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Long-Term Integrated Sampling to Characterize Airborne Volatile Organic Compounds in Indoor and Outdoor Environments

by

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A la mémoire de ma mère de qui je ne suis qu'un simple fruit de la nature. Elle a su être pour moi une grande source de motivation et d'inspiration ce qui m'a toujours poussée vers l'équilibre, la réussite et le bonheur.

Pour toi ma mère

ABSTRACT

Sampling methods used for the assessment of exposure to volatile organic chemicals (VOCs) in the workplace or for environmental studies are now limited to an upper integrative sampling time of 24 hours or less. Generally, these methods lack versatility and are difficult to use. A passive sampler that can extend sampling periods was developed as part of this research. This novel sampler relies on capillary tubes to restrict and control ambient air entry into an evacuated sample container.

A mathematical model was derived by modifications to the Hagen-Poiseuille and ideal gas laws. This model defines the relationship between container volume and capillary geometry (length/internal diameter) required to provide selected sampling times. Based on theoretical considerations, simulations were performed to study the effects of dimensional parameters. From these results, capillaries having 0.05 and 0.10 mm internal diameters were selected according to their ability to reduce sampling flow rates and to increase sampling times. Different capillary lengths were tested on various sampler prototypes. It was found that a constant sampling flow rate was delivered when a maximum discharge rate was established under the influence of a pressure gradient between a vacuum and ambient pressure. Experimental flow rates from 0.018 to 2.6 ml/min were obtained and compared with model predictions. From this comparison, empirical relationships between capillary geometry and maximum discharge rate given by the pressure gradient were defined. Essentially, based on these empirical relationships, capillary sampling flow controller specifications can be calculated to offer extended integrated sampling periods. On this basis, sampler prototypes were configured for stationary sampling and personal sampling.

Studies, based on theory, have indicated that factors such as temperature, humidity and longitudinal molecular diffusion are not likely to influence the passive sampling process. Subsequent experiments confirmed that temperature changes should not significantly affect flow rates delivered by controllers, and that molecular diffusion does not have any impact on the representativeness of long-term samples. Recovery tests provided acceptable results demonstrating that selected capillaries do not contribute to adsorption that could seriously affect the validity of this sampling approach.

Field demonstration studies were performed with both stationary and personal sampler prototypes in the indoor and outdoor environments. The performance of the sampler compared favorably, and in some instances, exceeded that of accepted methodology. These novel samplers were more reliable, had greater versatility and principally, allowed sampling periods extending from hours to a month. These inherent qualities will assist industrial hygienists and environmentalists in the study of emission sources, pollutant concentrations, dispersion, migration and control measures. This novel sampler is presently the only device available for the effective study of episodic events of VOC emission.

Selected capillary geometries acting as a restriction to the entry of ambient air into evacuated sample container can provide a simple, versatile and reliable alternative for the collection of VOCs. This approach can contribute to a better understanding of VOC effects on human health and the environment.

RÉSUMÉ

Les méthodes d'échantillonnage intégré utilisées pour déterminer l'exposition aux composés organiques volatils (COVs), qu'elles soient appliquées en milieu de travail ou pour l'étude de la protection de l'environnement, sont toutes présentement limitées à une durée d'échantillonnage inférieure à 24 heures. Ces méthodes sont généralement complexes à utiliser et peu polyvalentes. Dans le cadre des travaux de recherche, un échantillonneur passif permettant de prolonger la durée de collecte a été développé. Le principe de cet échantillonneur s'appuie sur l'utilisation de tubes capillaires pour restreindre et contrôler l'entrée de l'air ambiant à l'intérieur d'un réservoir initialement sous vide.

Un modèle mathématique a été dérivé à partir de modifications à la loi d'Hagen-Poiseuille et celle des gaz parfaits. Ce modèle définit la relation entre le volume du réservoir utilisé et la géométrie d'un capillaire (longueur/diamètre interne) nécessaire pour fournir la durée d'échantillonnage désirée. Sur la base de considérations théoriques, des simulations ont été réalisées afin d'étudier l'influence des paramètres dimensionnels. À partir de ces résultats, des tubes capillaires possédant un diamètre interne de 0.05 mm et 0.10 mm ont été sélectionnés en fonction de leur capacité à réduire considérablement les débits volumétriques, pour ainsi accroître les durées d'échantillonnage. Différentes longueurs de ces deux capillaires ont été testées en laboratoire à l'aide de prototypes. Il est prouvé qu'un débit d'échantillonnage constant est généré durant une période pour laquelle un écoulement optimal s'établit sous l'influence d'un gradient de pression entre le vide et l'atmosphère. Des débits d'échantillonnage expérimentaux variant entre 0.018 et 2.6 ml/min ont été obtenus et comparés aux prédictions mathématiques. Ces comparaisons ont permis de définir des relations empiriques entre la géométrie d'un capillaire et l'écoulement optimal fourni par le gradient de pression. Essentiellement, il est démontré que les spécifications d'un contrôleur capillaire peuvent être adéquatement calculées pour offrir des durées prolongées d'échantillonnage intégré. Sur cette base, des prototypes ont été configurés pour l'échantillonnage stationnaire et l'échantillonnage personnel.

Des études s'appuyant sur des considérations théoriques ont démontré que des facteurs tels la température, l'humidité et la diffusion moléculaire longitudinale ont peu d'influence sur le processus d'échantillonnage passif. Des expériences ont confirmé que les changements de température n'affectent pas significativement les débits générés par les contrôleurs, et que la diffusion moléculaire n'a pas d'impact sur la représentativité des échantillons collectés à long terme. Des essais de récupération ont fourni des résultats satisfaisants, démontrant ainsi que les capillaires utilisés ne contribuent pas à des phénomènes d'adsorption pouvant nuire à la validité de cette méthode d'échantillonnage.

Des études de démonstration sur le terrain ont été menées dans des environnements extérieurs et intérieurs, à l'aide de prototypes pour l'échantillonnage stationnaire et personnel. La performance des échantillonneurs s'est comparée favorablement aux méthodes approuvées. Les nouveaux échantillonneurs sont fiables, polyvalents et ils permettent surtout d'étendre la durée d'échantillonnage de quelques heures jusqu'à un mois. Ces qualités intrinsèques peuvent aider les hygiéniste industriels et les environnementalistes pour étudier les sources d'émissions, les niveaux de pollution, la dispersion et la migration ainsi que les mesures de contrôle. Le nouvel échantillonneur est présentement le seul outil disponible pour étudier efficacement les événements épisodiques d'émission de COVs.

La sélection d'une géométrie de tube capillaire agissant comme restriction pour l'échantillonnage passif de l'air ambiant à l'intérieur d'un réservoir initialement sous vide est une alternative simple, polyvalente et performante pour collecter les COVs. Cette approche peut permettre de mieux comprendre l'influence des COVs sur notre environnement et notre santé.

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Finally, my last word is for my son, Dominic. He is too young to understand but he was able to inspire me with the courage and determination needed to attain these achievements.

<u>Note to the reader:</u> this thesis includes in appendix-1 a manuscript to be published:

Capillary Sampling Flow Controller (CSFC)
for the Time Integrated Passive Collection of Gas and Ambiant Air

US Patent Application, Serial No. 08é646,073
Inventor: Philippe Simon and Jean-Pierre Farant

The contribution from the co-author, Jean-Pierre Farant, was essential. He supervised and supplied materials and equipment required to conduct research studies. The responsibilities for this invention are acknowledged as follows: P.Simon 90%, J.P. Farant, 10%.

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LIST OF NOTATIONS

A	Cross-sectionnal area (m^2)
A_E	Term for Eddy's diffusion in Van Deemter equation (m)
B	Term for longitudinal diffusion in Van Deemter equation (m^2/s)
c_i	Concentration of a VOC ($\mu g/m^3$)
C	Term for mass transfer in Van Deemter equation (s^{-1})
CF_i	Correction factor for the contribution of a VOC from the dilution gas (ng)
D_i	Diffusion coefficient of a VOC (m^2/s)
D_f	Dilution factor for the analysis of subpressurized samples
D_z	Diffusion coefficient in axial coordinates (m^2/s)
$HETP$	Height equivalent to a theoretical plate (m)
K_1	Constant in the volumetric sampling flow rate time function of the model (m^3/s)
K_2	Constant in the volumetric sampling flow rate time function of the model (s^{-1})
K_3	Constant in the sampling pressure time function of the model ($kg \cdot m^3/s^2$)
K_4	Constant in the sampling pressure time function of the model ($kg \cdot m^3/s$)
K_5	Constant in the sampled volume time function of the model (m^3)
K_6	Constant in the sampled volume time function of the model ($m^{-3} \cdot s^{-1}$)
K_{exp}	Experimental constant for the empirical model
L	Lenght of inlet restrictive deactivated fused silica capilliary column (m)
L_d	Length of path over which diffusion occurs in passive diffusive sampler (m).
m_i	Mass of analyte that diffuses (μg)
M_i	Mass of a VOC in gas samples injected in the GC/MS (ng)
Md_i	Mass of a VOC in dilution gas (ng)
n	Number of moles (mole)
nb	Number of theoretical plates
$n(t)$	Molar content time function (mole)
P_0	Inlet pressure inside capillary (Pa)
P_f	Final pressure after dilution (atm)
P_L	Outlet pressure inside capillary (Pa)
P_s	Final pressure after the sampling process (atm)
P_{atm}	Atmospheric pressure (Pa)

$P(t)$	Pressure time function (Pa)
Q	Volumetric flow rate (m^3/s)
Q_{exp}	Experimental volumetric flow rate (ml/min)
Q_{th}	Theoretical volumetric flow rate (m^3/s)
$Q(t)$	Volumetric sampling flow rate time function (m^3/s)
r	Radial distance in cylindrical coordinate (m)
R	Internal radius of restrictive deactivated fused silica capilliary column (m)
$\mathbb{R}$	Gas constant for air ($N \cdot m/mole \cdot K$)
Re	Reynolds number
T	Temperature (°K)
$\bar{V}$	Molar volume of air ($m^3/mole$)
$V(t)$	Sampled volume time function (m^3)
V_d	Volume of dilution gas injected in the GC/MS (m^3)
V_f	Final sampled volume (m^3)
V_{inj}	Volume of sample injected in the GC/MS (m^3)
V_s	Canister sampler volume (m^3)
v_z	Velocity of fluid in longitudinal direction (m/s)
$<v>$	Average velocity of the fluid (m/s)
z	Longitudinal distance in cylindrical coordinate (m)

Greek characters

θ	Angle in cylindrical coordinate (radian)
τ_{rz}	Shear stress (N/m^2)
ρ	Fluid density (kg/m^3)
π	3.14159...
μ	Viscosity of air (poise)

Indices

i: refers the variable to each of the target VOCs analysed

Abbreviations

CSFC	capillary sampling flow controller
DSI	direct split interface
GC	gas chromatograph
FID	flame ionization detector
GM	geometric mean
GSD	geometric standard deviation
ID	internal diameter
MCM	moisture control module
MS	mass spectrometer
mu	mass unit
OD	outside diameter
P&T	purge and trap injector
QA	quality assurance
QC	quality control
SS	stainless steel
UHP	ultra high purity
TLV	threshold limit value
TWA	time weighted average
VOCs	volatile organic compounds

1-INTRODUCTION

1.1-Statement of the problem

Volatile organic compound (VOC) exposure can be an important human health risk. Although low levels of many VOCs are found in drinking water or food, ambient air can be the major contributor to the overall absorbed dose. Thus, for many airborne organic chemicals, regulations are applied to mitigate the potential health hazards from inhalation. The effects of VOCs on our environment are also well documented. Many contribute, to different degrees, to global warming and/or to the stratospheric ozone layer depletion. Furthermore, VOCs participate in the photochemical formation of atmospheric oxidants (tropospheric ozone) which are strong respiratory irritants. Based on these facts, stringent controls have been increasingly implemented to reduce emissions.

Air quality studies have been routinely conducted to assess exposure to VOC's both indoors and outdoors. In both instances, previous research has clearly demonstrated that integrated sampling time is critical to the development of an effective survey strategy (Roach, S.A., 1977). Statistically, it is recognized that increasing sampling time contributes to a reduction in the variability of the measurements obtained to define exposure (Spear, R.C. et al., 1986), or to establish background levels (Zimmer, C.E. and R.I. Larsen, 1965). Temporal fluctuations will affect the number of samples required to evaluate mean airborne concentrations and to characterize their distributions (Rao, S.T. et al., 1991). Theoretically, air quality studies would need less observations with long-term integrated sampling to detect statistically significant differences between sampling sites. Arguments to increase sampling periods can also be found in toxicology. It has been suggested that sampling time should be adapted to represent human uptake, distribution and elimination kinetics in order to relate exposure measurements to total body burden (Saltzman, B.E., 1970; Rappaport, S.A., 1988). For many toxic airborne chemicals, longer sampling periods would provide a better estimate of adsorbed dose, and therefore improve the evaluation of potential risk from chronic exposure. Presently, all VOC sampling methods are limited to an upper integrated sampling time of 24 hours or less. This is mainly due to a physical barrier to the achievement of lower sampling flow rates. Current technologies apparently cannot provide an accurate convective ambient air flow rate below 2 ml/min.

Two sampling approaches are now used to collect VOCs during field surveys. Methods rely either on sorbent materials to concentrate target pollutants, or on evacuated containers to collect whole air samples (Jayanty, R.K., 1989). Active or passive techniques can be implemented with both approaches. Sorbent-based methods are widely used in industrial hygiene. Active methods using calibrated pumps to deliver constant flow rates to sorbent materials are considered as state-of-the-art. Passive devices are also popular because of their simplicity, low cost and convenience. However, with this method, the sampling rate which is controlled by diffusion is less precise and reliable when compared with convective flow rates obtained from a pump. Globally, both these methods lack versatility. Sorbent materials must be chosen based on the nature of VOCs to be collected, that is, their volatility and whether they are polar or non-polar. Environmental factors such as atmospheric humidity and temperature also significantly affect measurements. Furthermore, sorbent capacity sometimes limits sampling periods in the heavily polluted environments usually encountered in industrial workplaces and, often samples are lost because of overloading. Conversely, whole air collection methods are more widely used in environmental studies, mainly because better sampling containers namely, summa canisters, were developed. Summa canisters were shown to maintain the integrity of most VOCs during sampling and storage periods (Oliver, K.D. et al., 1986; Brymer, D.A. et al., 1996). Recently, the final draft for U.S.EPA method TO-15 was released in which sampling procedures based on the use of these canisters were defined to measure 97 VOCs listed as hazardous airborne pollutants in Title III of the US Clean Air Act amendments

(U.S. EPA, 1995). Active or passive whole air methods can be used and in both cases, flow controllers such as mass flow controllers or critical orifices govern the process. The sampling flow rate delivered by these electronic or mechanical devices directly affects integrated sampling periods. In fact, the level at which they maintain a relatively constant volumetric flow rate dictates sampling times. Active sampling systems using pumps provide pressurized samples in summa canisters. This method may be more effective in controlling sampling times, but it is generally more expensive and cumbersome. Passive methods are simpler to use. They provide subpressurized integrated samples based on the period when maximum flow rates are discharged. The sampling approach with summa canister is considered a gold standard because of its reliability and non-specificity (Des Tombes, K. et al., 1991; Tang, Y.Z. et al., 1996). However, both approaches lack versatility because of the limited range of flow rates delivered by present flow controllers.

