a Carbopack B column with desorption at 280°C onto a cold (-120°C) capillary interface, this unit being heated subsequently to 250°C to transfer the VOCs to the GLC for analysis by PID.

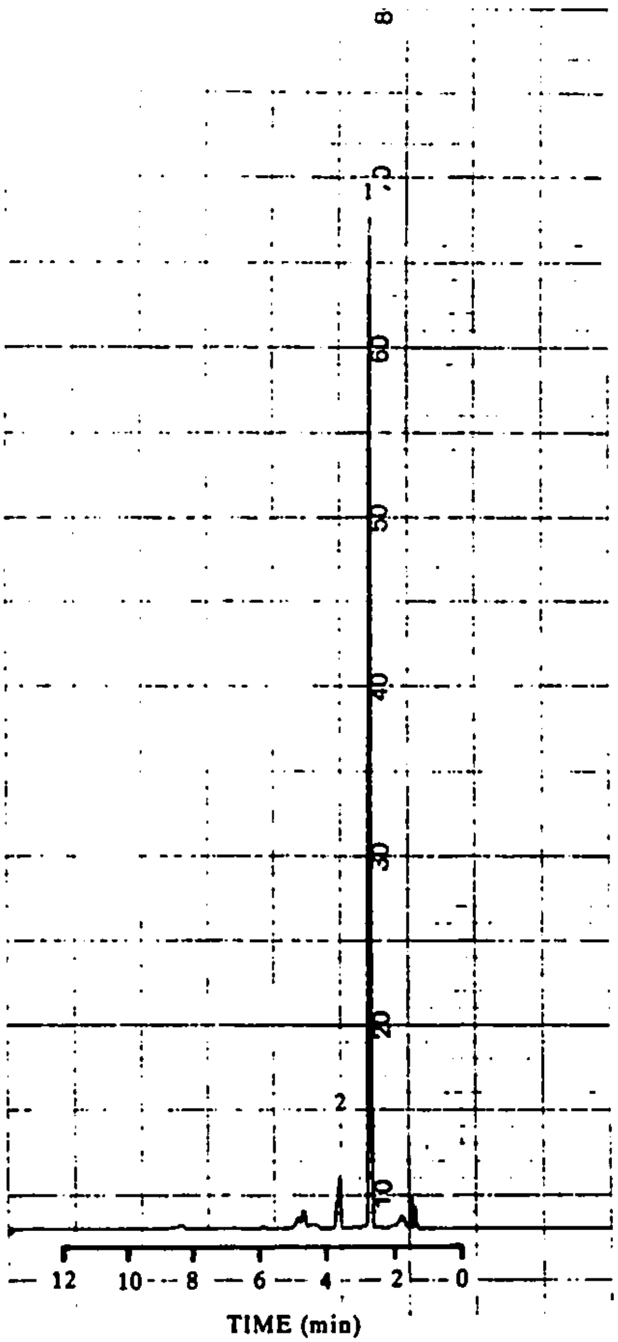


Fig.39 A chromatogram showing the thermal desorption (300 °C) of a two-layer charcoal cloth blank sample in a cassette, transferring any VOCs to a carbopack B column with desorption at 280 °C onto a cold (-120 °C) capillary interface with subsequent heating to 250 °C to transfer any VOCs to the GLC for analysis by PID.

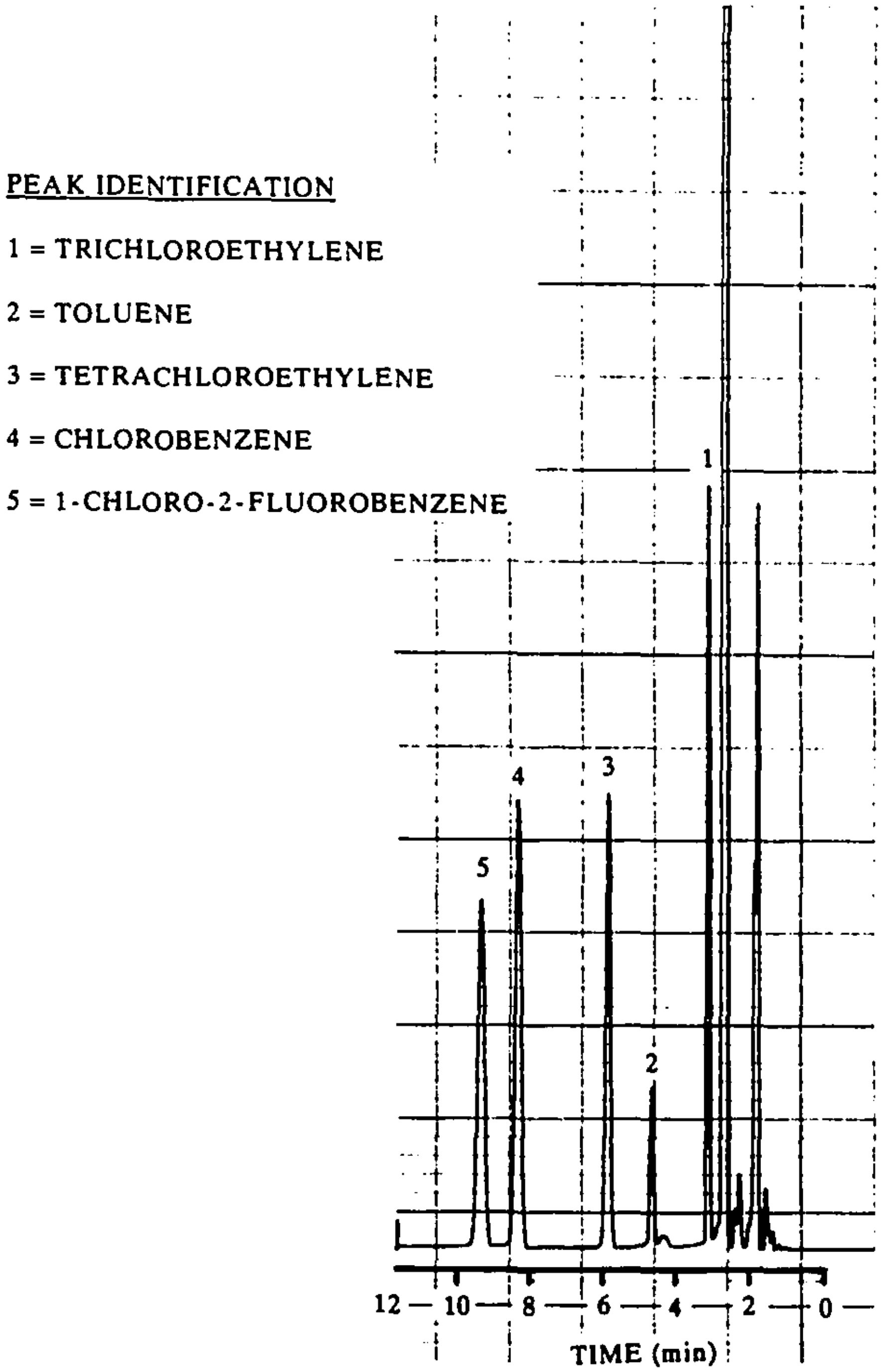


Fig.40 A chromatogram of the thermal desorption (300 °C) of a standard mixture of VOCs applied to a two-layer charcoal cloth in a cassette, transferring any VOCs to a carbopack B column with desorption at 280 °C onto a cold (-120 °C) capillary interface with subsequent heating to 250 °C to transfer any VOCs to the GLC for analysis by PID.

Considering the chromatogram of blank charcoal cloth (Fig.39), two unknown peaks appeared on the chromatogram. The first peak (retention time of 2.7 min) had the same retention time as benzene; the other peak (retention time of 3.8 min) did not interfere with the VOCs of interest. The chromatogram of standard VOCs, thermally desorbed from charcoal cloth (Fig.40), had an off scale peak at the same retention time (2.7 min) as benzene. As a result, the recovery of benzene from charcoal cloth by thermal desorption could not be determined. The other chemicals identified were trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and 1-chloro-2-fluorobenzene. The toluene was the smallest peak among all peaks identified while the o-xylene peak disappeared completely. If o-xylene was removed from charcoal cloth and transferred to the trap, it should be removed from the trap and shows an o-xylene peak on the chromatogram, as was seen in Fig.38. If o-xylene was spiked on the trap, it was desorbed readily by heating at 280 °C for 20 min. Therefore, o-xylene might still be adsorbed on the charcoal cloth and was not removed by the operational conditions used.