There is obviously a need for more flexible sampling strategies for both industrial hygiene and environmental investigations. A method that would allow a longer sampling time would improve air quality studies in both instances. Whether personal or stationary sampling is required, extended sampling durations can be a more meaningful and cost effective approach to evaluate and characterize airborne VOCs.

1.2-Objectives of the study

This research attempts to answer several questions related to the use of capillary tubings as restrictive flow rate controllers for the sampling of ambient air into evacuated containers, a process which is driven by a pressure differential. The concept is new and has never been investigated before.

The main objectives of this research are summarized as follows:

1) to develop and evaluate a capillary flow controller for the long-term integrated passive sampling of VOCs using evacuated sampling containers such as summa canisters;

2) to demonstrate the applicability of long-term integrated passive samplers using a capillary sampling flow controller (CSFC).

Specific secondary objectives relevant to this research are as follows:

- to study the influence of design parameters on the achievement of controlled low flow rates provided by selected capillary geometries;
- to derive mathematical equations that establish the relationship between sampling times and flow controller design parameters;
- to configure and assemble passive sampler prototypes;
- to estimate the effect of environmental factors on the validity and the reliability of long-term passive samplers;
- to evaluate the representativeness of gas samples collected in summa canisters over extended sampling periods;
- to test prototypes in field surveys and compare integrated passive sampler performances with currently approved sampling methods;
- to develop laboratory analytical procedures that will achieve the GC quantification of long-term samples.

1.3-Organization of the thesis

This thesis is divided into six chapters and four appendices. A brief description of each chapter and appendix follow:

Chapter 1:	Introduction. Establishes the nature of the problem being investigated and the objectives of this research.
Chapter 2:	Literature review broken down into two sections. Section 1 provides a synthesis of relevant factors involved when airborne VOCs are monitored to characterize exposures outdoors and indoors. Section 2 provides a review of active and passive sampling methods.
Chapter 3:	Material and methods divided into two sections. Section 1 concerns laboratory techniques and materials used to conduct sampling studies. Section 2 describes equipment and procedures used to analyse samples.

This research's findings can be more effectively reported and discussed as two distinct entities. Thus, the next two chapters will deal with the development and design of a novel flow controller and present results of the validation studies conducted with the device respectively.

Chapter 4:	Results concerning the development of a new device for long-term integrated passive sampling of ambient air VOCs: the Capillary Sampling Flow Controller (CSFC). This chapter is broken down into two sections. The first section presents prototype configurations and mathematical model equations used to design passive samplers. Section 2 gives simulation results and experimental findings for the study of capillary geometry effects on flow rates and sampling times.

Chapter 5: Results and discussion related to validation studies conducted to evaluate the applicability of the novel sampling method. The first two sections concern theoretical and experimental validation studies. The last section describes the results of field demonstration studies performed with prototypes in indoor and outdoor environments.

Chapter 6: Conclusion. This chapter presents conclusions derived from the findings arising from this research. Suggestions for further studies and contribution to knowledge are also included.

Appendix 1: Invention's manuscript submitted for patents in U.S. and Canada.

Appendix 2: Calibration curves used to quantify 54 selected VOCs by GC/MS.

Appendix 3: Experimental results obtained by testing inlet restriction capillary geometries with evacuated sampling containers.

Appendix 4: Test results for prototypes reported by an external laboratory.

2-LITERATURE REVIEW

Airborne volatile organic compounds (VOCs) are a source of health hazards. Among this broad class of chemicals, many species are known to cause various health outcomes. VOCs are present as either gases or vapors and they are mainly absorbed via the respiratory tract. Chemicals such as benzene, vinyl chloride, carbon tetrachloride, perchloroethylene, methylene chloride and 1,2-dibromoethane among others, are classified as known or suspected human carcinogens by public health and environmental authorities (ACGIH, 1993; Canada Gazette, 1989). In excess of a threshold value, exposure to VOCs (aromatics, halides, aliphatics) will affect specific target organs: liver, central nervous system (CNS), blood (NIOSH, 1990).

Monitoring methods have been developed to determine airborne VOC concentrations. Different approaches are used whether workplace exposure is assessed or outdoor levels are characterized. Moreover, in such environments, the concentrations of airborne VOCs differ by several orders of magnitude and the monitoring objectives adopted by industrial hygienists and environmentalists may also differ. In each discipline, it appears that sampling methodologies are limited to an upper integrated time interval. To compare the sampling approaches, important factors in each area of expertise will be defined, and the technical aspects of the methods which are presently used will be discussed.

2.1.-Airborne VOCs

VOCs are emitted by a large number of sources, and exposure occurs in nearly all types of environments. The environments are characterized by their level of contamination which varies considerably depending on location. The highest levels of airborne VOCs exposure are found in industrial settings where such chemicals are handled or produced, and where the average concentration of these VOCs are typically in parts per million (ppm). On the other hand, VOCs are at lower levels in outdoor ambient air where many species can be measured in the parts per billion (ppb) range. Furthermore, if urban and rural areas are compared, it is still possible to see parts per trillion (ppt) for some of these chemicals in the cleanest outdoor atmosphere (Tremblay, J. and T. Dann, 1995).

Airborne VOCs are also found in various indoor environments. Offices (Hodgson, A.T. and J.M. Daysey, 1989; Weschler, C.J. et al., 1990; Ekberg, L.E., 1994) and residences (Seifert, B. and D. Ullrich, 1987) were shown to contain many sources of emissions which contribute to increased exposure.

Whether high or very low concentrations are measured, the most common property of airborne VOCs is the great variability of their concentration in time. Before sampling approaches are discussed in detail, some of the common objectives of field investigations will be described. The factors which affect the temporal and spatial aspects of concentrations will also be defined.

2.1.1-Workplace

Airborne VOCs are sampled in the workplace to characterize a potential health hazard. Regulations are applied to work environments to protect an employee's health. These regulations specify limits or standards which should not be exceeded to prevent adverse health effects. Limits are established for short-term peak exposure as well as for workshift average exposure: the time-weighted-average (TWA). Well established sampling and analytical methods have been developed to determine the concentrations of selected VOCs (NIOSH, 1984; OSHA, 1985; IRSST, 1993). They can assist professionals in adopting the appropriate survey strategy. Most of these methods are valid for concentrations ranging from 1/10 below to several times above the acceptable levels: the threshold limit value (TLV).

Even though stationary samples are invariably collected during industrial hygiene investigations, personal sampling is preferred to estimate the exposure. Exposure assessment may be the main reason for conducting workplace studies. Two approaches are used. If the health risk associated with a specific job classification is judged to be homogeneous, a representative number of workers are selected. Otherwise, the workers at greater risk are monitored (Norwood, S.K., 1987). In all instances, an appropriate number of samples are required to obtain an adequate estimate of the central tendency (mean) and the dispersion (standard deviation) which can represent workers' exposure over time. These sampling strategies consider the time and space variations in exposure: fluctuations in processes (production rates), maintenance, seasonal changes in ventilation and a worker's personal habits (Damiano, J., 1989). In such cases, periodic measurements are required to provide an adequate estimate of long-term exposure.

With such strategies, results from random samples collected on several workers assigned to specific job categories are pooled to obtain the probability distribution. Data are expressed as a lognormal density function where this type of distribution best characterizes the presence of airborne VOCs in atmosphere (Ott, W.R., 1990). A well designed sampling strategy results in greater confidence in the data obtained for appropriate decision making.

The monitoring of VOCs in an industrial environment can have several other objectives. It can provide historical records of working conditions which can serve as the basis for epidemiological studies. It can also be used to determine the effects of process changes, to identify emission sources for appropriate control implementation and to verify the effectiveness of control measures.

2.1.2-Ambient air

VOCs are receiving greater attention from public and environmental authorities because of their importance as airborne toxicants, in ground level ozone and in the depletion of stratospheric ozone. Initial monitoring efforts were first directed toward the characterization of source emissions (stack sampling), and regulations were developed to mitigate their release and to reduce air quality degradation (Montreal Urban Community, 1988).

Recently, ambient air quality criteria, which included some target VOCs, were adopted by the Ontario Ministry of the Environment (1992). Defined to protect the environment and human health, these guidelines suggest acceptable limits that are applicable for different averaging times (annual, 24 hours, 1 hour, 10 minutes). They are used by environmental authorities to provide a certificate-of-approval to industries which demonstrate that airborne releases will not exceed ambient air criteria at fence line.

Airborne VOCs are measured in outdoor environment for many different purposes. Monitoring is performed to determine present conditions and trends (Singh, H.B. et al., 1981; Olier, J.P. et al., 1989), and to provide input data on air quality for the validation of large interdisciplinary urban models (Munn, R.E., 1981). Studies are also conducted to apportion point and fugitive sources using chemical mass balance receptor modeling (Aronian, P.F. et al., 1989; McClenny, W.A. et al., 1989; Middleton P. et al., 1990). The results obtained from this methodology are used to estimate the major VOC contributors to the urban levels. With such receptor models, Scheff was able to rank the proportion of specific categories of emissions (vehicle exhausts, gasoline vapors, refineries, chemical industries, waste water treatments, vapor degreasing) for some predetermined locations (Scheff, P.A. and M. Klevs, 1987; Scheff, P.A. and R.A. Wadden, 1993; Wadden, R.A. et al., 1994).

VOCs are also known as ozone precursors. They play an important role in the formation of atmospheric oxidants such as tropospheric (ground level) ozone (Manahan, S.E., 1994). Airborne VOCs react photochemically in the atmosphere with nitrogen oxides and each chemical has an hydroxyl radical rate constant which characterizes their reactivities (Allen, P.D. et al., 1989). Based on this fact, alkanes and alkenes along with some aromatic chemicals contribute more to this problem than other fractions of total VOCs such as halogenated hydrocarbons (Dann, T. et al., 1989). Many environmental studies monitor ozone precursor VOCs along with other air pollutants (ex. NO_x, O_3) to characterize the relationships between these chemicals in the atmosphere (Altshuller, A.P., 1989; MacGregor, L. and H. Westberg, 1990; Altshuller, S.L. et al., 1995).

Chlorinated and brominated volatile organics are of greater concern because of their potential health effects. These halogenated airborne VOCs and some aromatic hydrocarbons (ex.benzene, toluene, xylene) are monitored in exposure assessment studies performed to supply data for risk analysis (Paustenbach, D.J. et al., 1990). Unit factors per concentration of hazardous VOCs are developed to estimate human cancer risk at low exposure levels (Kolluru, R.V., 1991). Based on toxicology, this approach usually assumes chronic (life-time) exposure.

There are several common elements in the different environmental studies in which VOC levels are monitored in outdoor ambient air. First, stationary samples are invariably collected. Also, considering the complex mixtures of VOCs, most strategies attempt to measure simultaneously a large number of selected VOCs. The list of chemicals varies according to the study objectives. For example, the United States Environmental Protection Agency (U.S.EPA) specifies two separate methods whether 41 target air toxics or 52 selected ozone precursors are monitored. These methods use similar sampling approaches, but the analytical procedures differ. U.S.EPA has also received the mandate (section 112 of the Clean Air Act) to protect public health from exposure to 189 hazardous air pollutants (Berry, D.K., 1986). Efforts are continuously made to improve methods, to increase the detection limits and to quantify more airborne hazardous VOCs from a unique sampling approach (McClenny, W.A., 1995). As the analytical technology progresses, a more complete contaminant profile of airborne volatile organics can be observed.

Finally, the other common characteristic of ambient air sampling strategies is that similar parameters will influence the large variability of airborne VOCs in the atmosphere. In outdoor air environmental studies, the space-time relationship is affected on a minute-to-minute basis by wind direction and speed changes. A daily cycle is present because of other meteorological considerations (night-time stability, day-time convection, morning-time peak emissions: temperature inversion) and fluctuations in emission rates, mainly due to traffic (U.S.EPA, 1989a). 24-hour integrated samples are recommended to attenuate the natural daily cycle effects. Meteorological conditions have a direct influence on the exposure (Carter, R.E. et al., 1993). Apart from wind speed and direction, mixing height is another important variable in the transport and dispersion of air pollutants (Seinfeld, J.H., 1986). In a wider time frame, outdoor levels of airborne VOCs are subjected to strong seasonal variations, concentrations being significantly higher during winter (Hartwell, T.D. et al., 1987; Lindskog, A. and J. Moldanova, 1994). This observation is partly explained by large-scale meteorological factors, by modifications in rates of chemical transformations, and by the variation in emission rates, principally from fossil fuel combustion.

Proper sampling strategies should take into consideration these facts. Usually, a large number of samples are required to estimate the variability with confidence (Lioy, P.J., 1988).

2.1.3-Indoor air quality

Inside buildings or residences, VOCs are suspected to cause mucous membrane irritation and neuropsychological effects when concentration of mixtures are high, but still significantly lower than workplace standards (Mølhave, L. et al., 1991). Individual susceptibility is an important factor in these health outcomes frequently associated with the Sick Building Syndrome (Kjaergaard, R.K. et al., 1991). The sampling approach must deal with the fact that no single chemical has been identified as the causative agent. Therefore, total VOCs obtained from analytical quantification is often reported in these studies (Lenderer, B.P. et al., 1993). Again, to relate these outcomes to exposure, the sampling approach should attempt to characterize events where airborne VOC concentrations produce an adverse health effect.

Products such as paint, furniture, draperies and carpets (Bayer, C.W. et al. 1988; Wallace L. et al., 1987; Schaeffer, V.H. et al., 1996), building materials such as particle board (Merrill, R.G. et al., 1987), adhesives (Sanchez, D.C., 1987), photocopy machines (Leovic, K.W. et al., 1996) and heating systems have been identified as major VOC sources. The methods used to characterize VOCs in indoor air are usually derived from both industrial hygiene and environmental practices.

Although some objectives and practices are basically different, the studies of airborne VOCs in ambient air, office or residences have several common features when compared with workplace monitoring. The fundamental principles of sampling methods used in each area have many similarities.

2.2-Sampling methodology for VOCs

A significant overlap exists between air monitoring methods used to sample airborne VOCs for industrial hygiene surveys and for environmental studies. Two technical approaches are used in both instances: active or passive integrative sampling methods. Presently, the most popular approach is based on the collection of VOCs on solid sorbent materials. Airborne pollutants are trapped and concentrated in the field using a porous sorbent. The alternative is to collect air samples inside a vessel which is suitable for maintaining the stability of VOCs prior to laboratory analysis. Both approaches have advantages and limitations. It is obvious that, in the selection of an appropriate method, one must keep in mind the fact that one of the main characteristic of airborne VOCs is their great variability: the concentrations fluctuate in time based on the many factors described above.

The collection of an atmospheric sample for the quantitative or qualitative evaluation of airborne VOCs should also ensure that the procedure will result in a valid observation. The precision from subsequent analytical characterization will greatly depend on sampling errors (Kratochvil, B., 1987). In fact, during the past ten years, analytical methodologies were developed to achieve the desired resolution and sensitivity, and data banks began to appear (Shah, J.J. and H.B. Singh, 1988, U.S. EPA, 1988). Different methodologies may be used when the characterization of VOCs is required. Capillary gas chromatography (GC) plays an important role in the analytical procedure. In recent years, mass spectrometry (MS) detection following GC separation has demonstrated its use in identifying man-made toxic organic chemicals from several environmental sample matrices, including ambient air.

2.2.1-Active sampling techniques

The standard approach which relies on active sampling techniques can be ascribed to airborne contaminants collection methodologies which require the use of mechanical systems to obtain a time integrated concentration of VOC.

2.2.1.1-Sorbent sampling

Solid sorbent materials represent the main element in many of the technical approaches used to sample VOCs. Solid sorbents are porous materials such as charcoal, polymers, graphitized carbons, silica gel and alumina. They are characterized by their high surface area. The retention capacity of sorbents is dependent on the adsorbates, which means that each VOC species interacts differently with the support material.

Sampling tubes are used with pumps that force air to pass through the porous sorbent material. For a given volume of air collected over an integrated sampling period using a constant precalibrated flow rate, VOCs are trapped in the sorbent tube and can be quantified using the appropriate analytical procedures. In the laboratory, VOCs are recovered before they are analyzed by GC using either solvent or thermal desorption techniques, depending on the sensitivity required. With the sorbent method, the sampling flow rate needs to be well controlled to minimize errors. To this end, critical orifices are used to stabilize and reduce the convective air flow generated by the pump (Zimmerman, N.J. and P.C. Reist, 1984).

Introduced in 1968, this active sampling method is widely used in workplace monitoring (Langhorst, M.L. and L.B. Coyne, 1989), for personal or environmental time-weighted average (TWA) assessment of exposure to organic vapors. For this purpose, activated coconut charcoal shell sorbent tubes are used under specific sampling conditions to ensure that target VOCs in a measured ambient air volume are adsorbed on this high surface area material. Active sorbent sampling has been used for the preconcentration of VOCs in ambient air since the early 1980s. It coincided with the development of new sorbent materials, and of new analytical methodology using pre-column direct thermal desorption instead of solvent desorption of concentrated analytes.This latter technique emerged with the development of more appropriate sampling cartridges to overcome observed contamination problems associated with direct injection to GC/MS (Russwurm, G.M. et al., 1981). The development of new porous polymer sorbents having lower affinity for water also had an impact. The factors that influence this process were also better characterized: cartridge diameter, bed depth, sorbent mesh size versus pressure drop and breakthrough volumes of several chemicals versus temperature (Krost, K.J. et al., 1982). These studies pointed out an inherent sampling error related to the accurate measurement of air volume, leading to the use of more precise mass flow controllers instead of calibrated pumps (Walling, J.F. and A.E. Bond, 1984a). The first accredited ambient air VOC sampling and analytical procedures appeared as method TO-1 and TO-2 (U.S.EPA, 1984a, U.S.EPA, 1984b).

As one of the most widely used methods in VOC determination, active solid sorbent sampling offers many advantages. The possibilities of sampling large volumes of air and the fact that sorbent materials are the first element in the sampling train are some examples. Some of the major disadvantages include adequate retention versus breakthrough characteristic for each VOC, blank contamination, and artifact formation during storage of analytes. Poor recovery following desorption should also be mentioned, principally for polar VOCs. These are all factors that affect analytical quality assurance (QA) and will require more stringent control.

Sample breakthrough indicates that the capacity of the sorbent bed is insufficient for some constituents of the collected gas matrix. In industrial hygiene, sorbent tubes contain a second layer which is analyzed separately. This is used to confirm that less than 10% breakthrough has occurred. It can validate that first layer results are representative of VOC contents in the air volume collected during the total integrated sampling time. In environmental monitoring, assessment of toxic VOCs in ambient air using thermally desorbable traps requires good judgement in evaluating sampling volume because breakthrough verification cannot be systematically performed. Replicate samples with different air volumes were proposed as an alternative for the breakthrough determination (Walling, J.F., 1984b). However, this procedure greatly increases efforts and expenses associated with QA/QC. Prediction of breakthrough can theoretically be calculated based on expected contamination profiles, levels of individual VOC, their retention characteristics and the sorbent used. However, the VOC mixture composition is a critical factor and breakthrough may not only be dependent on analyte concentration (Peters, R.J.B. and H.A. Bakkerren, 1994). It should be noted that breakthrough problems predominantly occur with highly volatile organic compounds. In essence, when VOCs are collected in ambient air using active preconcentration on sorbent materials, sample validity is greatly dependent on the total volume of air which is passed through the sorbent cartridges. Mistakes can easily occur because the optimal collected volume is a function of VOC levels present in the sampled atmosphere. That last variable is not known until sampling has been conducted.

With sorbent material, blank contamination can be encountered. However, appropriate corrections can be made if the baseline level is well quantified. An analytical baseline relies mainly on the purity of chemicals involved in cleaning and desorbing procedures (Chuang, J.C. et al., 1990).

Many assessment studies were conducted using this sampling technique. In industrial hygiene, this sampling approach was part of many workplace investigations where workers' exposure was assessed, and examples are too numerous to be cited here. In environmental studies the situation is different because the measurement of low contaminant levels is technically challenging. First used to establish outdoor air levels (Harkov, R. et al., 1983), this technique was also applied to characterize indoor/outdoor VOC personal exposure (Hartwell, T.D. et al., 1987a; Hartwell, T.D. et al., 1987b; Hartwell T.D. et al., 1992), to determine source strength of consumer products (Bayer, C.W. et al., 1988) and building materials (Wallace, L. et al., 1987), to estimate the impact from traffic sources (Zweidinger, R.B. et al., 1988), in new office buildings (Hodgson, A.T. and J.M. Daisey, 1989) or transportation activities (Chan, C.C. et al., 1993; Lawryk, N.J. and C.P. Weisel, 1996; Jo, W.K. and S.J. Choi, 1996). Active sorbent sampling also contributed to source-receptor air pollution exposure model studies in Chicago (Aronian, P.E. et al., 1989) and in a heavily industrialized location in the Kanawha Valley (Cohen, M.A. et al. 1989a; Cohen, M.A. et al. 1991a;Cohen, M.A. et al. 1991b).

Investigations are continuously being made in the field of sorbent materials. Compared with activated charcoal, porous polymer sorbents have lower sorbent capacity. However, they also have less affinity for water and direct thermal injection of analytes into a GC is more easily achievable. This was probably the main factor for the selection of porous polymers such as ®Tenax for ambient air assessment of air toxic levels by active field preconcentration techniques. However, studies on ®Tenax have shown inconsistent results with some aromatic and halogenated hydrocarbons. Unidentified chemical reactions which generated artifacts were proposed as one explanation by Walling (Walling, J.F. et al., 1986). Other types of porous polymers (®Chromosorb, ®Porapak) were studied and described (Rao, N.V. and M. Sriram, 1986). Generally, the temperature limits are relatively low (<300°C) and thermal cleaning procedures are often not sufficient to efficiently remove compounds with high boiling points.

Graphitized carbon materials have proven their utility when one considers their high surface areas, their very low affinity for water and their very high degradation temperatures (Raymond, A. and G. Guiochon, 1976). A comparison between ®Tenax TA and a type of this new sorbent material (i.e. Carbotrap, ®Supelco) was performed and results indicated a promising future for graphitized carbon material, principally in handling very volatile molecules (Rothweiler, H. et al., 1991). Multilayer sorbent cartridges of either porous polymer and/or graphitized carbon materials of different types are now applied to VOC trapping (Heavner, D.L. et al., 1992). New types of carbon-based sorbents (Carbosieve and Carboxen, manufactured by ®Supelco) are still being tested (Vahdat, N. et al., 1995), and better analytical resolution of chemicals is being achieved (Helmig, D. and J.P. Greenberg, 1994). Depending on the chemicals needed to be trapped, chemists can develop and prepare their own recipes of sorbents and many commercial preparations of multilayer sorbent sampling cartridges can readily be prepared or purchased.

Nevertheless, active sampling methods using graphitized carbon or any other sorbent material are prone to similar limitations. For instance, sampling flow rates are dictated, to a certain extent, by a given sorbent material's retention capacity and the choices involved are difficult to make. Invariably, integrated sampling periods cannot be extended to more than a few hours.

2.2.1.2-Whole air sampling

Active collection of whole air samples without field preconcentration was first attempted using glass bulbs and sampling bags. However, these procedures did not adequately ensure sample integrity prior to analysis (Jayanty, R.K., 1989). With these devices, VOCs may be lost in condensed water vapors on glass or bag surfaces (Groves, W.A. and E.T. Zellers, 1996).

Whole air sampling for VOCs became reliable with the recent development of stainless steel summa passivated canisters (Oliver, K.D. et al., 1986). The inner metal surface of the sampling vessel is coated with a thin layer of pure chromium-nickel oxide and electropolished to minimize active sites. In this way, the stability of many organic compounds is preserved and storage intervals are increased. Figure 2.1 presents a diagram of a 1 liter summa canister. The evacuated canisters are available in different volumes and, for practical reasons, the 6-liter container is the most commonly used for outdoor air applications. The first canister-based method was initially summarized in method TO-14 (U.S.EPA, 1984c) as part of U.S.EPA's *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Winberry et al., 1988).

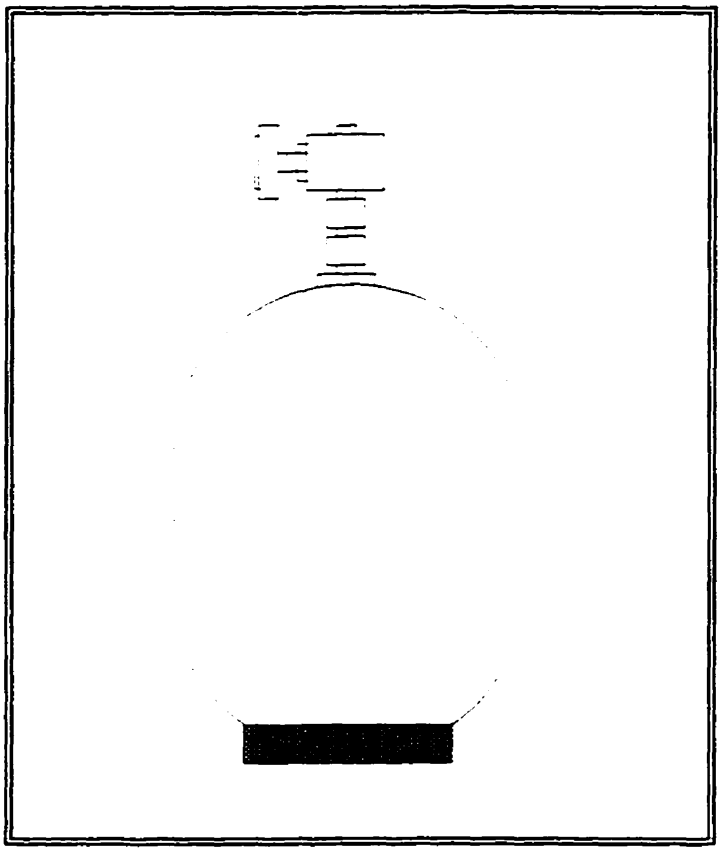

Figure 2.1: Illustration of a summa canister

This device can be used for whole air active sampling. To collect time integrated samples, air can be pressurized in the vessel with commercial sampling units equipped with a pump and a timer (Krasnec, J.P., 1988). These units can be used in many locations because they can be battery operated. Figure 2.2 shows the configuration of such a sampler. After initial development, this active sampling device was modified to prevent contamination from the sampling train (McClenney, W.A. et al., 1987).

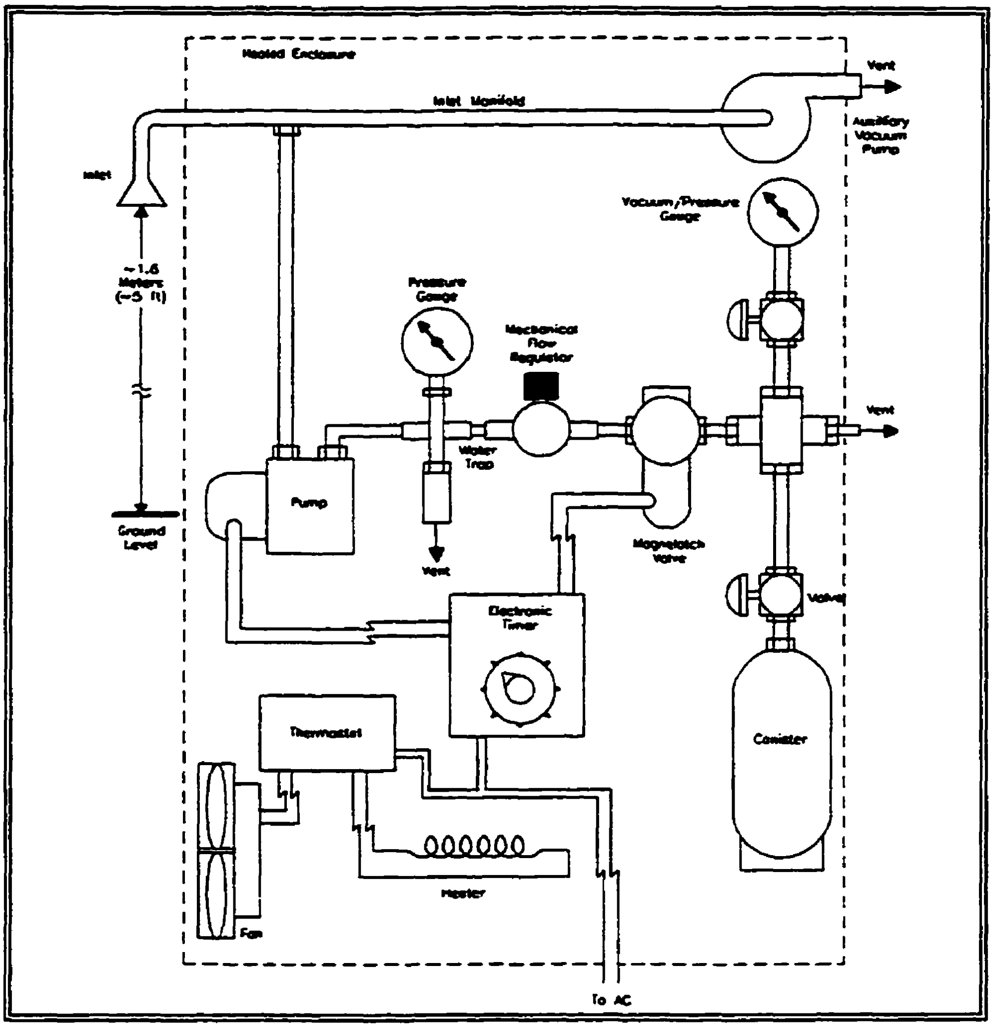

Figure 2.2: Sampler configuration for subatmospheric pressure or pressurized canister sampling using active device (U.S.EPA, 1984c)

These active samplers are available in two types of configurations: 1-Multi-canister samplers that can collect replicate samples and/or consecutive samples at one given sampling point (Krasnec, J.P, 1989, Krasnec, J.P., 1993). 2-Weatherized versions that can be controlled to collect in-sector/out-sector ambient air samples related to specific wind patterns (McClenny, W.A. and J.D. Pleil, 1990). The latter version is suitable for monitoring upwind/downwind VOCs near fugitive sources such as hazardous waste or sanitary landfill sites.