The average percent recoveries of four different concentrations of VOCs in a mixture were plotted as bar graphs from three replicate determinations in Fig. 41 (A-D). The recovery of benzene could not be determined at all VOC concentrations studied. The recovery of trichloroethylene and chlorobenzene fluctuated in the range of 70.3- 89.8% and 64.0-

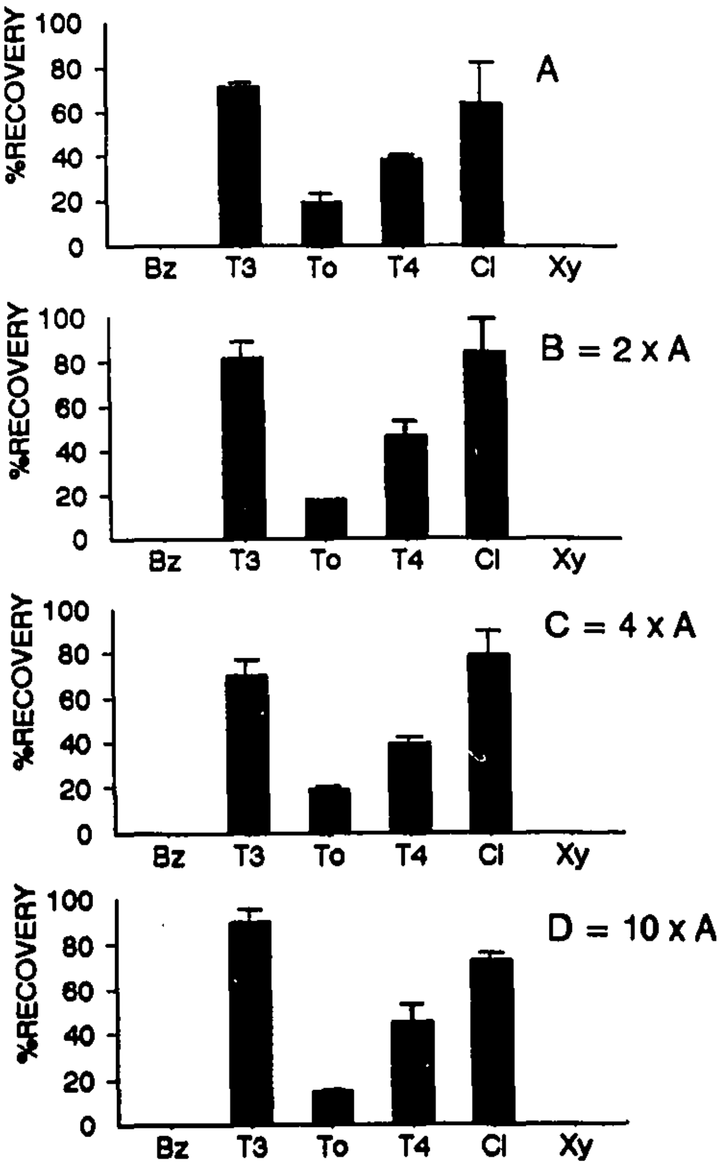


Fig.41 The average percent recovery of standard VOC mixtures from pretreated charcoal cloth (two layers) following thermal desorption from the cassette desorber to Carbopack B column, to capillary interface and analysis by GLC/PID. These concentrations of VOCs in standard A were benzene (Bz), 0.3 ug; trichloroethylene (T3), 0.75 ug; toluene (To), 0.63 ug; tetrachloroethylene (T4), 1.5 ug; chlorobenzene (Cl), 0.88 ug and o-xylene (Xy), 0.88 ug. Concentrations of VOCs applied in standards B, C and D were two-fold, four-fold and ten-fold higher than those of A. The results were obtained from 3 replicate experiments at each concentration.

85.1% respectively. Chlorobenzene showed the greatest variation of percent recovery which was not shown in the graph. The recovery of tetrachloroethylene ranged from 38.7 to 46.8% and toluene gave the lowest percent recovery (14.7-19.7%). The recovery of o-xylene from thermal desorption was zero at the concentration of 0.88-8.75 ug. As the concentration of VOC mixture increased, the percent recovery of VOC mixture did not increase. The percent recovery of VOC mixture showed similar pattern for all VOC concentrations tested.

B. Method Reliability

The accuracy and precision of four VOCs (trichloroethylene, toluene, tetrachloroethylene and chlorobenzene) could be determined as percent recovery and coefficient of variation respectively over sampling times of 10, 20 and 30 min. The accuracy and precision of the method for sampling this VOC mixture by charcoal cloth cassette and analyzing by thermal desorption are shown in Table 23. The recovery of the VOC mixture for 10-min sampling at the concentration range of 1.5 to 4.3 ug was in the range of 89.4 to 99.0% and the coefficient of variation ranged from 10.0 to 21.9%. For 20-min sampling, the VOC concentration ranged from 3.5 to 10.2 ug, gave similar percent recovery (89.0-99.6%) and slightly greater range of coefficient of variation (6.0-24.9%). At the greatest VOC concentration studied (4.8-13.6

Table 23 The Accuracy and Precision of the Method for Sampling VOC Mixture by Charcoal Cloth Cassette and Analysis by Thermal Desorption.

VOCs*	ug Expected $\bar{X}$ ± SD	ug Found** $\bar{X}$ ± SD	%Recovery $\bar{X}$ ± SD	%CV
<u>10-min Sampling</u> (n=4)				
T3	2.3 ± 0.3	2.3 ± 0.7	99.0 ± 16.9	17.1
To	1.5 ± 0.2	1.5 ± 0.3	97.1 ± 22.4	23.1
T4	4.3 ± 0.6	4.0 ± 0.8	91.1 ± 9.1	10.0
Cl	2.1 ± 0.5	1.8 ± 0.4	89.4 ± 19.6	21.9
<u>20-min Sampling</u> (n=4)				
T3	5.4 ± 0	5.0 ± 0.6	92.6 ± 11.0	11.8
To	3.5 ± 0	3.4 ± 0.4	96.7 ± 12.6	13.0
T4	10.2 ± 0	9.1 ± 0.6	89.0 ± 5.4	6.0
Cl	5.1 ± 0	5.1 ± 1.3	99.6 ± 24.8	24.9
<u>30-min Sampling</u> (n=4)				
T3	7.5 ± 0	7.6 ± 0.9	100.5 ± 11.0	10.9
To	4.8 ± 0.1	4.9 ± 1.0	101.2 ± 17.3	17.1
T4	13.6 ± 0.5	12.3 ± 2.7	89.7 ± 17.9	20.0
Cl	6.8 ± 0.5	6.3 ± 0.6	92.3 ± 12.6	13.7

* T3 = Trichloroethylene

To = Toluene

T4 = Tetrachloroethylene

Cl = Chlorobenzene

** These values were corrected for desorption efficiency.

ug), the percent recoveries of VOC mixture were greater than 89.7% and the coefficient of variations were between 10.9 to 20.0%. It is clear that the coefficients of variation were very wide at all concentrations studied. This was probably because the model 3 cassette desorber could not provide sufficient heat to the charcoal cloth layer and the heat was not evenly distributed over the surface of the charcoal cloth. The reliability of the method was also calculated in terms of overall precision and overall system accuracy. The overall precision and accuracy of the method for 10, 20 and 30-min sampling using charcoal cloth cassette, thermal desorption with model 3 cassette desorber and analysis of VOC mixture with GLC/PID is shown in Table 24. The concentration of VOCs generated ranged from 0.80 to 2.6 mg/m^3 and gave an overall precision which ranged from 13.36 to 20.72% and for an overall accuracy of more than 26.28%. The NIOSH accuracy criteria was not satisfied if the overall system accuracy was more than 25%. Chlorobenzene had the greatest percent overall precision and system accuracy probably because of the wide variation of replicate determinations. The overall percent accuracy of toluene was 35.7 probably because the percent recovery of toluene by thermal desorption was very low (14.7-19.7%).

3.3 Reactivation/Re-use of Charcoal Cloth

With solvent extraction, the properties of charcoal cloth were irreparably altered so that the cloth could not be re-

Table 24 10,20 and 30-min Sampling, Average Precision and Accuracy of Thermal Desorption and Analysis of VOC Mixtures Captured on Charcoal Cloth.*

VOCs**	Concentration tested(mg/m^3)	Range tested(ug)	$\%\hat{B}$***	Precision $\%\overline{\overline{CV}}_T$+	Accuracy %O.S.A++
T3	1.20-1.38	2.11-7.55	-0.03	13.55	26.58
To	0.80-0.90	1.34-4.90	-0.02	18.22	35.73
T4	2.25-2.60	3.96-14.33	-0.10	13.36	26.28
Cl	1.10-1.30	1.81-1.7.55	-0.07	20.72	40.68

* Operating conditions at the temperature of 20-23°C and a flow rate of 200 ml/min.