Audits were performed on summa canister samplers and reliability problems were found only when dry air mixtures were handled (Clark, P. et al., 1989). This sample container has many advantages when compared to solid sorbents: it is rugged, easy and safe to use, more than one injection can be performed from the sample container, storage stability is good, no breakthrough occurs and reusability cleanup procedures are simple to perform. The disadvantages include the fact that they are bulky, costly, and the container is the last element in a sampling train such that the sample is more likely to be contaminated by a component of the sampler. Finally, they were initially found to be not suitable to collect polar compounds (McClenny, W.A. et al., 1991). However, they were recently tested with 194 VOCs including reactive compounds such as aldehydes, ketones, alcohols and mercaptans. This study demonstrated that canisters are a viable collection and storage media for a broad range of airborne organic chemicals including polar compounds (Brymer, D.A. et al., 1996).

This active sampling methodology is used by Environment Canada as part of their pollution measurement program to characterize VOCs throughout the country. Twenty-four hour integrated samples are obtained on a weekly basis, predominantly at urban sites and at some rural locations (Wang, D. et al., 1989). In the United States, method TO-14 and target ozone precursor VOCs accredited methodology (method TO-12) both involve passivated canisters (U.S.EPA, 1987). Some VOC ambient air assessment studies were performed to evaluate a population's environmental exposure using this sampling procedure (Grosjean, D. and K. Fung, 1986; Edgerton, S.A. et al, 1989; Michael, L.C. et al., 1990). However, this method is not commonly used for that purpose. Monitoring units are expensive and relatively disturbing (noisy, obtrusive) for participants of residential indoor VOC measurements. They were applied in defining VOC exposures during car transportation activities (Chan, C.C. et al., 1989; Conner, T.L. et al., 1995). These are the few examples of the application of these sampling devices in the indoor environment.

Although they were specifically developed for ambient air sampling, summa canisters were also applied to stack sampling (Gholson, A.R. et al., 1989), subsurface evaluations for VOC contamination (Kirshen, N. and E. Almasi, 1992), measurements of toxic organic contaminants in raw landfill biogas (Solecky, M.F. et al., 1992; Steenkamer, A. et al.. 1994) and in the monitoring of flux chambers dedicated to the estimation of liquid-gas and soil-gas VOC emission rates of environmental area sources (Gholson, A.R. et al., 1991; Reinhart, D.R. et al., 1992). An expired breath sampler prototype was also designed and successfully tested with evacuated canisters (Pellizzari, E.D. et al., 1990).

Most reference methods used for the determination of total non-methane organic compounds (TNMOC), consisting of a carbon based estimation of the total organic compound contents of ambient air or other gaseous mixtures, involve evacuated stainless steel vessels (U.S.EPA, 1993; U.S.EPA, 1994a; U.S.EPA, 1994b). In fact, canister samplers were partially developed as a result of limitations observed during tentative TNMOC level determinations using bag samplers (Cox. R.D. et al., 1982).

Summa canister based active methods provide versatility and confidence for the quantification of VOCs in different environments. The estimation and definition of exposure to a mixture of toxic organic chemicals involve many variables, and in the selection of methodologies to be applied for a predefined purpose, this device can play an important role. Therefore, summa canisters are becoming the standard approach for the accurate and precise quantification of low VOC levels in ambient air.

In practice, the use of either active sampling techniques (preconcentration on sorbent materials or collection of whole air sample) may be relatively expensive for large scale field studies. Also, it should be noted that they are both limited to a relatively short integrated sampling time (<24 hours).

2.2.2-Passive sampling techniques

Compared with active sampling techniques, the operation of passive samplers does not require any source of power and generally, their cost is much lower. Field preconcentration of VOCs on sorbent material can be achieved on the basis of diffusional motion, and the collection of whole air samples can be performed by mechanically controlling the pressure gradient between the atmosphere and an evacuated container.

2.2.2.1-Diffusion on sorbent

The fundamentals of passive sampling with sorbent material is based on the natural diffusion of compounds of interest from its immediate surroundings onto a sorbent. The sampling flow rate or uptake rate of a target airborne contaminant depends on its diffusion coefficient, and is governed by Fick's first law of diffusion. This law can describe the movement of a compound through air due to concentration gradients. For passive sorbent samplers, the equation used is stated as follows:

$$\frac{m_i}{tA}=D_i\frac{c_i}{L_d} \qquad \text{(eq.2.1)}$$

where m_i is the mass of analyte that diffuses (μg), t is the sampling interval (s), A is the cross-sectional area through which diffusion occurs (m^2), D_i is the diffusion coefficient (m^2/s), c_i is the ambient concentration of analyte, (μg/m^3) and L_d is the diffusion path length (m). For such samplers, the main design parameters are the exposed sorbent area

(A) and the length of the diffusion pathway (L_d). The geometry of the sampler and the diffusion coefficient will both determine the uptake rate or sampling rate of analytes (Fowler, W.K., 1982).

This device has become the sampler of choice for the evaluation of full-shift personal VOC exposures because it is simple to use, light and non-obtrusive. Nevertheless, the overall sampling accuracy is estimated at approximately ±25% which is significantly higher than the more conventional charcoal tube methods (±15%). In laboratory experiments, both approaches usually show good agreement (Leinster, P. et al., 1987; Pristas, R., 1991). However, more variability is observed with passive samplers during field testing, principally when exposed to complex mixtures (Saarinen, L. et al., 1987; Purdham, J.T. et al., 1994).

Even though they were designed for personal monitoring of time weighted average (TWA) occupational exposures to organic vapors, these passive samplers are also used for air quality measurements in residential environments and outdoor air. In many instances, sampling time exceeds 8 hours to collect enough materials for analysis. It has been demonstrated that for low VOC levels typically found in ambient air, sampling intervals as long as 8 weeks would not overcome the sorbent capacity of commercial samplers manufactured for industrial hygiene investigations (Shields, H.C. and C.J. Weschler, 1987).

Only a few examples of their applications in long-term monitoring have been reported. This sampling technique has been used successfully for indoor air quality studies in buildings having health and comfort complaints (Weschler, C.J. et al., 1990). Another environmental study showed that the passive samplers were reliable in assessing indoor residential VOC concentrations, but the measurement of the outdoor profile was more difficult to resolve (Cohen, M.A. et al., 1989b). Under such conditions, systematic biases were found with these devices even though they were shown to be a useful tool for the synchronic determination of VOCs at different locations (Monn, C. and M. Hangartner, 1996).

Recently, 757 households randomly selected around the country were sampled for a 24-hour period using these passive samplers. The investigators were able to report the levels of 52 VOCs, providing an interesting insight into the magnitude and the intensity of exposure inside residences (Otson, R. et al., 1994; Fellin P. and R. Otson, 1994). However, more work is needed to ensure the validity of this technique, principally when it is used to quantify many VOCs, and when the sampling time is extended to more than a work shift period to provide an appropriate sensitivity.

Passive sorbent badges are a valuable alternative to sample VOCs in environments where their levels are presumably higher than what is observed in ambient air. They are now widely used in indoor air quality studies where they allow the collection of a larger sample size and significantly improve exposure assessments.

Almost every commercial passive sampling device requires solvent desorption of analytes prior to gas chromatographic analysis. This is one of the limitations. Low detection limits are difficult to attain because of the dilution inherent to this procedure (Coutant, R.W. and D.R. Scott, 1982). Thermally desorbable passive samplers were developed to overcome this deficiency (Gonzalez, J. and S.P. Levine, 1986), but were never tested in long-term monitoring for VOC measurements. It should be mentioned that in the design of thermally desorbable passive samplers, the cross-sectional area through which diffusion occurs is greatly reduced for practical considerations and hence the sampling uptake rate is smaller.

A constant uptake rate is usually assumed for calculating field sample final concentrations, although the diffusion coefficient is strongly dependent on some physical parameters.

Furthermore, ambient temperature will influence the uptake rate and it may be considered as another limitation.

The main problem with increasing sampling time is that theoretically the uptake rate tends to slowly decrease under static concentrations (Coutant, R.W. et al., 1986a). But more importantly, it was shown that under fluctuating concentrations, the deviations can result in more important biases, principally if peak levels occur in the first part of extended sampling periods (Coutant, R.W. et al., 1986b). This remains a major drawback in obtaining precise data using diffusive sorbent samplers for long term monitoring.

Furthermore, relative humidity was shown to affect the sampling rate. For some VOCs, deviations as great as 41 percent were observed at different humidity levels in experimental test chambers (Cohen, M.A. et al., 1991c). It was also demonstrated that during long exposures, ozone can degrade trapped analytes and produce artifact chemicals, principally if a porous polymer is used as the sorbent sampling material (Cao, X.L. and C.N. Hewitt, 1994). These undesired reactions are likely to create a bias in measurements. Finally, other drawbacks related to active sorbent sampling also apply to this method. As mentioned earlier, sorbent materials are generally not good for very volatile contaminants, and desorption problems occur with polar compounds and overloading can take place.

Passive sorbent samplers were shown to be reliable enough in the workplace and are now used by industrial hygienists to determine target VOCs. However, the prediction of diffusional migration may lead to large errors when extended sampling periods of days or weeks are used to assess low levels of various chemicals to characterize exposure in the environment. Nevertheless, these samplers are becoming increasingly popular for such applications primarily because they are inexpensive, easy to use and extended sampling time can be obtained. More research needs to be done before passive sorbent samplers become widely accepted outside occupational environments (Brown, R.H. and M.D.

Wright, 1994).

2.2.2.2-Pressure gradient sampling

Evacuated sample containers such as summa canisters can be filled passively by the convective motion of air driven by a pressure gradient (McClenny, W.A. and R.J. Paur, 1988). The ambient air flow can be reduced with mechanical flow controllers. In active air sampling, critical orifices, hypodermic needles or other tight restrictions are used to reduce the sampling flow rate (Huygen, C., 1970; Brenchley, D.L., 1972). With passive sampling methods, the orifice size and the sampler's volume dictate the time interval (Eaton, H.G. et al., 1976). However, 24-hour integrated samples are difficult to obtain with 6-litre canisters because commercial flow controllers have serious limitations to deliver very low flow rates (Rasmussen, R.A. and R. Stanton, 1995).

With this technique the sampling flow rate is assumed to be constant until approximately half of the vessel is filled. An integrated sample is obtained during this period when a critical flow is established. In the laboratory, the sample is pressurized with purified air to obtain an aliquot that can be withdrawn for analysis. This operation dilutes the sample by a factor of 2 to 4, and increases the detection limit for the quantification of analytes. However, as a result of all the work that was conducted recently to increase the resolution of GC/MS analysis (Gordon, S.M. et al., 1989; Kirshen, N. and E. Almasi, 1992; Pleil, J.D. et al., 1991; Brittain R. and C Feigel, 1994), this dilution no longer has a significant effect on results.

Besides the critical orifice, a typical sampling train includes an inlet filter to prevent the entry of particulates, and a vacuum gauge to record initial and final pressure. This sampling technique is often selected: the sampling train is easier to clean prior to use in the field than those used with an active technique. It is also simpler to use and, finally this approach is considerably less expensive.

The whole air collection method is not as popular in industrial hygiene, even if this sampling approach was initially developed to characterize workplace hazards. An evacuated stainless steel sampler was first reported by Miller as a simple method to collect instantaneous or grab samples for the quantification of gas and vapors (Miller, R.W. et al., 1976). A pocket size stainless steel vessel using an inlet critical orifice was also developed to collect personal passive integrated samples over a full workshift (Eaton, H.G. et al., 1976). However, at the time it was reported, the procedures to determine the pressure were not precise enough, and the sampler was never accepted. Also, with the reduced container volume, the size of critical orifice which is theoretically required to sufficiently extend the sampling time (>8 hrs) becomes so small that particulates can physically interfere by blocking the entry of sampled air. It is also difficult and expensive to manufacture.

This passive sampling approach is presently limited by the availability of reliable mechanical flow controllers. It was never used for personal monitoring. At higher VOC levels such as those found in workplaces, the physico-chemical interactions with inner surfaces of the sample container would be less critical to measurement precision. Materials such as stainless steel (Denyszyn, R.B. and T. Sassaman, 1987) and aluminum (Gholson, A.R. et al., 1990) can preserve the VOC mixture's integrity if their surfaces are well polished. The summa passivation technique used with canisters becomes more important when ppb levels of VOCs are sampled.

This passive sampling technique for the collection of low VOC levels is presently limited by an upper sampling interval (<24 hours). The analysis of gas aliquots by GC/MS certainly gives a more accurate VOC profile measurement in the environment than any other characterization obtained from diffusive sorbent samples. However, the technique would greatly benefit from the development of an inlet flow controller which would allow longer integrated sampling times.

2.2.3-Other considerations

In many instances, a sampling approach which allows an evaluation of mean exposure and an estimate of long term trends would be desirable. In such cases, sufficient data have to be collected to characterize exposure distributions over time. Mean exposure is determined from integrated samples which are usually collected over long averaging times. In the workplace, VOCs are sampled over an entire workshift, whereas in environmental exposure assessment, a 24-hour sampling time is often desired.

Fundamentally, the averaging time of airborne VOCs has a great impact on the variance of the exposure distribution (Saltzman, B.E., 1970). Without affecting the mean results. the extension of sampling time tends to reduce standard deviation and attenuates fluctuations which are observed within a group of shorter averaging time samples (Zimmer, C.E. and R.I. Larsen, 1965). This theoretical aspect of air sampling can indirectly influence the number of samples required to obtain a significant difference between mean exposures when statistical inference is used to compare populations or to test for compliance (Rao, S.T. et al., 1991).

The effects of averaging time have another dimension which is based on the pharmacokinetic relationships between the airborne VOC concentrations and those which contribute to cumulative human dose. This approach introduces the rate of body accumulation of contaminants in the sampling design through the use of biological half-life (Rappaport, S.M., 1988). For chronic toxicants (benzene, carbon tetrachloride and others), these elimination times should dictate the best average sampling period for the results to be interpreted in terms of consequent effects on the body burden. The concept is based on the fact that the human body physiologically dampens exposure variability and sampling strategies should also smooth out short-term fluctuations.

The ACGIH long term limits (TLVs) refer to the average concentration for a normal 8-hour workday and 40-hour workweek. This reference concerning a 40-hour workweek exposure partly supports the concept that longer sampling periods should be used to characterize atmospheric VOCs. As stated by Roach, the choice of averaging period taken on such a basis is preferable to an arbitrary choice of 15 minutes, 8 hours or a period chosen for the convenience of the sampling instrument, analytical procedures or measuring personnel (Roach, S.A., 1977).

In practice, the selection of such a sampling period may not be possible. Technically, all sampling methods have flow rate limitations which have an impact on the averaging time. Presently, all active technical approaches cannot be extended to a 24-hour sampling period. Solid sorbent methods depend greatly on the flow rate used. The selection of averaging time is also a function of the analytical sensitivity required since enough VOCs need to be collected to obtain valid results. This dependency on analytical procedures is less critical in the case of whole air collection methods. Theoretically, it should allow more versatility in the choice of a sampling period. However, whole air collection methods are also limited to an upper sampling time by the mechanical flow controllers presently used to restrict flow rate.

The sampling methods cannot only be compared on the basis of their ability to achieve an appropriate sampling time. Other factors such as cost and precision play a role in the selection of a method. Since budgetary constraints always interfere with study designs, the cost associated with the sampling method becomes a factor to consider. Active sampling techniques use equipment that require an important initial investment. This method also requires properly trained technicians. Of all the technical approaches, the use of passive sorbent badges is the most cost effective sampling method: they are simple to use and affordable. Since strategies should always try to increase sample sizes, more measurements can be obtained with these passive monitors for a given cost when compared with active techniques. Unfortunately, these monitoring devices were never shown to be reliable enough to sample low VOC levels found in urban ambient air. Based on these considerations, passive sampling using an evacuated container such as a summa canister becomes the most economical method.

Precision and accuracy are other factors to be considered in decision making leading to the selection of a sampling method. Sampling errors are classified as either systematic or random. Systematic errors introduce a bias in the measurements. They cause a measured value of a VOC profile to always fall above or below the true value, and they can only be prevented or minimized by constant vigilance. This implies that appropriate flow rate and time measurements are performed and that pressure and temperature conditions are considered in calculating concentrations. Random errors can never be totally eliminated, but their magnitude may be reduced by careful work. They are assumed to be normally distributed around the true value. To date, passive sorbent badges based on diffusive flow to collect VOCs have the highest random sampling errors.

Measurement errors are also attributable to analytical procedures. However, the variability introduced by the time-space concentration fluctuations can be far more important than the ones attributed to the collection and quantification processes (Nicas, M. et al., 1991). Every VOC sampling approach is dependent on the analytical procedures and overall precision can be optimized by spike and recovery testing, by internal standardization and by an accurate control and validation at every step of the analytical process (Adkins, J.E. and N.W. Henry, 1993).

2.3-Summary

For a valid assessment of VOC exposure, the sampling method should be simple and reliable. With a monitoring technique that could achieve long term integrated sampling, one could gather sufficient information to better characterize the intensity and duration of VOC exposures. It could increase the reliability of comparing the levels measured in a particular environment with the outcomes that are observed. This could also improve the dose-response relationship used to determine the threshold limit value of such chemicals.

Presently, active sampling techniques are widely used in various environments. Whatever the monitoring objectives, they constitute the most precise approaches. They remain the state of the art method to sample airborne VOCs. Two different technical approaches are applied depending on the level of contaminants to be measured. However, active sampling with sorbent tubes or with canisters lack versatility and simplicity.

Following the Total Exposure Assessment Methodology (TEAM) studies that provided most of the available data on human VOC exposure outside the workplace, Wallace and coworkers pondered whether a few repeated short-term measurements (12 hours) within the same population could be used to estimate the long term exposure distribution (Wallace, L. et al., 1994). They demonstrated that in the absence of true long term measurements, the prediction of chronic risk may be impossible to validate.

The presence of VOCs in the environment is a matter of public health. The question of whether VOC levels can significantly increase health risks in indoor/outdoor environments is an important concern. Most of the studies performed to date have relied on very poor estimates based on limited set of measurements obtained during relatively short time intervals (< 24 hours).

When VOC source emissions are highly variable, as is the case during most investigations, the air sampling strategy requires a sufficient temporal scale to attenuate fluctuations. Variability can be explained by transport parameters (meteorological and climatic conditions) and by source kinetics (emission rates). Longer sampling periods can dampen most short-term variations to provide better mean VOC profile estimates. With toxicants such as VOCs, the argument for longer integrated measurements is also supported by the biological response observed from health studies.

> "When evaluating long-term inhalation exposures, sample results should be representative of the long-term average air concentrations at the long-term exposure points." (U.S.EPA, 1989b)

In the development of an overall strategy of sample collection, temporal and spatial considerations are of prime importance. One needs to adopt sampling strategies which recognize the inherent statistical nature of assessing exposure.

> "More efficient air sampling programs can be designed, and clearer interpretations of their data made, if important theoretical aspects are clearly understood. The choice of a sampling time is an important decision affecting the results. Empirical and theoretical calculations show that the averaging effect of sampling time attenuates responses to short period fluctuations in pollutant concentrations." (Saltzman, B.E., 1970)

Presently, active sampling devices consist of high-tech, cumbersome and expensive equipment that can, at best, efficiently collect only 24-hour integrated samples. With these methodologies, the sampling period is limited by technological difficulties for the achievement of low and precise flow rates. Sample sizes are also reduced when the equipment costs required for an extensive field study are considered.

A similar problem exists in occupational hygiene with sampling methodologies used by industrial hygienists. As stated by Rappaport in an extensive review of the subject:

> "Indeed, there is a critical need for inexpensive monitoring procedures of modest precision which require a minimum of calibration and interpretation and which can be used by individuals without professional qualifications....devices which can be worn over periods of weeks or months so that true long-term monitoring can be achieved." (Rappaport, S.M., 1991)

In fact, passive sorbent badges can be used for such sampling, but as noted in the literature review, many factors tend to accentuate the poor reliability of such devices in fluctuating conditions (humidity and concentrations) over long sampling periods. Passive sorbent badges can hardly qualify as a solution to the problem. Otherwise, subpressurized integrated passive grab samples can be collected using critical orifices, but maximum sampling duration will be much less than 24 hours.

The problem still remains. Can long-term mean VOC exposures be measured with reliability and simplicity, thus allowing that their impact on human health and/or on our environment can be readily assessed?

3-MATERIAL AND METHODS

The research described in this thesis resulted in the design of a novel flow controller based on selected capillary geometries which allow the long-term sampling of gaseous contaminant using summa canisters. A full description of this invention, the Capillary Sampling Flow Controller (CSFC), is to be found in the patent manuscript. The reader is invited to consult this document presented in Appendix 1. The design and development of this flow controller are reported in chapter 4 and its validation is discussed in chapter 5. The equipment and the procedures used to conduct experiments to fulfill the study objectives are now described.

3.1-Sampling set-ups and procedures

Different configurations of passive samplers using evacuated vessels were tested with the novel flow controller to determine the sampling flow rate achievable and to evaluate the integrated sampling time attainable. Protocols were also developed for the treatment of samplers before and after analysis and of collected samples prior to analysis.

3.1.1-Dynamic testing of flow controllers

Capillary Sampling Flow Controllers (CSFC) designed with different geometries (lengths and internal diameters) of deactivated fused silica columns (©J&W Scientific) were connected to evacuated sample containers. Different canister volumes were tested: 100 ml, 500 ml, 1 l, 6 l. In addition to summa canisters, 150 ml rectangular pocket size containers machined from stainless steel 316 (SS) were also tested. Connections between capillaries and containers were made with stainless steel gas tight reducers (©Swagelok) using graphite-vespel ferrules (© Chromatographic Specialities). A pressure reading device was connected between the flow controller and the evacuated vessel to monitor the change of internal pressure with time. Two different types of device were used: a Bourdon type mechanical pressure gauge (°Matheson, model 63-3704) and an electronic pressure transducer (°Omega, model PX-615) connected to a read-out box. Both devices were calibrated to read in the range of 1 to 3 atmospheres. Tests were performed to verify that the connections were leak-proof: each system was capped at the entry, and the container's valve was opened to verify that it could maintain vacuum during a sufficient period of time (ex.: overnight). When the sampler was determined to be leak-proof, the system was uncapped and testing was started by opening the container's valve. The variation in internal pressure was monitored as a function of time. The pressure readings were used to calculate the sampled volume. The following relationship based on the ideal gas law was used:

$$V(t)=V_s\frac{P_{atm}}{P(t)} \qquad \text{(eq.3.1)}$$

where $V(t)$ and $P(t)$ are respectively the gas volume and the internal pressure which change over time inside the container, P_{atm} is the atmospheric pressure and V_s is the sampling vessel volume. During the initial phase, where a linear relationship was observed between the sampled volume $V(t)$ and the sampling time, experimental flow rates were derived from the slope (linear regression) and sampling times were determined based on the size of each container. Capillary geometry (length and internal diameter) was first predicted using a mathematical model developed to characterize the relationship between the size of the vessel and sampling time (Chapter 4). Experiments were conducted to verify model predictions for sampling periods of hours, days and weeks.

3.1.2-Sample preparation

Two different sample preparation procedures were used during sampling studies.

3.1.2.1-Sample container cleaning

The sample containers were cleaned and evacuated before each sampling experiment was conducted. The cleaning procedure involved emptying each vessel and filling it with humid clean gas (pure nitrogen, air or helium) while heating the reservoir.

A cleaning system was designed and assembled. Figure 3.1 shows a diagram of the experimental set-up. It consisted of a manifold made of stainless steel, equipped with two shut-off valves on each side and a pressure gauge (° Matheson, model 63-3704) connected to the sample container. On one side, a vacuum was supplied by a high capacity two-stage rotary pump (°Edwards, model E2M-1.5). A particulate and vapor filter was installed on-line to protect the pump. On the other side, ultra high purity (UHP) nitrogen was delivered at 3.7 atm (40 psi) through an organic adsorbent trap (activated charcoal bed) and a humidifying chamber. The humidifying chamber was filled with clean deionized water previously boiled and purged with dry UHP nitrogen. A sintered stainless steel diffuser (7 μm) immersed in the water was used to saturate the gas flow. This experimental setting was manually operated by opening one valve at a time and by monitoring the internal pressure of the container. The valve's position (on/off) was changed on either side when vacuum was attained or when containers were pressurized to 2.4 atm (20 psi). All lines were cleaned with a proper source of heat (electrical heating gun, flame torch) to minimise contamination from previous operations. These procedures were adapted from an existing method (U.S.EPA, 1984c).

It should be noted that set-ups and procedures described above were used for the development of the new flow controller. As mentioned earlier, the results from these studies are reported in chapter 4. Other procedures and set-ups including analytical systems were used to validate the sampling method using the CSFC. Validation studies are reported in chapter 5.

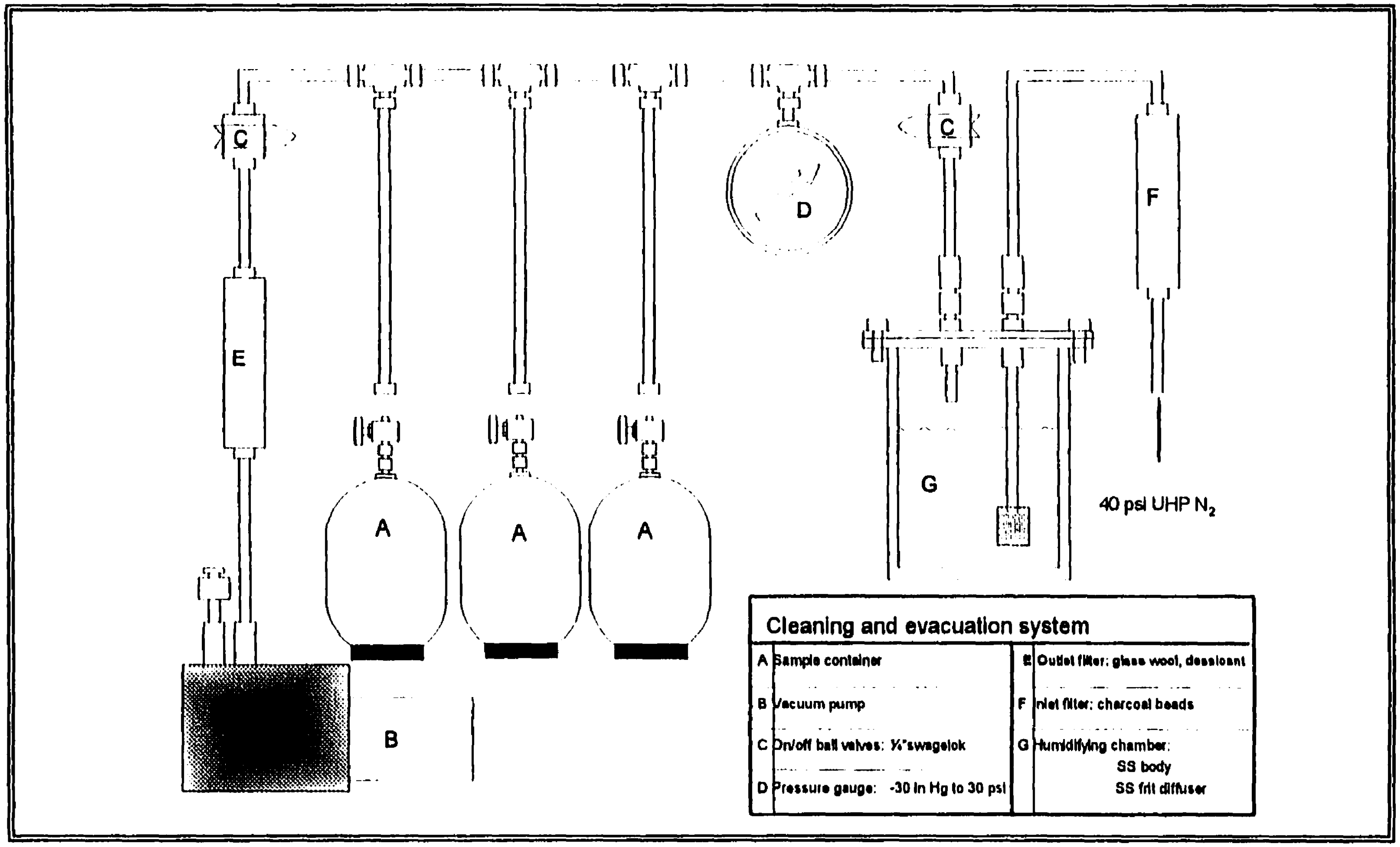

Figure 3.1: Experimental set-up to clean and evacuate sample containers

3.1.2.2-Sample dilution

A sample preparation procedure is required prior to gas chromatographic analysis. The samples collected using the CSFC are pressurized. The containers must be subpressurized to inject the sample in the analytical system. To achieve this, samples were diluted using humidified clean UHP nitrogen. The initial internal pressure was monitored, then the vessels were filled to approximately 1.3 atm (5 psi). A dilution factor was calculated using the following relationship;

$$D_f = \frac{P_f}{P_s} \tag{eq.3.2}$$

where D_f is the dilution factor, P_f is the final pressure after dilution and P_s is the final internal pressure in the container (following passive sampling with the CSFC). This factor is normally between 2 and 4. For example, given a situation where the internal pressure for a collected sample is 0.5 atm and this container is then filled to 1.34 atm (P_f), the dilution factor (D_f) is calculated to be 2.68. This factor is critical to the quantitative measurements of long-term integrated samples collected with the CSFC. It has to be considered when GC/MS analysis is used to determine the airborne VOC concentrations in outdoor or indoor environments.

3.2-Analytical systems and procedures

To quantitatively analyse air samples collected with long-term passive samplers, experimental systems were setup and/or modified to satisfy some of the technical requirements associated with low VOC level analysis. The analytical systems described below were installed and operated as part of validation and field demonstration studies (Chapter 5).

3.2.1-Injection devices for GC/MS

Injection devices have to be installed on a gas chromatograph (GC) to allow direct gas sample transfer. Some of these devices are also used to concentrate organic pollutants to ensure that a sufficient amount of analyte reaches the GC detector. The latter must attain an appropriate limit of detection since the concentrations of VOC in ambient air are measured in $\mu g/m^3$ (i.e. parts per billion {ppb} and even parts per trillion {ppt}). Sample concentration is achieved either with cryogenic or multisorbent trapping. This step is normally followed by thermal desorption which introduces analytes into the GC and completes the injection sequence. Finally, when a mass spectrometer (MS) is coupled to the GC, water management procedures are also required to ensure an adequate sensitivity and a good resolution at the detection level.