** T3 = Trichloroethylene
To = Toluene
T4 = Tetrachloroethylene
Cl = Chlorobenzene

*** $\%\hat{B}$, Mean bias (error) = $\mathcal{E} n_i B_i / \mathcal{E} n_i$, n = 4

$\%B_i$ = 100(Found-Expected)/Expected

\+ $\%\overline{\overline{CV}}_T$ = The precision of the sampling and analytical method

$\%\overline{\overline{CV}}_T = [\mathcal{E}(CV_i)^2 f_i / \mathcal{E} f_i]^{1/2}$, n = 4 , f = 3

++ O.S.A. = Overall system accuracy

O.S.A. = $[1.96(\overline{\overline{CV}}_T)$ + Absolute mean bias,$|\hat{B}|]$

used. If the two layers of charcoal cloth could be left _in situ_ in the stainless steel cassette, this would simplify sampling but raises the question whether or not the charcoal cloth can be used repeatedly, subjecting it to frequent re-heatings at 300°C to desorb any adhering VOCs from previous analysis. Experiments were conducted in which the two-layer charcoal cloth was alternately heated and cooled 1, 5, 10 and 20 times to 300°C to simulate re-activation of the cloth. At each time interval, the breakthrough times and volumes were assessed as indicators of change in the physical and chemical properties of the cloth, using the VOC mixture in a generated air sample as the test standard materials. The results shown in Fig.42 indicate that repeated heating up to 10 times increased both parameters, hence the efficiency of the cloth, but that, with 20 re-heatings, the breakthrough time and volume was slightly reduced but remained considerably higher than the control values determined for freshly activated cloth.

4. APPLICATION OF CHARCOAL CLOTH CASSETTE

An assessment of paint vapour exposure using both a charcoal cloth cassette and charcoal tube to collect solvent vapours was conducted on March 10, 1993. The results are shown in Table 25. Sample collection by both methods was performed at the same site (Fig.11, site A) and was initiated 30 min after the painting was finished. With solvent

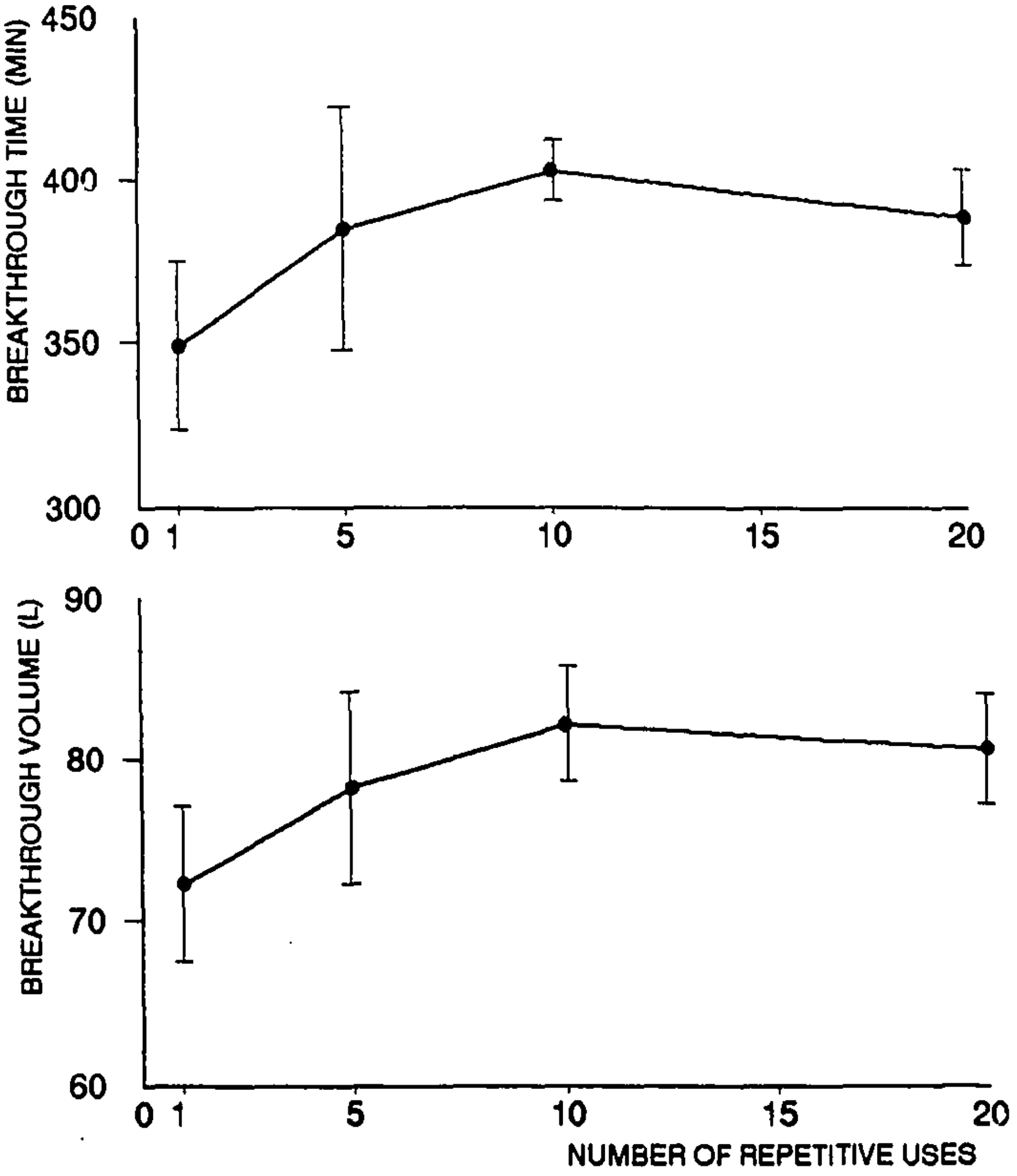


Fig.42 The assessment of thermal stability of charcoal cloth (two layers) following repeated (1, 5, 10, 20 times) thermal desorption (60 °C - 300 °C) by measuring the breakthrough time (min) and volume (L) of a standard mixture of VCCs generated in a chamber and passed through the charcoal cloth cassette. The times and volumes shown are the averages ± standard deviations for three experiments for each point.

Table 25 Assessment of Paint Vapour Exposure Using Charcoal Cloth Cassette and Nutshell Charcoal Tube Sampling After Painting.

	Solvent Desorption*		Thermal Desorption*	
	p,m-xylene (mg/m^3)	o-Xylene (mg/m^3)	Toluene (mg/m^3)	Chlorobenzene (mg/m^3)
Charcoal Cloth Cassette Sampling (Site A)				
Sampling Time (min)				
15	<0.83	<3.33	1.25	0.03
30	<0.42	<1.67	0.67	0.20
45	<0.28	<1.11	0.20	0.03
60	<0.21	<0.83	0.23	0.15

Nutshell Charcoal Tube Sampling (Site A)

Sampling Time (min)	Total Xylene (mg/m^3)
30	0.61
30	0.61
30	0.40
30	0.40
30	0.20

---

*Limits of Detection

o-Xylene (hexane desorption) 10 ug

p,m-Xylene (hexane desorption) 2.5 ug

Chlorobenzene (thermal desorption) 0.025 ug desorption of the charcoal cloth by hexane, the amounts of xylenes were below the detection limits for o-xylene (10 ug) and p- and m-Xylene (2.5 ug) due to the dilution by the extraction solvent and a low percent recovery (10%) of xylenes from charcoal cloth. However, the nutshell charcoal tube extracted with carbon disulfide yielded concentrations of total xylene in the range of 0.20-0.61 mg/m^3. The concentration of xylenes obtained with the charcoal cloth and the nutshell charcoal tube sampling and analysis after solvent desorption was very low, reflecting the use of a good ventilation system in the paint room.

Avoiding the difficulties of extracted sample dilution by using thermal desorption, the results obtained from charcoal cloth sampling are also shown in Table 25. Xylenes were not removed from charcoal cloth by thermal desorption under the conditions used. However, low levels of toluene and chlorobenzene (corrected for desorption efficiency) were detected ranging from 0.20 to 1.25 mg/m^3 and from 0.03 to 0.2 mg/m^3 respectively. The catalyst used in the paints for troop carriers does not contain toluene or chlorobenzene but toluene was a component in a primer material used earlier by the painters and chlorobenzene has been detected as an impurity in paint mixtures.