Samples collected on a long-term integrated basis were injected into the GC/MS using a purge and trap (P&T) concentrator. This equipment is normally used to extract VOCs from liquid or solid samples that are placed in purge vessels. A purge gas is introduced into the sample at a constant flow rate to flush out the volatile contaminants which are then concentrated on a sorbent trap to be later thermally desorbed and injected into a chromatograph. This system was modified to allow gas sample injections.

The modifications included the replacement of a purge vial located on the autosampler (©Teckmar, LSC 16) with stainless steel lines and connectors, a septum adaptor and a three-way valve. Also, the vent port of the P&T (©Teckmar, ALS 2000) was connected with Teflon tubing to a mass flow controller (MFC), followed by a diaphragm vacuum pump (©Thomas Instrument, model 2107CE20). The MFC (©Tylan, FC-260) calibrated to read between 1 and 100 ml/min based on nitrogen was connected to a read-out box (©Tylan, RO32). Figure 3.2 shows a schematic flow sheet of these modifications. This part of the set-up was previously reported (Stephenson, J.H.M. et al., 1990).

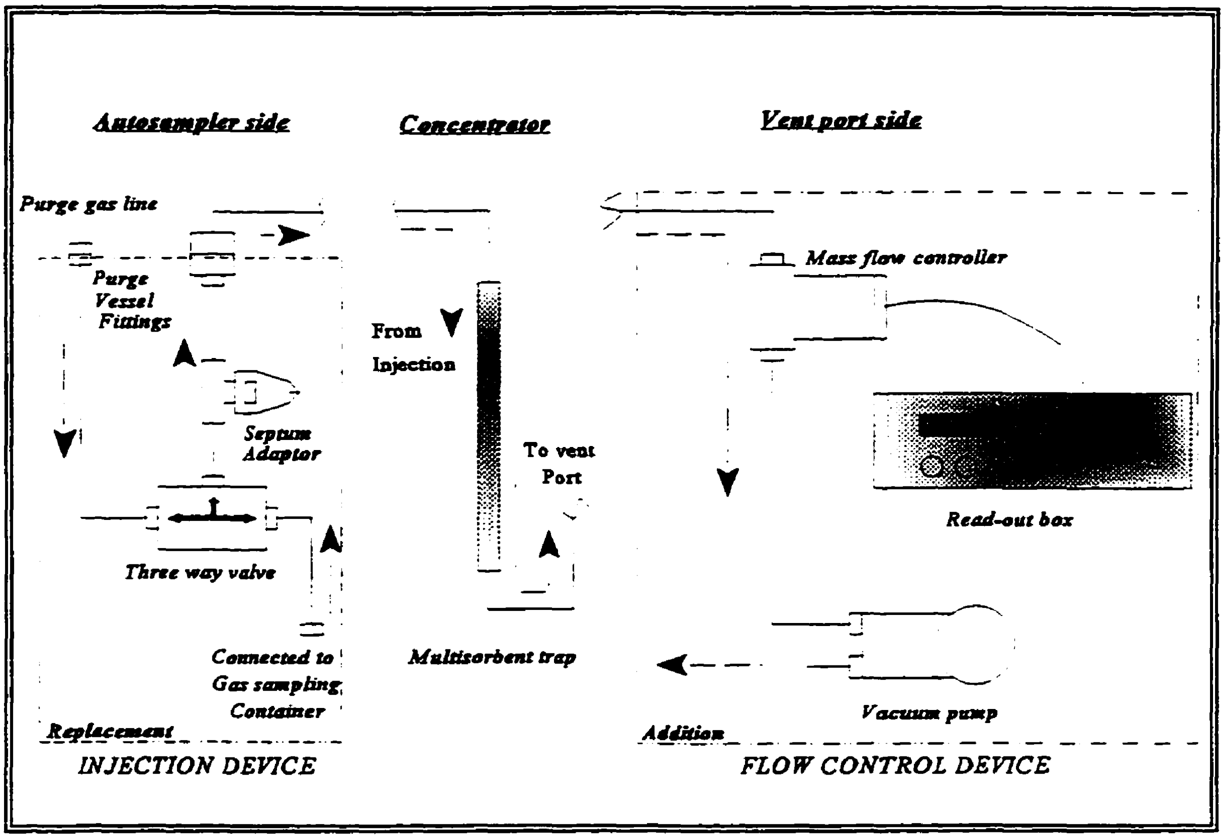

Figure 3.2: Schematic flow sheet for the modification of purge and trap concentrator

Two types of injections were made using this system. In cases where high VOC concentrations were suspected (ex. industrial hygiene samples), a gas aliquot was withdrawn using a 10-ml gas tight syringe (©Hamilton) through a septum adaptor installed on the sample container. This volume was then injected through another septum adaptor installed on line with the purge gas (see figure 3.2). The three-way valve was kept at the purge gas position to flush the samples into the multisorbent trapping bed. A purge time of 2 minutes and a 20 ml/min flow rate were used.

For the other type of injection, a vacuum pump was used to withdraw a large volume of gas (15 ml to 1500 ml) from the sampling vessel. This type of injection was used for ambient air samples where low level detection limits are required. The sample container was connected to the three-way valve using an appropriate line. The injection was accomplished by switching the valve's position from purge gas to sample container. Gas flow was controlled at 15 ml/min by adjusting the set point of the MFC on the read-out box. Purge time was selected from 2 minutes to 100 minutes depending on the sample volume to be injected. Lines were flushed with purge gas for one minute before and after injection to prevent carry over. Injection volumes were calculated using the flow rate and the injection time (ex: 60 minutes at 15 ml/min gives 900 ml of gas sample injected).

Method sequences were programmed directly on the control board of the P&T for automation. This modified injection unit was used according to the conditions shown in Table 3.1.

Table 3.1: Operating conditions for the P&T injection devices

Parameters	Set point	Units
Purge flow	15-20	ml/min
Purge time	2-100	minutes
Dry purge time	4	minutes
Desorb preheat	175	°C
Desorb temperature	250	°C
Desorb time	4	minutes
Bake temperature	350	°C
Bake time	10	minutes
Transfer lines temperature	110	°C
Valve temperature	150	°C

Dry nitrogen was used as the purge gas. A UHP grade nitrogen, treated for organic vapors, oils and greases, and water using appropriate cartridges, was provided at 2.4 atm (20 psi). Graphitized carbon multisorbent traps (°Supelco, vocarb 3000, vocarb 4000) were used for sample concentrations. These cylindrical traps were 30 cm long by 0.32 cm outside diameter (12 inches long by 1/8 inches OD). Two techniques were used for water management. Dry purging was sequenced after injection to flush residual oxygen, carbon dioxide and water vapor that could have remained in the trap. This approach was reported to be effective (McClenny, W.A. et al., 1995). Also, a moisture control module (MCM) was operated to minimise water entry into the GC during desorption. The MCM (°Teckmar) which uses a temperature effect to condense water vapor, was programmed to operate from 75°C during injection to 5°C during desorption.

The P&T injector was interfaced to the GC/MS. Other modifications were required to enhance the resolution of VOC at sub ppb level. A focussing step is needed to increase the separation of very volatile chemicals such as some Freons and vinyl chloride (low boiling points) at the head of the GC column. This can be achieved either by using cold trapping at the column or by providing a high desorption velocity. The latter option was selected.

The connection between the GC and the P&T was adapted to control desorption velocity. A direct split interface (DSI) was installed at the GC injection port. The GC carrier gas line was bypassed at the injector level (after the flow controller) and connected to the desorption gas port of the P&T. The heated transfer line following the multisorbent trap was then connected to the entry of the split/splitless injector. All connections were made using zero dead volume stainless steel unions. Figure 3.3 shows a diagram of the DSI.

With this interface, adjustment of the split ratio (the ratio between the carrier gas flow rate to the injector and to the GC capillary column) made using the GC's mechanical flow controller, provides a means to regulate the desorption flow rate on the P&T concentrator.

Increasing the split ratio involves a higher thermal desorption velocity and a better focussing of light molecular weight chemicals. However, this decreases the sensitivity of the analysis because the portion of the sample carried to the detector is proportionally reduced. A compromise value between stable flow rates and good separation of very volatile chemicals was selected.

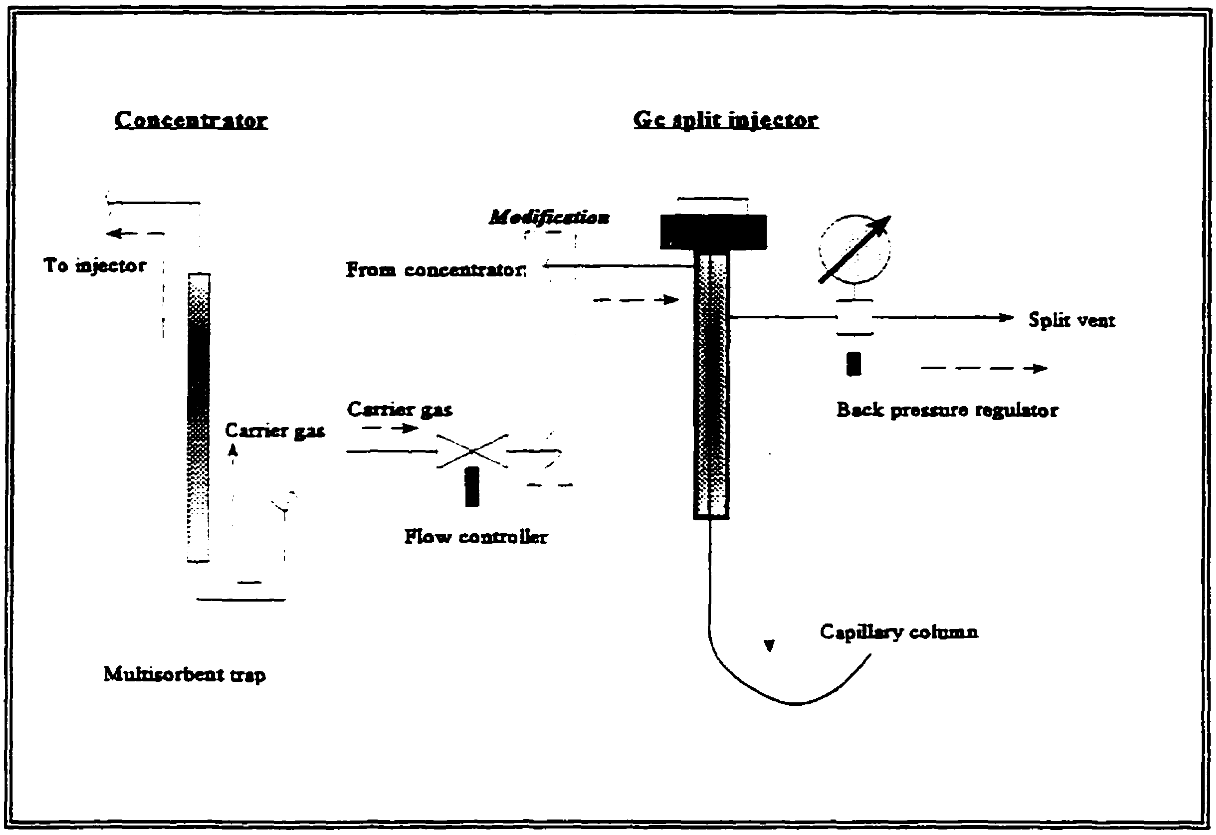

Figure 3.3: Schematic flow sheet of the direct split interface between the purge and trap concentrator and the GC/MS

The split vent flow was measured at the vent port using a mass flow metre (©Alltech) and was adjusted to 10 ml/min. The back pressure regulator of the GC, which controls the helium flow rate (carrier gas) into the column, was maintained at 1.68 atm (10 psi).

Gas sample injection ports were installed on a purge and trap concentrator and modifications were made to interface this experimental set-up to a GC. The injection devices were operated to introduce long-term integrated gas samples in a GC/MS for VOC quantification.

3.2.2-GC/MS operation for VOC determination

Mass spectrometers are detectors where molecules are bombarded and fragmented into ion clusters. Under specified conditions, each molecule has its own fragmentation pattern called the mass spectrum and substances can be partly identified based on this fingerprint. In combination with a GC where chemicals are separated depending on their affinity for a stationary phase, an MS provides a very effective tool to identify and quantify VOCs in environmental samples.

A gas chromatograph (®Varian 3400) coupled with a benchtop mass spectrometer (®Varian Saturn) was used for VOC analysis. The chromatograph was equipped with a DB-624 capillary column (®J&W Scientific) having the following dimensions: 60 metres long, 0.25 mm internal diameter, 1.8 μm film thickness. A deactivated fused silica capillary column (1 metre) was used as a transfer line to the detector. Both columns were connected using a universal glass union (®Chromatographic Specialities). The split/splitless injector was maintained at 125°C. The oven temperature program for VOC separation is given in Table 3.2.

The GC runs lasted 33 minutes. A signal was sent from the P&T to start the GC synchronously with desorption when both systems were ready. An autosampler (®Varian 8100) was also installed on the GC injection port for the automatic injection of solvent samples.

Table 3.2: Operating conditions for the GC oven

Start temp.	**End temp.**	**Rate**	**Times**
°C	**°C**	**°C/minute**	**minutes**
35	35	0.0	5.00
35	50	4.0	3.75
50	220	10.0	17.00
220	220	0.0	7.25

The ion trap manifold of the mass spectrometer was maintained at 125°C and the heated transfer line was maintained at 220°C. The mass spectra were obtained from electronic ionization and the emission source was set between 30 and 100 μA. The voltage for the electron multiplier was selected between 1400 and 2200 volts to obtain the best sensitivity from the detector. The amplitude read back voltage was kept at 4.0 volts. The target value for the automatic gain control was 20 000 total ion counts. The default segment break values were modified for the following mass range: segment 1-) 1 to 71; segment 2-) 71 to 79; segment 3-) 79 to 150; segment 4-) 150 to 650. This scan function was implemented to maximize the ion trap detector potential for low molecular weight chemicals.

Full scan mass spectra were obtained along with chromatograms. The specifications used for the data acquisition are shown in Table 3.3.

The lower scanned masses limit was defined at 46 mu mainly to reduce the baseline signal due to carbon dioxide, air and water. However, for some tests, this setting was reduced to 26 mu to allow the observation of a spectrum in the lower mass range. The higher mass value was selected considering the profile of VOC spectra where the larger ions do not normally exceed 300 mu.

Table 3.3: Operating conditions for the mass spectrometer

Parameters	**Set point**	**Units**
Acquired time	33	minutes
Filament delay	200	seconds
Acquired mass	46 to 300	mass unit (mu)
Scan rate	0.7	second/scan

The GC/MS was controlled from a computer station using the commercial software (°Varian, Saturn ver. 1.1). Figure 3.4 shows the overall analytical system used. The injection method was stored in the P&T controller. The GC and MS methods were loaded from the computer. A data file was saved for calculations for each injection made under predefined conditions.

3.2.3-Quantification of VOCs

Calibration curves were prepared for the quantification of 54 hazardous VOCs. The concentration of each airborne VOC was calculated from these calibration curves based on the volume of sample injected. Retention times and mass spectra were used to confirm the presence of chemicals in the samples[1]. Table 3.4 shows each VOC with the mass of the predominant ion used for their quantification. External calibration curves were obtained by injecting known concentrations of standard solutions into the GC/MS. The mass of the predominant ion specific to each chemical was plotted against its peak area.