Since the concentrations of VOCs in the paint room after the painting operation appeared to be very low, short-term sampling of paint vapour by charcoal cloth cassette should be carried out during painting as well as immediately after painting. An example of a chromatogram showing the VOC mixture detected during and after painting is shown in Fig.43. The two chromatograms showed similar patterns of VOCs. Some of the chemicals on the chromatogram could not be identified. The VOCs identified were toluene, m-xylene, p-xylene and o-xylene at the retention time of 4.6, 8.9, 8.9, and 10.8 min respectively. m-Xylene and p-xylene had exactly the same retention time under the optimal conditions employed. Since concentrations of vapours were expected to be high during the painting operation, nutshell charcoal tubes were attached to the outlet end of the cassettes to check for possible breakthrough of VOCs. No breakthrough occurred, the concentration of total xylenes desorbed from the charcoal tubes (n=3) being <0.002 mg/m^3.

The VOC concentrations during and after the painting operation sampled by charcoal cloth cassette are shown in Table 26. The concentrations of toluene at site B, C and D during painting were 9.6, 7.0 and 2.1 mg/m^3, respectively (See Fig.11 for location). The concentrations of total xylenes were rather high (68.9, 245.0 and 65.0 mg/m^3 at site B, C and D respectively) but the value still considerably lower than the threshold limit value of xylene (434 mg/m^3).

Following completion of the painting and with the troop carrier still in the ventilated room, charcoal cloth cassettes were used to collect VOC vapours at sites B, C and D for a 3-

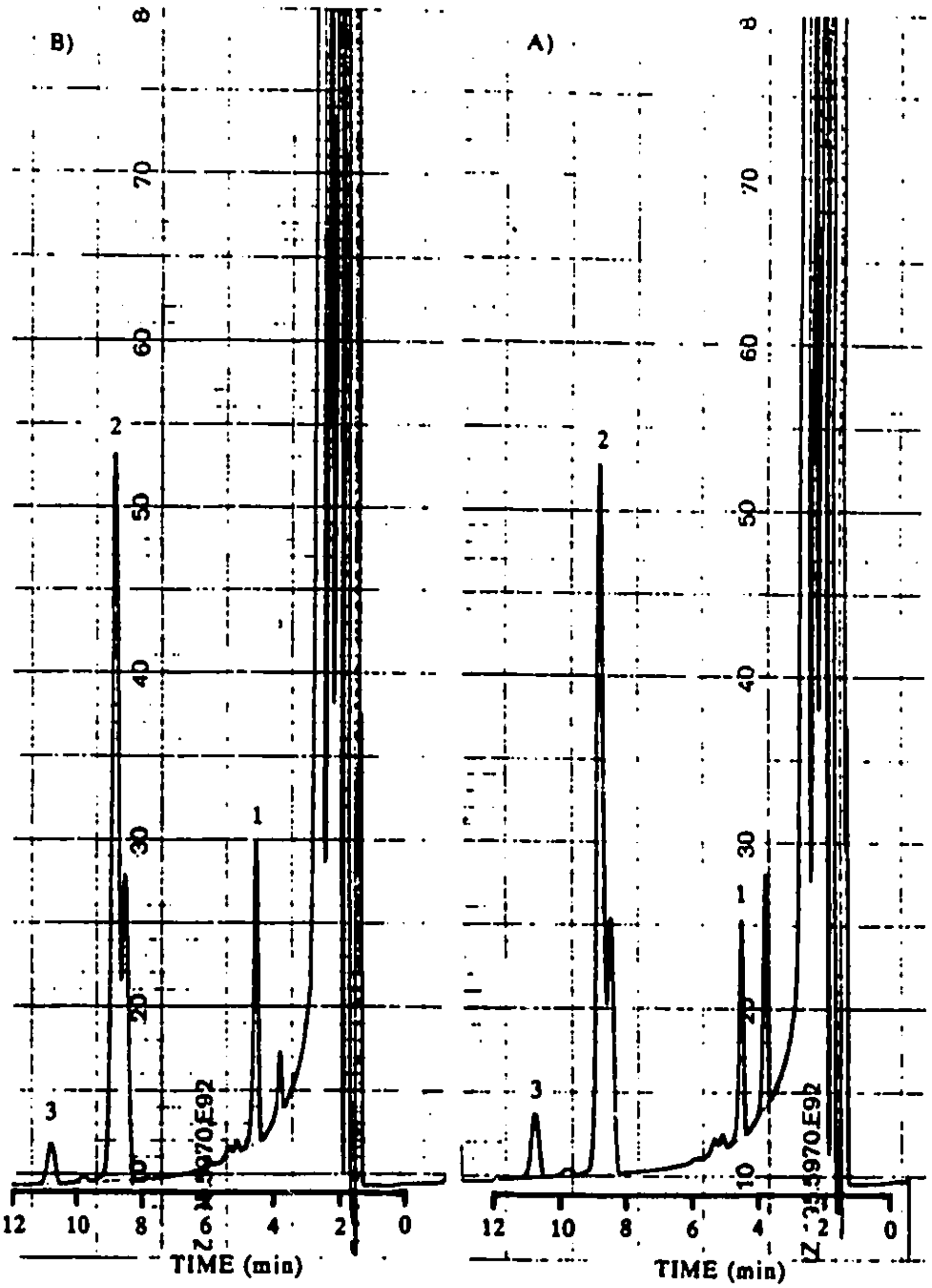


Fig.43 Chromatograms of solvent vapours from paint captured on charcoal cloth (two layers) (A) during painting (B) after painting, the cloth being thermally desorbed using the standard, optimal conditions established for this technique. See results, page 166. The chemicals detected were toluene, p-,m-xylene and o-xylene in peaks 1, 2 and 3 respectively.

Table 26 Assessment of Paint Vapour Exposure Using Charcoal Cloth Cassette and Nutshell Charcoal Tube Sampling During and After Painting.

		VOC Concentration (mg/m^3)		
	Toluene	p,m-Xylene	o-Xylene	Total Xylene
Charcoal Cloth **During Painting (24-min Sampling)** Sampling Location				
B	9.6	53.0	15.9	68.9
C	7.0	205.2	39.8	245.0
D	2.1	50.8	14.2	65.0
After Painting (180-min Sampling) Sampling Location				
B	1.6	6.9	1.4	8.3
C	1.5	4.8	1.0	5.8
D	0.6	5.6	0.8	6.4

Nutshell Charcoal
After Painting (30-min Sampling)
Sampling Location E and F

Sample Number	Average Total Xylene Concentration (mg/m^3)
1	90
2	20
3	8.2
4	8.3
5	7.2
6	4.9

hr period (Table 26). During this same time period, two nutshell charcoal tubes were hung on the structure of the troop carrier, samples of the air being collected over consecutive 30 min intervals for 3 hr (See Fig.11, Sites E and F). These results are also shown in Table 26 and demonstrated that the concentrations of total xylenes decreased with time (Fig.44). Comparing the 24-min samples collected by charcoal cloth cassette and the first 30-min sample collected by nutshell charcoal tube, the concentrations of total xylenes were similar (68.9 and 65.0 mg/m^3 versus 90 mg/m^3). The higher level detected by nutshell charcoal tube is understandable since the units were much closer to the source of the vapours (See Fig.11). The results from the 180-min sampling by charcoal cloth cassette and the sequential 30-min samplings by nutshell charcoal tubes from 90 min onward were also comparable despite the position of the devices and reflect the use of an efficient ventilation system in the painting room.