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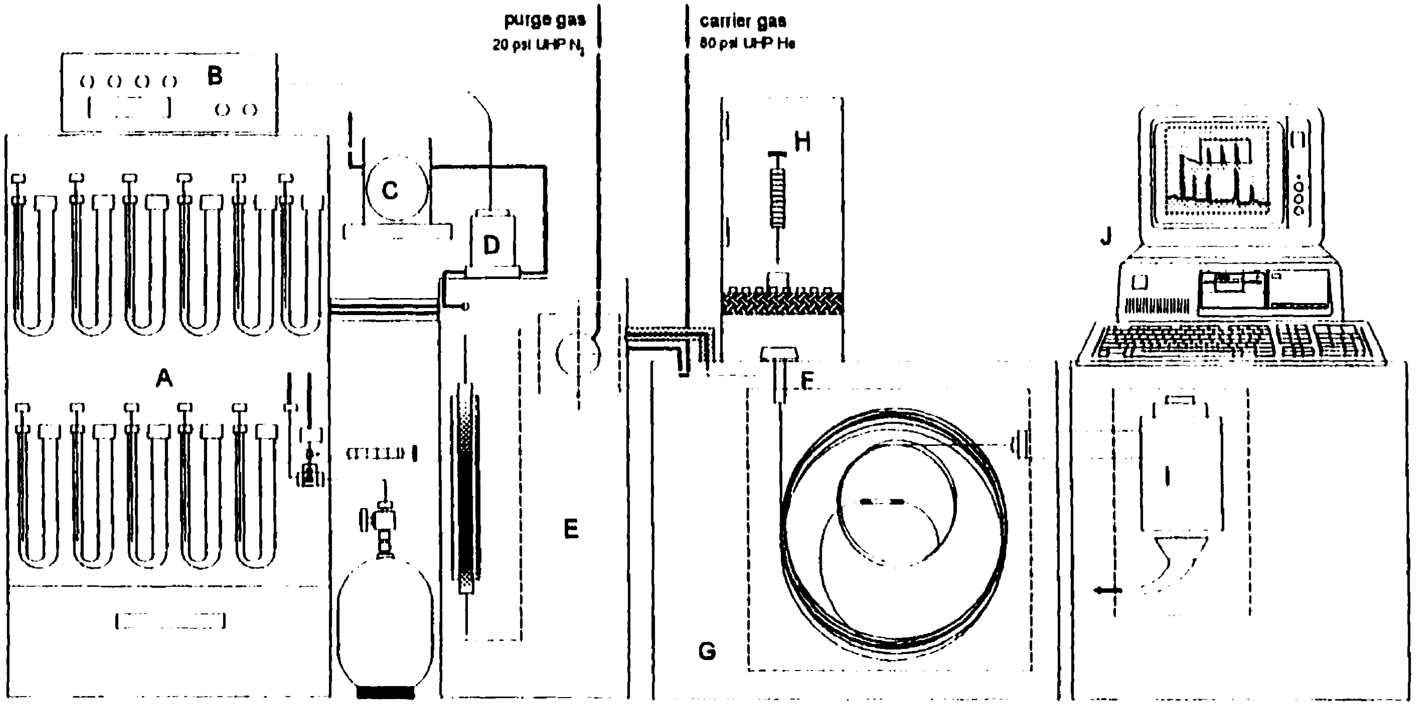
[1] For the retention times, a search window of 40 seconds was assigned, and for the mass spectra, a fit threshold value of 700 was defined for the comparison with specified cracking pattern of target molecules.



Modified P&T injector connected via DSI for GC/MS determination of Volatile Organic Compounds

Air samples injection system		Separation and detection system	
A	Modified purge and trap autosampler	F	Direct splitt interface between GC and P&T
B	Flow measurement read-out box	G	Gas chromatograph: oven, columns
C	Diaphragm vacumm pump	H	Autosampler syringe injector
D	Mass flow controler	I	Mass spectrometer detector
E	Purge and trap concentration and desorption unit	J	Computer control station

Figure 3.4: Experimental system used to analyse VOCs in gas samples

Table 3.4: List of VOCs with their predominant mass ion

List of VOCs analyzed by GC/MS			
Chemicals	**Mass**	**Chemicals**	**Mass**
Dichlorodifluoromethane	85	Chlorobenzene	112
Chloromethane	51	1,1,2,2-Tetrachloroethane	131
Vinyl chloride	62	Ethylbenzene	91
Trichlorofluoromethane	101	m,p-Xylene	91
1,1-Dichloroethene	61	Styrene	104
Carbon disulfide	76	o-Xylene	91
Dichloromethane	49	Bromoform	175
trans-1,2-Dichloroethene	61	Isopropylbenzene	105
1,1-Dichloroethane	63	1,1,2,2-Tetrachloroethane	83
2,2-Dichloropropane	77	1,2,3-Trichloropropane	75
Bromochloromethane	49	Bromobenzene	77
Chloroform	83	4-Chlorobenzene	91
1,1,1-Trichloroethane	97	1,3,5-Trimethylbenzene	105
Carbon tetrachloride	117	2-Chlorotoluene	126
Benzene	78	ter-Butylbenzene	119
Trichloroethene	130	n-Propylbenzene	120
1-2,Dichloropropane	63	1,2,4-Trimethylbenzene	105
Dibromomethane	93	4-Isopropyltoluene	119
Bromodichloromethane	83	1,3-Dichlorobenzene	146
trans-1,3-Dichloropropene	75	1,4-Dichlorobenzene	146
Toluene	91	n-Butylbenzene	91

List of VOCs analyzed by GC/MS			
Chemicals	**Mass**	**Chemicals**	**Mass**
cis-1,3-Dichloropropene	75	1,2-Dichlorobenzene	146
1,1,2-Trichloroethane	97	1,2-Dibromo-3-chloropropane	75
1,3-Dichloropropane	76	1,2,4-Trichlorobenzene	180
Dibromochloromethane	129	Hexachlorobutadiene	225
1,2-Dibromoethane	107	Naphthalene	128
Tetrachloroethene	166	1,2,3-Trichlorobenzene	180

Two different types of solutions were used. First, standards added to water were injected into the system using the P&T. Six commercially available standard mixtures containing several VOC at a concentration of 2000 μg/ml with a certified precision superior to 97% (°Supelco, VOC calibration standard kit) were mixed in a 10-ml volumetric flask and sucessive dilutions were made with HPLC grade methanol. From this stock solution, five standards having concentrations between 1 ng/ml and 100 ng/ml were prepared in separate flasks and one μl of each was added with a calibrated syringe to separate purge vials containing 5 ml of deionized water. These purge vessels were installed on the P&T autosampler and VOCs were purged into the multisorbent trap for 11 minutes at 40 ml/min. They were then desorbed and injected into the GC/MS using the conditions described above. Appendix 2 contains the calibration curves obtained for each VOC using this approach.

These calibrations were verified with a gas standard solution. A cylinder containing a subset of 40 VOCs at 100 ppb in pressurized dry nitrogen was used (°Supelco, TO-14 calibration mix). A pressure regulator was installed on the container to deliver this gas mixture at approximately 2.4 atm (20 psi). Connections were made to inject this blend through the three-way valve (modified injection port on the autosampler) and the procedures used were similar to those employed for the analysis of long-term gas samples. Different volumes were injected at 15 ml/min by varying the purge time. The total mass of each analyte from an injection was calculated (using conversion factors from ppb to mass per volume units[2]) and compared to the calibrations obtained using the water method.

The noise baseline of the analytical system was considered during calculations. Blank run analysis were made to estimate the signals generated by potential chemical contaminations from the purge gas, solvents used for dilution and from the purge water. For most of the listed chemicals, no contamination was observed. However, trace signals were measured for dichloromethane, benzene and toluene. A significant amount of chloroform was found in the purge water. Finally, the response for carbon disulfide was too erratic to conduct a precise quantification. This solvent was often used in the same laboratory for other types of analysis and is probably the cause of this problem. Baseline contamination was substracted from the calibration curve for each of these chemicals.

The target VOC masses (M_i) in the injected volume (V_{inj}) taken from the gas samples were obtained from peak integrations and calculations using the calibration curves. To estimate the final concentration in field samples, the dilution factor (D_f) was applied and the VOC contamination in the dilution gas was substracted. To account for this, a correction factor was estimated using the following procedure. A canister was filled with the dilution gas and a precise volume (V_d) was injected in the system. The dilution gas impurities were characterized and the mass of VOC contaminant (Md_i) was determined. For each VOC, a correction factor (CF_i) was calculated according to equation 3.3:

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[2] To convert from ppb(v) to $\mu g/m^3$, the molecular weight of substances is divided by the molar volume of air at selected temperature.

$$CF_i = \frac{Md_i}{V_d}(V_{inj} - (\frac{V_{inj}}{D_f})) \qquad \text{(eq.3.3)}$$

The following relationship was used to determine the concentration of selected VOCs (c_i) in gas samples collected using the CSFC:

$$c_i = (\frac{M_i - CF_i}{V_{inj}})D_f \qquad \text{(eq.3.4)}$$

Even if stringent procedures are used to provide the cleanest source of gas for the pressurization of gas samples (see section 3.1.2), it appears that the correction factor must be used, principally when low VOC levels are measured as in the outdoor environment. The highest GC/MS analytical sensitivity was obtained for VOCs not present in the dilution gas. However, chemicals such as dichlorodifluoromethane, dichloromethane, benzene, toluene, xylenes and tetrachroethylene were sometimes found as impurities. Fortunately, the measured VOC levels in dilution gas injections were much lower than those measured in field samples.

The ratio between the measured amount of analytes in the gas samples (M_i) and weighted mass contribution from the dilution gas impurities (Cf_i) was normally below 0.2. If the relative amount of a specific VOC in an injected sample volume (V_{inj}) did not represent more than 80% of what was found as impurities from pressurization procedures, the results were discarded and the concentration of these chemicals was not reported because of uncertainties.

Considering the impact of supplied materials (gas and liquids) for the maintenance of the GC/MS and the handling of subpressurized long-term passive samples, the limit of detection and the analytical precision were increased for some VOCs. However, for most chemicals where no signal was observed in blank analysis (purge gas, purge water, standard dilution solvent and samples dilution gas), the instrument detection limit was approximated to 0.2 ng. Based on the fact that 1 litre of gas was injected into the system, the method detection limit was estimated at 0.2 μg of VOC per cubic metre of ambient air ($\mu g/m^3$). This maximum sensitivity was determined from the MS baseline response obtained using the predefined operating conditions[3]. Otherwise, for chemicals that were detected as impurities in the analysis, this limit was increased to a conservative value of 1 $\mu g/m^3$.

3.2.4-GC/FID for methane detection and quantification

Methane was also analysed in long-term samples collected in the vicinity of a sanitary landfill to assess its use as a marker for biogas emissions. A one-ml sample was withdrawn from either sample bags or summa canisters using a gas-tight syringe and injected directly through the septum of the split/splitless injector. Isothermal chromatographic conditions (oven: 40°C, detector: 200°C, injector: 120°C), a Vocol column (30 metres by 0.53 mm ID, 0.3 μm film thickness) and a split ratio of 1:25 were used. The signals from the flame ionization detector (FID) were obtained and integrated into an area count. Detector flow rates were controlled at the following setpoints: make-up gas - 30 ml/min; hydrogen - 30 ml/min; air - 300 ml/min.

The area count from field samples were compared to the responses from similar injections of a 100 ppm CH_4 in dry nitrogen (°Supelco, Scott gas cylinder). A one point calibration was used to quantify the level of methane. The dilution factor (see eq.3.2) was then

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[3] The peak heights obtained from the injection of a 1 ng standard were compared with the minimum response of the detector observed for blank runs, and the threshold value was assigned at three times the signal to noise ratio.

three times the baseline signal to noise level, the limit of detection was estimated at 1 ppm. This method's limit was sufficiently low to characterize observable methane variations near a landfill site.

3.2.5-Quality control and maintenance

The analytical systems described above were used for qualitative and quantitative studies as part of the novel sampler's validation. Efforts were made to ensure that observations were representative and could be reproduced. Procedures were implemented to control and optimize the validity of the quantification process. Strategies were mainly applied to verify the signals obtained from the analytical system detectors. Several of these procedures were associated with the mass spectrometer.

First, commercially prepared stock standards certified traceable to a NIST Standard Reference Material were systematically used to prepare calibration curves. Calibrations were periodically made to verify the detector stability. Baseline signals obtained from the dilution, dry purge and carrier gases were determined and considered in calculations. Replicate sample injections were performed on a routine basis. Recovery studies were conducted (see section 5.2.2). External standards were injected along with samples under similar operating conditions in every quantitative investigation. Ideally, the quality control procedures would also have included surrogates, internal standards and external laboratory controls. More sophisticated analytical quality controls are usually required to provide compliance results. However, at this stage, it was felt unnecessary to implement these procedures. The main objective of this research was to develop a long-term sampler, not to characterize VOCs.

Procedures were also implemented to maintain mass spectrometer conditions. A mass calibration was performed on a daily basis, or before every new set of injections. A builtin program was used under regulated conditions to introduce a calibration compound (FC-43) into the ion trap. These results were used to establish the relationship between the electronic detector responses and related mass fragments. Also, the air and water levels were verified at the detector to ensure that they were within acceptable limits. The presence of leaks in the system (lines from the gas cylinders to the injection port, the GC and to the ion trap) is critical for an MS detector. Also, parts of the analytical system were replaced on a regular basis (1-6 months) to maintain an acceptable sensitivity: septum, liner, sorption trap and transfer line. Finally, routine maintenance was performed on the MS's filament, multiplier and vacuum pumps to keep the detector under ultimate conditions.

The sampling and analytical systems and conditions described in this chapter were used to demonstrate that capillaries can be designed to achieve long integrated passive sampling periods. The theoretical and practical results from this research are now presented and discussed.

4-DESIGN AND DEVELOPMENT OF A LONG-TERM SAMPLER: RESULTS AND DISCUSSION

This research project is based on an idea which originated from the following questions concerning the use of an evacuated sample container for the sampling of ambient air. Can sampling time be extended by using an appropriate geometry of capillary tubing connected to an evacuated container? Will this new type of flow controller allow long-term integrated passive sampling of gaseous airborne contaminants such as VOCs? In essence, this novel flow controller involves a capillary tubing whose determinate length and diameter allow a specific flow rate and will be herein called a Capillary Sampling Flow Controller (CSFC).

The CSFC was developed as an inlet restriction for the entry of gas into an evacuated sample container. The pressure gradient between the container and ambient air provides the driving force for the gas flow. An appropriate selection of capillary geometries affords commensurate constant low flow rates which extend integrated sampling periods.

Theoretical and experimental investigations were performed to elucidate this novel sampling process and to answer questions raised by it. In this chapter, the approaches used for the design of a flow controller for long-term passive sampling will first be presented. Experimental and theoretical results obtained for the relationships between capillary geometries and integrated sampling times are then compared.

The initial research results were filed to protect intellectual property during the early stages of this project (Simon, P. and J.P. Farant, 1995). These procedures were conducted by the University according to their policy on inventions. Recently, the Capillary Sampling Flow Controller (CSFC) was the object of patent applications (Simon, P. and J.P. Farant, 1996a) which received a Notice of Allowability (Murphy, K.P., 1996).