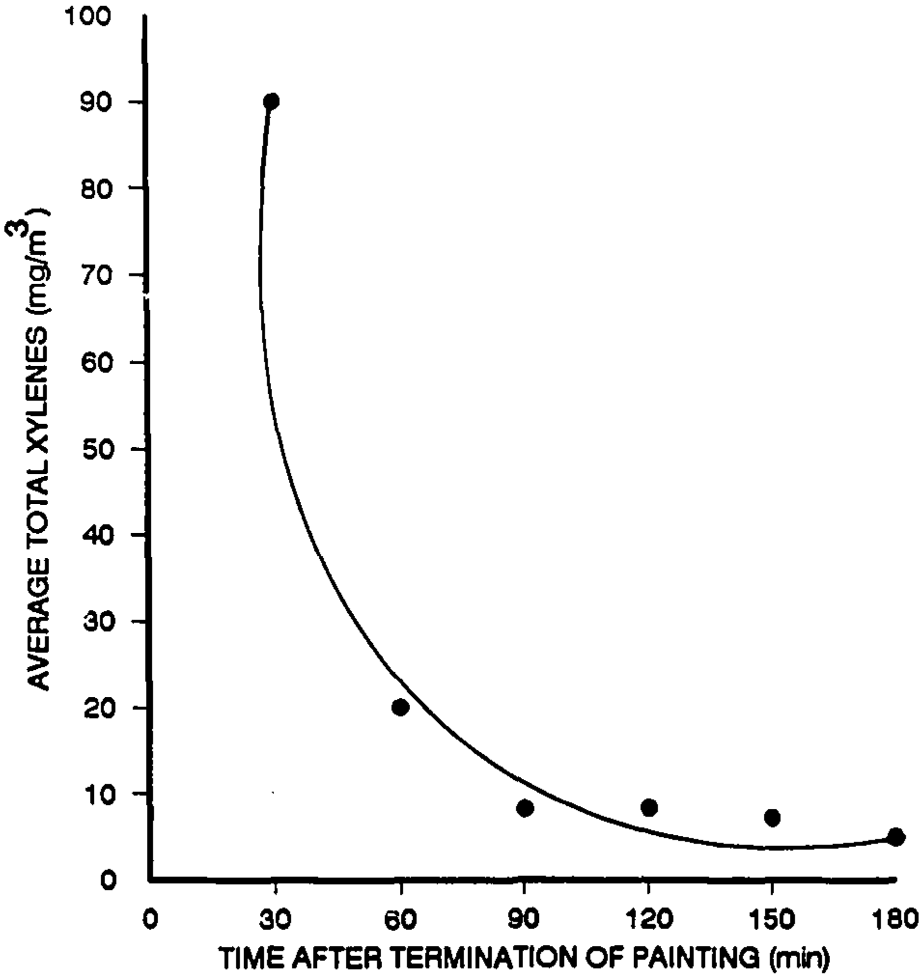


Fig.44 Average total xylenes using nutshell charcoal tube sampling in the paint room after painting.

DISCUSSION

The hypothesis of this project was that charcoal cloth was as good as or better than NIOSH nutshell charcoal as an adsorbent for a sampling medium for air quality analysis in the workplace and home environments at either high or low levels of contamination. To test this hypothesis, it would be essential to make a comparison of the two media under a variety of physical conditions, using different concentrations of a number of volatile organic chemicals to assess the ability of activated charcoal in these two forms to capture and retain agents potentially hazardous to human health. Such studies would necessitate the investigation of different techniques by which these chemicals could be qualitatively and quantitatively removed from the charcoal medium for subsequent analysis.

Volatile organic chemicals (VOCs) are always present in the environment as mixtures rather than as individual compounds (Amman et al., 1986; Molhave et al., 1984; Wallace et al.,1989). Six, low molecular weight chemicals were selected for study. All of these chemicals have extensive industrial use. They are also commonly found in recirculated indoor air in buildings as a consequence of volatilization from new fabrics, office equipment, building materials, etc. and they have been shown to elicit adverse health effects (Samet et al., 1987; Turiel, 1985; Amman et al., 1986). These particular VOCs are sensitive to analysis by a photoionization detector attached to a gas-liquid chromatograph, thereby permitting the quantitation of low levels that might be encountered in office buildings, light industry, the home, etc. Since these VOCs are present in the atmosphere as mixtures, they should be studied as such rather than as individual chemicals. There may be significant chemical interactions that would influence their capture and subsequent recovery, separation and analysis.

Considering the adsorption capacity of these two types of charcoals, Maggs reported that the saturation vapour adsorption of charcoal cloth for benzene and chlorobenzene spanned the range of adsorption by various types of commercial granular charcoal (Table 27). Another study showed that the adsorption capacity of the Porton Down charcoal cloth diffusive sampler for benzene, trichloroethylene and tetrachloroethylene was at least two-fold lower than nutshell charcoal (Table 28). The authors suggested that the adsorption capacity of charcoal cloth was not an accurate measure of the capacity of the cloth for diffusion sampling but that it could be a useful guide (Purnell et al., 1981). The adsorption capacity for toluene (220 mg/m^3) of the first-designed cassette containing 3-layer charcoal cloth compared with 150-mg nutshell charcoal tube was 24.0 and 27.4%, respectively (Fig.17). The difference in adsorption properties by nutshell charcoal and charcoal cloth may be related to the bed geometry of the former. With the

Table 27 The Vapour Adsorption at Saturation Vapour Pressure of Benzene and Chlorobenzene on Charcoal Cloth and Granular Charcoal.

Charcoal	% Vapour adsorbed (W/W)	
	Benzene	Chlorobenzene
Cloth P57 (1)	35.4	43.1
Cloth P57 (4)	67.3	86.9
Cloth P66	45.8	57.0
Cloth P68	29.2	36.8
Cloth P69	44.7	55.0
Granular A	-	47.0
Granular B	-	68.0

Data from Maggs et al.,1977

Table 28 Comparison of Breakthrough Volume and Adsorption Capacity of Charcoal Cloth Cassette, Porton Down Charcoal Cloth Diffusive Sampler and Nutshell Charcoal Tube for Selected VOCs at Low Humidity.

VOCs	Concentration (mg/m^3)	Breakthrough Volume (L)	Adsorption Capacity (%)
Charcoal Cloth			
Benzene**	65	40	2.6
Trichloroethylene**	546	12	6.6
Toluene*	963	19	27.0
Tetrachloroethylene**	689	32	22.0
Nutshell Charcoal***			
Benzene	149	45	6.7
Trichloroethylene	2266	19	43.1
Toluene	2294	12	27.5
Tetrachloroethylene	2749	21	57.7

* Charcoal Cloth Cassette

** Porton Down Charcoal Cloth Diffusive Sampler (Purnell et al.,1981)

*** NIOSH, 1977

redesigned charcoal cloth cassette, the adsorption capacity of toluene was 27%, a value comparable to nutshell charcoal tube (27.5%) (Table 28). Using the VOC mixture (benzene, trichloroethylene, toluene, tetrachloroethylene, chlorobenzene and o-xylene) at the concentration ranges of 38.5-212.0 and 52.3-239.7 mg/m^3, the adsorption capacity of 2-layer charcoal cloth (67.8 mg) and 100-mg of nutshell charcoal was 25.8 and 38.3% respectively (Table 17, 18 and 29). With one chemical, e.g. toluene, the adsorption capacity of charcoal cloth (2 layers) was comparable to that of nutshell charcoal (100 mg) but there appeared to be significant differences when mixture of chemicals in air was sampled. As shown in Tables 17 and 18, the adsorption capacities for toluene in the mixture were 3.6% and 5.1% for charcoal cloth and nutshell charcoal, respectively. There appears to be considerable competition between the components in a mixture for available binding sites.

Generally, the adsorption capacity of charcoal for VOCs is increased with increasing VOC concentrations. The adsorption of activated charcoal (37.5 g) for trichloroethylene at the concentrations of 303, 987 and 1331 mg/m^3 was 29, 40 and 43% respectively (Werner, 1985). For nutshell charcoal (900 mg), the adsorption capacity of 48, 38.8 and 23.2% was observed for tetrachloroethylene at the concentrations of 2698, 837 and 288 mg/m^3 respectively (Guenier and Muller, 1984). Similar results were obtained

Table 29 Comparison between the Properties of Charcoal Cloth and Activated Charcoal[*].

Physical properties	Charcoal cloth	Activated charcoal
Adsorption capacity for the mixture of VOCs[**]	25.8%	38.3%
Pressure differential across the device (inch of water)[+]	0.1	2.4
Storage stability of charcoal-adsorbed VOCs (days)[++]	>32	>35

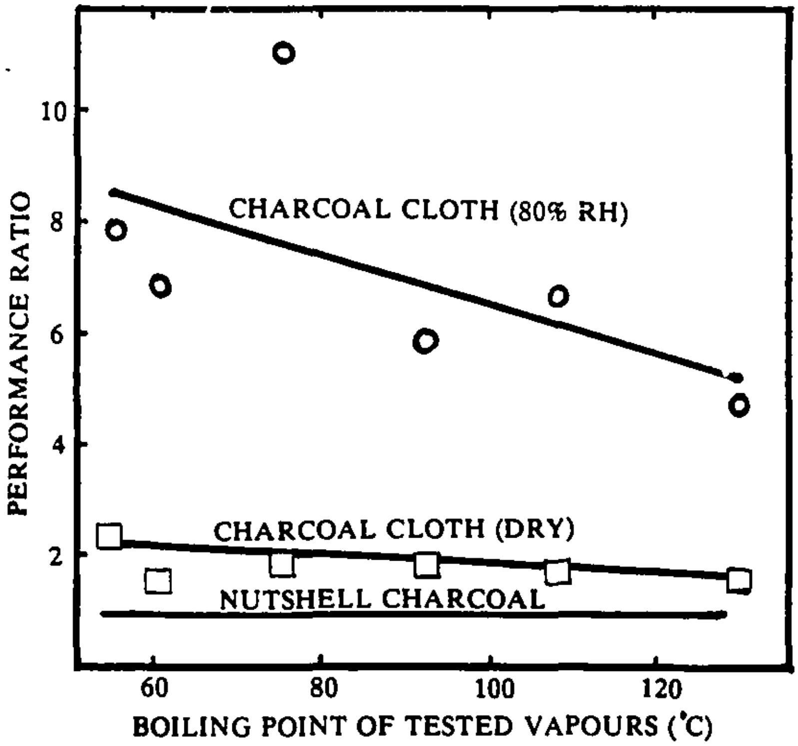
[*] Data are taken for the highest concentrations of chemicals in the mixture, the results appearing in Tables 17 and 18.

[**] The percent adsorption capacity represents average values from three replicate experiments with each medium (2-layer charcoal cloth, 100-mg nutshell charcoal)

[+] The values presented represent the average pressure differential obtained from three replicate experiments.

[++] See Fig.30 for charcoal cloth.

with charcoal cloth (Fig.21 and Table 17). However, adsorption on activated charcoal of any type usually is reduced with an increase of relative humidity (RH) because water vapour competes for the available binding sites on charcoal and causes a deactivation of the medium (Werner, 1985). The performance of charcoal cloth for adsorption of six individual chemicals (chlorobenzene, methoxyflurane, trichloroethylene, carbon tetrachloride, chloroform and halothane) was better than granular nutshell charcoal by a factor of 2 and 5 at "dry" condition and at 80% relative humidity respectively (Fig.45) (Charcoal Cloth Ltd, 1983). Charcoal cloth was considered less affected by preadsorbed moisture than nutshell charcoal (Smith and Davies, 1983 and Charcoal Cloth Ltd, 1983). Saalwaechter et al. (1977) also reported that experiments using toluene at high humidity resulted in a marked decrease in breakthrough volume of nutshell charcoal. When the relative humidity was increased from 7 to 94%, a reduction of greater than 50% in breakthrough capacity was observed (Saalwaechter et al., 1977). Werner (1985) also reported that the adsorption capacity of activated charcoal for trichloroethylene (293-303 mg/m^3) was reduced from 28.6 to 2.7% when the relative humidity increased from 5 to 85%. For charcoal cloth in this study, the adsorption capacity of toluene (128-150 mg/m^3) decreased slightly with increasing amount of water vapour, an overall reduction of only 17.4% being observed between 0 and 80% RH (Fig.20D). The



TESTED VAPOURS	BP °C
HALOTHANE	56
CHLOROFORM	60-62
CARBON TETRACHLORIDE	76-77
TRICHLOROETHYLENE	87
METHOXYFLURANE	105
CHLOROBENZENE	130-133

Fig.45 Performance ratio vs boiling point values for a range of vapours. Performance ratio is defined as the ratio of breakthrough time for charcoal cloth and breakthrough time for nutshell charcoal.

adsorption capacity of 2-layer charcoal cloth (67.8 mg) for toluene (963-977 mg/m^3) was 14.2% reduction when the relative humidity was changed from 0 to 40% RH (Fig.21D).

The rate at which air will pass through the medium will be governed by the thickness (the weight) of medium used in sampling, thicker "beds" raising the resistance to air flow. The pressure differential across the standard nutshell charcoal tube and charcoal cloth cassette was 2.4 and 0.1 inches of water respectively at a flow rate of approximately 200 ml/min (Fig.18 and Table 29). This result confirmed earlier statements that charcoal cloth had very low air flow resistance of approximately 0.1 mm per cm/s per layer of cloth (Table 10) (Maggs et al., 1977). Such observations would indicate that, if need be, many layers of charcoal cloth could be used without impairing the flow rate significantly.

Since it is possible that considerable time might elapse between sampling and analysis, it is important to know if the adsorbed VOCs would remain on the cloth medium and can be quantitatively recovered. The stability of adsorbed VOCs on charcoal cloth exceed a month when stored in tightly sealed glass vials at either refrigerated or at room temperature. The percent recovery of the VOC mixture, shown in Fig.30, ranged between 92.5 and 104.1% using solvent (hexane) desorption. In contrast, for petroleum derived charcoal, trichloroethylene showed no loss during 92 days of storage at room temperature but 15% of trichloroethylene had migrated to the back-up section at the end of the time period (Saalwaechter et al., 1977). Toluene showed no significant loss from nutshell charcoal after five weeks of storage at room temperature (Saalwaechter et al., 1977).

DESORPTION OF VOCs

1. Solvent Desorption

The removal of VOCs from an adsorbing medium prior to analysis is of considerable importance since the desorption efficiency would affect the final quantitative results of analysis. Solvent desorption has been a widely used technique for the removal of VOCs from charcoal (Crisp, 1980). Carbon disulfide has been the first choice as a desorbing solvent because of the absence of a large solvent peak when using gas chromatography with flame ionization detectors, the short retention time on most analytical columns and the ability to desorb "nonpolar" compounds (Rudling and Bjorkholm, 1986). However, carbon disulfide presents an explosive hazard in the laboratory, it is also very volatile and difficult to handle and is a known neurotoxicant, two properties of sufficient concern to merit the search for a different desorbing solvent. The desorption efficiency of VOCs from activated charcoal using carbon disulfide was more than 92% (Table 30). Charcoal cloth gave similar results of more than 98% desorption efficiencies using carbon disulfide as the solvent (Cohen and Popendorf, 1989). Purnell et al. (1981) also reported that

Table 30 Desorption Efficiencies of Various Compounds from Activated Charcoal and Charcoal Cloth by Solvent Desorption.

Chemicals	%Desorption Efficiencies*							
	Activated charcoal (Extracted with CS_2)					Charcoal cloth		
						CS_2	Hexane	Pentane
	1	2	3	4	5	6	7	8
Benzene	96	96	100	96	100	100	100	90
Trichloro.	97	97	100	96	-	-	103	102
Toluene	96	96	98	92	100	98	93	90
Tetrachloro.	96	96	-	-	-	-	99	96
Chlorobenzene	-	-	-	-	-	-	83	71
o-Xylene	-	98	-	95	100	99	80	78

* 1, 3 and 4 cited by Crisp, 1980

2 White et al., 1970

5 and 6 Cohen and Popendorf, 1989

7 and 8 This study

the desorption efficiencies of benzene, trichloroethylene and tetrachloroethylene from charcoal cloth were 100 ± 5% with carbon disulfide.

In this study, pentane, hexane and cyclopentane were used as desorbing solvents because they gave small solvent peaks with gas chromatography using photoionization detection. The desorption efficiencies of six individual VOCs (10 mg) were greater than 71% by both pentane and hexane desorption (Table 30). The desorption efficiencies decreased when reduced amounts of chemicals were applied (Fig. 26). These results agreed with Melcher et al. (1978) and Saalwaechter et al.(1977) for some compounds (2-butanone and styrene) but not with White et al. (1970) and Krajewski et al. (1980). The latter groups reported that the desorption efficiency was not affected by the amount of analyte adsorbed. When the VOCs were studied as a mixture, at the same concentrations as individual VOCs, the desorption efficiencies of VOCs in a mixture were higher than those of individual VOCs (Figs.26 and 27). White et al. (1970) did not see the changes in desorption efficiencies when the substance was analyzed either as an individual or as a mixture.

These observational differences may be the consequence of different desorbing solvents being used or different amounts of the analyte being applied. It is difficult to compare results generated by different methods since the recovery yields of adsorbed compounds depend on the nature and the amount of the analyte, the presence of other adsorbed substances, especially polar compounds, the humidity of the sampled air, the ratio between the amount of charcoal and desorbing liquid and the time and temperature of desorption (Cocheo et al., 1987; Lautenberger et al., 1980; Mueller and Miller, 1979 and Melcher et al., 1978).

The adsorbed substances are generally eluted by a 1-3 ml volume of solvent, with a 1.0 ul aliquot being applied to the GLC/FID or PID for analysis. Both the dilution on desorption and the small volume of solution analyzed may result in the VOC concentration being below the limits of detection.

What would be desirable would be a technique that would quantitatively desorb the VOC from the medium without dilution, permitting the GLC analysis of all of the recovered analyte rather than a small aliquot (Gonzalez and Levine, 1986).

2. Supercritical Fluid Extraction (SFE)

The use of supercritical fluid extraction as a desorption technique has been increasing rapidly due to unique properties of various supercritical fluids employed. Such fluids as liquid carbon dioxide and nitrous oxide (N_2O) can behave both as liquids and as gases. SFE can be used to extract a wide range of both low and high molecular weight compounds. For low molecular weight n-alkanes, the average extraction recovery of nonane was 86% (Data from Dionex, 1991). When the number of carbon atoms in the molecule increased (decane), the recovery was increased to almost 100% because these chemicals were trapped efficiently in the collecting solvent (Data from Dionex, 1991). However, when SFE was used to extract a mixture of VOCs with 2 to 8 carbon atoms in the molecules from charcoal cloth, a number of serious methodological problems became evident. Extraction at higher pressures of liquid carbon dioxide resulted in increased flow rates of the gas and increased desorption efficiencies of VOCs but the collecting solvents (pentane, hexane and decane) could not efficiently capture the VOCs. Indeed, these VOCs and the collecting solvents were loss through the vent lines because the temperature of collecting solvents could not be cooled sufficiently to trap these VOCs (Figs.34 and 35). It was considered that the amount of collecting solvent (10 ml) would dilute the trapped VOCs even more than in the case of solvent desorption (4 ml). Adjustments to the commercially available SFE equipment could be made, e.g. reducing the size of the collecting tube to reduce the volume of collecting solvent required, partially obstructive the restrictors to yield lower flow rates, etc.; but the major problem remains. The SFE has serious limitations for very low molecular weight compounds even though it may perform adequately with higher molecular weight compounds such as polyaromatic hydrocarbon, pesticides, etc.

3. Thermal Desorption

The efficacy of thermal desorption is that, in theory, the technique should quantitatively remove the charcoal-adsorbed VOCs as vapours under elevated temperature, these vapours being transported by an inert carrier gas (helium, nitrogen) to a short column containing a suitable trapping medium followed by a heat-induced subsequent desorption directly into the analytical instrument. In this manner, the analytes of interest are carried quantitatively through these steps without dilution or loss. The major disadvantage is that only one analysis can be carried out on one sample. The results of thermal desorption experiments from several laboratories for individual VOCs and the mixture from this study are summarized in Table 31. Gonzalez and Levine (1986) desorbed benzene from activated charcoal disc (5 mm diameter X 0.58 mm disc) with 97% desorption efficiency. An apparatus for thermal desorption of solvents from activated charcoal was designed by Cocheo et al. (1987) which gave desorption efficiencies of individual VOCs (benzene and trichloroethylene) and a mixture of VOCs ranging from 99 to 101% (Table 31). Hori et al., (1989) desorbed two components of organic solvents from activated charcoal using an experimental design of thermal desorber, the desorption efficiencies ranging from 12 to 22% for o-xylene, 43% for toluene and 98% for benzene.

From the present experiments, the desorption efficiencies

Table 31 Desorption Efficiencies of Various Compounds from Activated Charcoal and Charcoal Cloth by Thermal Desorption.

	%Desorption Efficiencies				
	Activated charcoal				Charcoal cloth
Reference*	1**	2**	3***	4***	5***
Benzene	97	101	101	98	-
Trichloro.	-	99	99	-	72
Toluene	-	-	99	43-44	20
Tetrachloro.	-	-	99	-	39
Chlorobenzene	-	-	-	-	64
o-Xylene	-	-	-	12-22	0

* 1 Gonzalez and Levine, 1986 (Benzene conc., 0.03-4.02 ug)

2 Cocheo et al., 1987 (Benzene conc., 0.09 and trichloroethylene conc., 0.88 mg)

3 Cocheo et al., 1987 (Benzene conc., 0.09 mg; trichloroethylene conc., 0.88 mg; toluene conc., 1.13 mg and tetrachloroethylene conc., 0.74 mg)

4 Hori et al., 1989 (Benzene conc., 1.76 mg; toluene conc., 1.74 mg and o-xylene conc., 1.76 mg)

5 This study (Benzene conc., 0.3 ug; trichloroethylene conc., 0.75 ug; toluene conc., 0.63 ug; tetrachloroethylene conc., 1.5 ug; chlorobenzene conc., 0.88 ug and o-xylene conc., 0.88 ug)

** VOC was analyzed as individual VOCs

*** VOC was analyzed as a mixture of VOCs of a mixture of five VOCs ranged from 0 for o-xylene to 72% for trichloroethylene (Table 31). A considerably lower percent desorption efficiencies was observed than in the study of Cocheo et al. (1987) because the desorption conditions and the type of charcoal used were different. Cocheo desorbed the VOCs in a desorption tube (8 mm o.d.X 140 mm length) with a carrier gas flow rate of 300 ml/min, desorption oven temperature of 320°C, maximum pressure inside the desorption tube of 3.7 bar and the total desorption time of 260 sec. The time required for reaching thermal equilibrium was only 200 sec. In contrast, the cassette built for thermal desorption from charcoal cloth discs required 25 min to reach 300°C and the flow rate of carrier gas (helium) was only 10 ml/min. There was some question whether the heat was evenly distributed over the large surface of charcoal cloth, thereby permitting the charcoal cloth to retain some VOCs more strongly.

The low recoveries of components of the VOC mixture (Table 31) suggest that additional development will be required if the charcoal cloth medium is to be used for routine air sampling and VOC analysis. However, in the present study, the amount of adsorbed VOCs was considerably smaller than those reported in similar experiments conducted by other investigators (Table 31). The cassette desorber (Fig.8, Model 3) will require modification to have a less exposed area of charcoal cloth in the cassette, the generation of a more rapid higher and/ or more uniformly distributed heat and an optimal carrier gas flow to transport the desorbed VOCs onto the trapping (Carbopack B) column or dispensing with the use of the latter. Quantitative desorption from the Carbopack column has not proven to be a problem, results both in this study and that of Mangani and Mastrogiacomo (1982) showing 100% recovery for a variety of VOCs. Despite the rather crude cassette thermal desorption system developed in the laboratory for charcoal cloth, the results demonstrated a sensitivity 100-fold greater than that determined for solvent desorbed VOCs (Table 32). This demonstrates that VOCs can be thermally desorbed from charcoal cloth quantitatively without dilution by using the Carbopack B trapping column.

It was exceedingly difficult to confirm that the low recoveries were due to non-desorption from the charcoal cloth. The concentrations of VOCs used for the thermal desorption studies were low, such that removal of any residuals by solvent desorption would result in dilution to a point below the limits of detection. Throughout all of the experiments, o-xylene posed a particular problem, being extremely difficult to desorb from charcoal cloth under any conditions, possibly as a consequence of a strong chemical interaction with the carbon filters rather than the usual physical, though reversible, interaction generally associated with chemical-charcoal interaction.

Table 32 Detection Limits of Hexane Desorption and Thermal Desorption of the Mixture of VOCs*.

VOCs	Hexane desorption (ug)**	Thermal desorption (ug)***
Benzene	2.5	-
Trichloroethylene	2.5	0.025
Toluene	2.5	0.025
Tetrachloroethylene	2.5	0.05
Chlorobenzene	2.5	0.025
o-Xylene	10	-
p-,m-Xylene	2.5	-

* Detection limit in these substances refers to a peak of approximately 1.0 mm height visible at the appropriate retention time for each chemical in the mixture.

** Detection limit for a standard of 2.5 ug of chemicals (or 10 ug of o-xylene) in 4.0 ml of hexane, injecting a 1.0 ul sample of the mixture into the GLC/PID.

*** Detection limit of a standard mixture applied directly as a liquid (in hexane) to the Carbopack B trap and thermally desorbed into the GLC/PID.

FIELD TESTING

The proof of developing any new instrument or technique is to be able to take something from the laboratory into less controlled field conditions and demonstrate that it will function both qualitatively and quantitatively according to expectations. The performance of charcoal cloth cassette has been tested both in the laboratory and in the field. This sampling cassette was tested both in the laboratory and in one industrial setting, a vehicular paint shop. Using a dynamic vapour pressure system for mixed solvents, the recovery of six VOCs over sampling periods of 1,2 and 4 hr, extracted by hexane and analyzed by GLC, was greater than 78% (Fig.28). The overall system accuracy was satisfied according to NIOSH criteria for all compounds (<25%), except for o-xylene (Table 21). For short-term sampling (10-30 min), the accuracy of the method (recovery of the mixture of four VOCs by thermal desorption and analysis by GLC) was more than 89% but the precision of the method (variations between replications) was poor (6-25%) (Table 23). The overall system accuracy was above 25% for the four VOCs analyzed (Table 24). The large variations observed may reflect poor performance of the thermal desorbing cassette.

In the field, adsorption on charcoal cloth gave comparable results with that using nutshell charcoal tubes for for total xylenes even though the sampling times (Table 26) and sampling locations (Fig.11) for these two devices were different. The charcoal cloth cassette sampler also detected variations in room air concentrations dependent on the location of the sampling device and ventilation dynamics in the room. Total xylenes were highest at a site in a corner of the room than at sites near doors and the ventilation outlets (Fig.11 and Table 26). The charcoal cloth cassette sampler also adsorbed toluene and chlorobenzene at very low but quantifiable concentrations by thermal desorption and GLC/PID analysis (Table 25). Toluene was a component of a primer paint used earlier in the day. These preliminary results demonstrated that the charcoal cloth cassette can be used to collect high and low concentrations of VOCs in the field.

CONCLUSIONS

Charcoal cloth would appear to be a useful adsorbing medium for air sampling in both industrial and office building/home environments for either single chemicals or mixtures. The adsorption capacity and solvent desorption efficiency of charcoal cloth are comparable to those of nutshell charcoal. Charcoal cloth has a significant advantage in having very low pressure drop across the device. It could use many charcoal cloth discs. The unit cost of sampling would be less than using a NIOSH charcoal tube. Experiments have demonstrated that adsorbed VOCs can be quantitatively removed from the charcoal cloth at any time up to 32 days after sampling, provided that the discs are stored in sealed glass containers. With high levels of air contamination, short-term sampling with solvent desorption and GLC analysis will yield accurate, reproducible results with a high percent recovery of the adsorbed VOCs from the charcoal cloth. However, the major disadvantage of solvent desorption is the irreparable damage done to the charcoal cloth, making it useless for repeated use. The NIOSH-type, sampling tubes with nutshell charcoal cannot be reused. In contrast, with low-level air contamination situations, short- or long-term sampling coupled with thermal desorption and GLC analysis will result in an extremely sensitive and reliable analytical tool for air quality measurements for many low molecular weight VOCs with the exception of xylene. In addition, with thermal desorption, the charcoal cloth disc can be reactivated and reused for up to 20 times since the reheating of the discs does not appreciably alter the adsorption properties of the charcoal as determined by repeated measurements of breakthrough time and volume of standard VOC mixture.

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APPENDIX I

Breakthrough time(s) = time taken for VOCs to break through the adsorbent materials (min or hr)

Breakthrough volume = Breakthrough time x flow rate

= (min) x (ml/min)/1000

= L

Breakthrough capacity (Weight of trapped VOCs)

= Breakthrough volume x VOCs conc.

= (L/1000) x (mg/m^3)

= (m^3) x (mg/m^3)

= mg

Adsorption capacity = Weight of trapped VOCs/Weight of charcoal cloth

= mg/mg

Sample Calculation - Toluene

Toluene concentration = 222 mg/m^3

Flow rate = 209.8 ml/min

Breakthrough time = 423 min

Weight of cloth = 90.9 mg

Breakthrough volume = 423 x 209.8

= 88.75 L

Breakthrough Capacity= 88.75/1000 x 222

= 19.70 mg

Adsorption Capacity = 19.70/90.9

= 0.22

APPENDIX II

Sample Calculation - Benzene

Benzene conc. = 10.4 mg/m^3

Flow rate = 203.3 ml/min

Sampling Time = 60 min (1-hr sampling)

(1) Sampling Volume = Sampling Time (min) x Flow rate (ml/min)

= 60 (min) x 203.3 (ml/min) = 12198 ml

= 12198 (ml) x 10^{-3} (L/ml) = 12.20 L

= 12.20 (L) x 10^{-3} (m^3/L) = 0.0122 m^3

(2) mg Expected = Benzene conc.(mg/m^3) x sampling Vol. (m^3)

= 10.4 (mg/m^3) x 0.0122 m^3 = 0.1269 mg

ug expected = 126.9 ug

(3) % Error (Bias) (B_i) =100 (Found-Expected)/Expected

From Experimental Data (1-hr Sampling):

	ug Expected	ug Found
(1)	126.9	108.6
(2)	126.6	125.5
(3)	126.6	113.7
(4)	126.6	125.5
(5)	126.6	112.7
$\bar{X}$ ± SD	126.66 ± 0.13	117.20 ± 7.81
$\%CV_1 = SD\times100/\bar{X}$		6.70

Average benzene concentration found 117.20 ug (1-hr Sampling)

Average benzene concentration expected 126.66 ug (1-hr Sampling)

B_i = 100(117.20-126.66)/126.66

= -7.47%

(4) Mean Bias (Error), $\hat{B}$ = $\mathcal{E} n_i B_i / \mathcal{E} n_i$, n = number of replication

From Experimental Data (1-hr, 2-hr and 4-hr Sampling):

	ug Expected	ug Found	%Error (B_i)	%CV (n=5)
1-hr Sampling	126.66	117.20	-7.47	6.70
2-hr Sampling	289.52	302.28	4.41	6.60
4-hr Sampling	574.05	547.13	-4.69	5.52

$\hat{B}$ = [5(-7.47)+5(4.41)+5(-4.69)]/15

= -2.58%

(5) $\overline{CV}_T$ = $[\mathcal{E}(CV_i)^2 f_i / \mathcal{E} f_i]^{1/2}$

n = number of replication

f = degree of freedom = n-1

CV = coefficient of variation

$\overline{\overline{CV}}_T = [(6.70)^2 x4 + (6.60)^2 x4 + (5.52)^2 x4/12]^{1/2}$

$= [179.56 + 174.24 + 121.88/12]^{1/2}$

$= [475.68/12]^{1/2}$

= 6.30

$\overline{\overline{CV}}_T$ = precision of analytical and sampling method

(6) Overall system accuracy (O.S.A.)

$= 1.96(\overline{\overline{CV}}_T)$ + Absolute mean bias, $|\hat{B}|$

$= 1.96 \times 6.30 + 2.58$

$= 14.93$

APPENDIX III

Wheeler Equation For The Kinetic Adsorption Capacity of Adsorbent.

$$t_b = \frac{W_e W}{C_0 Q} - \frac{W_e \rho_B}{K_V C_0} \ln(C_0/C_X)$$

where

t_b = breakthrough time (min)

C_X = exit concentration (g/cm^3)

C_0 = inlet concentration (g/cm^3)

Q = volumetric flow rate (cm^3/min)

W = weight of adsorbent (g)

ρ_B = bulk density of the packed bed (g/cm^3)

W_e = kinetic adsorption capacity or equilibrium adsorption capacity at an arbitrary ratio of C_X/C_0 (g/g); and

k_v = first order constant of adsorption (per min)

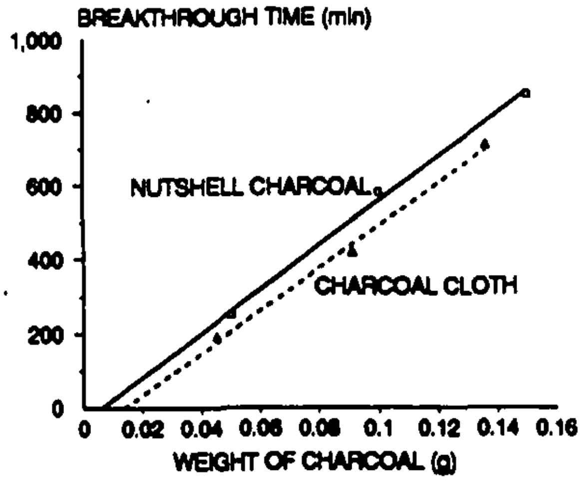

Fig.46 The relationship between breakthrough times (min) and weight (mg) of nutshell charcoal and charcoal cloth for toluene.