4.1-Design of a long-term passive sampler

The design of a long-term passive sampler, based on the use of selected capillary geometries as inlet restrictions for evacuated containers, required two separate considerations. First, materials appropriate for the assembly of flow controllers and long-term passive samplers was investigated. Configurations were designed for both stationary and personal sampling. Secondly, a mathematical model was developed to predict the capillary column lengths of a given internal diameter required to achieve a selected sampling period with a specific volume of sample container.

4.1.1-Configuration

A capillary sampling flow controller (CSFC) is essentially a selected length of capillary tubing connected to an evacuated container which can provide long-term integrated passive sampling. Two criteria are fundamental to the selection of materials used for the assembly. First, the connections must be gas tight. Also, all material surfaces should be as inert as possible to prevent any interaction with chemicals in the sample collected. Figure 4.1 illustrates a simple configuration of the flow controller.

Flow controllers are made using variable lengths of deactivated fused silica capillary columns. Such capillary tubings are often used in GC where they have been shown to be reliable to transfer analytes from the injector to the detector. They can endure temperatures up to 300°C without significant degradation. They are flexible but still very fragile. Different internal diameter sizes are commercially available. The smallest diameter was selected to provide the severe restrictions required to extend sampling times. Columns having internal diameters of 0.05 mm and 0.10 mm, with an external diameter of 0.4 mm were used in the configurations.

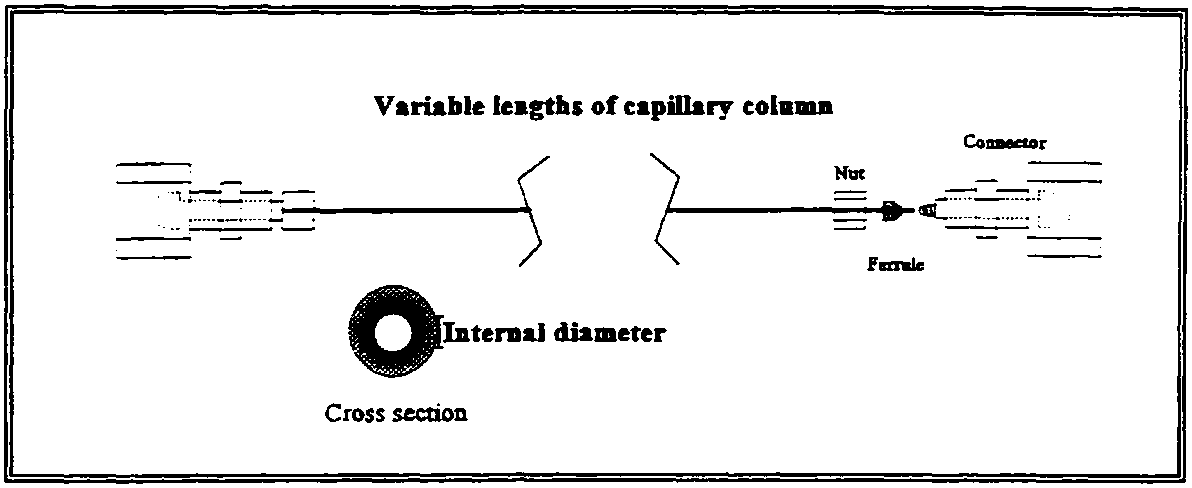


Figure 4.1: Schematic view of a capillary sampling flow controller (CSFC) used for long-term integrated passive sampling

The selected connectors are made of stainless steel (SS). Compared to brass, this material is more inert and it does not outgas like Nylon or Teflon at elevated temperatures. Graphite-vespel ferrules were used for the connections between the capillary and the connectors. The nuts were tightly screwed on the compression fittings to seal the capillary with the ferrule. This assembly was attached on one side to an evacuated sample container. An inlet filter was connected to the other side to prevent particulate from plugging the device.

For field applications, the capillary column used as a restrictor has to be protected from shocks and vibrations to prevent it from breaking during transportation and handling. Protecting shields were designed and two different assemblies were made. The general approach was to build a casing on which the connectors could be mounted and in which the capillary could be enclosed.

For one design, a small round box, 5 cm in diameter and 1.2 cm thick having a removable lid on one side, was machined from SS. Two reduction fittings were welded to the casing at a 90° angle with the capillary connections inside. The column was then installed. This casing was filled with a packing material (wool, other fibers or polymer foam) that absorbs vibrations and then capped. Note that square boxes were also made, the geometry of the housing being of secondary importance. This type of design was successfully tested in a vibration chamber. It was also shown to resist vibrations when a shuttle was launched into space (Cole, H., 1996).

The other design used to protect the capillary incorporates the latter in a plastic material such as epoxy, polyacrylic or other polymeric resins. This type of casing was cast with the capillary tubing and fittings installed in an appropriate mold using resin transfer molding. The mold was made of two identical aluminum parts. Figure 4.2 gives the schematic views of this mold. First, a selected length of column was rolled up to fit in the molding area (which has a diameter of 5 cm and a thickness of of 1.2 cm) and connected to the compression fittings. The two flow controller fittings were placed at a 90° angle in their respective spaces located on the mold's body. The two parts were finally assembled using three screws to enclose the capillary column.

The polymeric material was prepared according to the supplier's directions by mixing the ingredients (usually a polymeric resin and a hardener). The liquid solution obtained was rapidly injected with a 200-ml syringe from the bottom of the mold until some material came out of the vent port located on the opposite side. The polymer was allowed to dry (from 1 hour to 24 hours depending on the type of polymer) and then, the mold was dismantled.

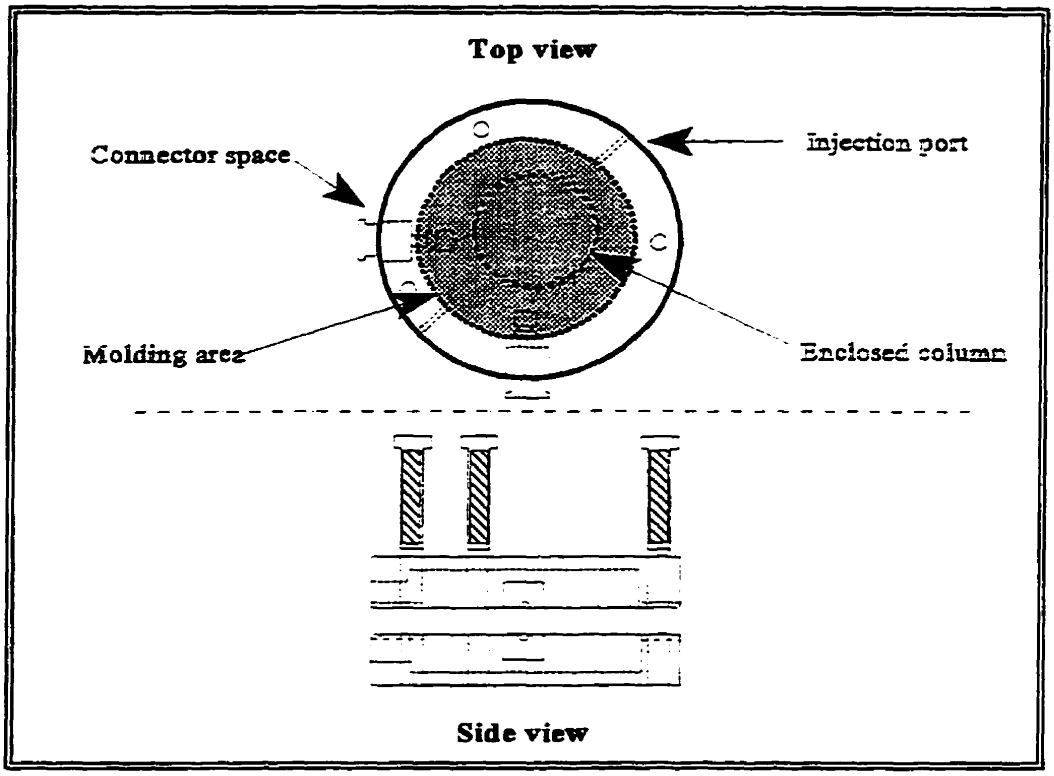


Figure 4.2: Illustration of the assembly used for casting the flow controller's plastic protection shield

The final product has the appearance of a hockey puck with two connectors on its circumference. Different materials can be used to mold units of the CSFC. Tests were made with epoxy and polyacrylic resins, and both results were satisfactory. The selection of the best resin to achieve this application was not investigated. To prevent contamination of the gas samples collected using these devices, the selected material should not outgas. This aspect was considered beyond the scope of this project. It should be part of an applied research program to specifically develop a commercial product. However, the tests that were performed showed that this type of protection shield can be used to configure units of CSFC without running the risk of contaminating collected samples.

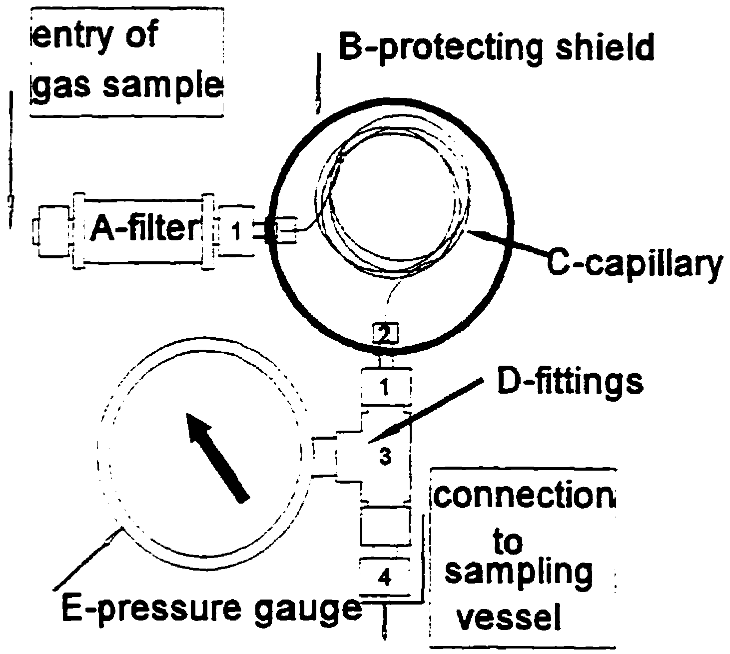
The two types of protection housing can be compared based on practical considerations. The stainless steel casing has the advantage of allowing the replacement of capillary columns. Capillaries can be changed according to the selected sampling period desired and the size of the sample container used, and the flow controller can be used in a variety of situations. However, the production costs are higher than those required for polymeric protecting shields. It should be noted that for the latter type of casing, once molded they can only be used according to design specifications. Also, if the capillary becomes contaminated by a chemical or plugged by particulate matter, these units can no longer be used. The major advantage of polymeric casings is certainly related to the fabrication cost. Nevertheless, both types of protection shields can be used.

The flow controllers were configured as a component of long-term integrated passive samplers for the collection of gaseous contaminants such as VOCs. The sampler configurations depend upon whether they are to be used for ambient air stationary sampling as part of environmental studies, or for personal sampling in industrial hygiene surveys. Each application has specific requirements and the design of samplers which use a CSFC differs accordingly.

4.1.1.1-Sampling train for stationary samples

Summa canisters have a proven reliability for the collection of whole air ambient samples for VOC analysis in environmental monitoring studies. A sampling train which includes the CSFC was designed for the collection of long-term integrated samples into these containers. A sampling train diagram is shown in figure 4.3. The finest available porosity (0.5μm) of a sintered stainless steel (SS) filter was connected at the gas inlet. This filter was selected mainly because it is made of an inert material: active sites on stainless steel are not numerous when compared with other possible filtering material such as cellulosic and polymeric fibers.

CSFC Prototype for stationary sampling with an evacuated Summa canister



A	filter	1/4" SS swagelok, 0.5 µm porosity, SS frit
B	protecting shield	a-SS cylindrical enclosure 50 mm OD * 12 mm width b-epoxy or polyacrilic mold 50 mm OD *12 mm width
C	capillary	deactivarated fused silica, 0.4 mm OD, variable ID
D	fittings	1-1/16"-1/4" SS swagelok reducer 2-1/16"-0.4 mm graphite-vespel ferrule 3-1/4"-1/4" SS swagwelok-NPT tee union 4-1/4"-1/4" SS swagelok union
E	pressure gauge	bourdon tube device, 1/4" NPT, -30" Hg to 30 psi

Figure 4.3: Sampling train for long-term integrated passive stationary sampling using summa canisters

The 0.5 μm filter's porosity was chosen to prevent particles from penetrating and eventually altering the sampling flow rate. A pressure reading device was installed between the flow controller and the container to allow monitoring of the internal sampler pressure. A mechanical pressure gauge (Bourdon type) calibrated by suppliers to read between approximately 0 and 3 atmospheres was selected. The stainless steel NPT connector of this pressure gauge was joined to an appropriate three-way connector using Teflon tape.

The sampling train was assembled to provide a leak proof system. This unit was then connected to an evacuated sample container of specific volume to offer long-term passive integrated sample ability. The container's size was selected according to the type of atmospheric environment which was monitored. For outdoor ambient air, six-liter summa canisters are often used. The injection volume of a gas sample required to achieve the selected sensitivity during chromatographic analysis is sometimes fairly large (>500 ml). For this reason, large sample containers are selected for these situations. However, for most indoor environments, injection volume can be reduced because the concentrations of target contaminants are higher. For industrial hygiene and indoor air quality assessments, the size of sample containers can range from 100 ml to 1 liter for convenience: larger sizes are too bulky to handle.

Simple procedures are required to operate passive stationary samplers. The valve of the evacuated sample container is opened to start the collection of the gas sample. The initial vacuum is measured. Once the selected sampling period is completed, the valve is closed and the internal pressure of the vessel is recorded again: a residual vacuum should be found when leaks did not occur. The sampling train is then removed from the container to be diluted and analyzed.

4.1.1.2-Personal samplers

A long-term passive sampler based on the flow controlling capability of the CSFC was designed to perform personal monitoring. In industrial environments, portable samplers worn by workers are used to collect breathing zone samples over entire workshifts. These exposure measurements are used to verify compliance or to assess worker exposures. The design respected these requirements.

The container was reduced to pocket size, equipped with a clip and worn at the worker's belt. A sampling line was connected between the CSFC and the filter on which a clip was also installed to attach the sample inlet to the worker's collar. The same type of filter and compression fittings were used as with stationary samplers. Figure 4.4 shows a diagram of a passive personal sampler prototype that was assembled and tested for the collection of whole air samples.

A pressure gauge was not included in this assembly to optimize the portability of the device and its acceptance by workers. A rectangular sampling vessel was machined from stainless steel (SS) according to the following dimensions: 10 cm by 8 cm by 2 cm. To install a 90° angled needle valve, a small piece of 0.63 cm outside diameter (OD) SS tubing (¼ inches OD) was welded symmetrically approximately one centimeter (cm) from the top corner of the metal box. The flow controller enclosed in a protection shield was connected between the valve and the sampling line. This line was selected to provide flexibility, resistance and more importantly, a low dead volume and an inert surface. It should be noted that the flow restriction of this line was negligible when compared to the one used in the CSFC. A Teflon tubing with an outside diameter of 1.58 mm and a internal diameter of 0.3 mm was preferred.

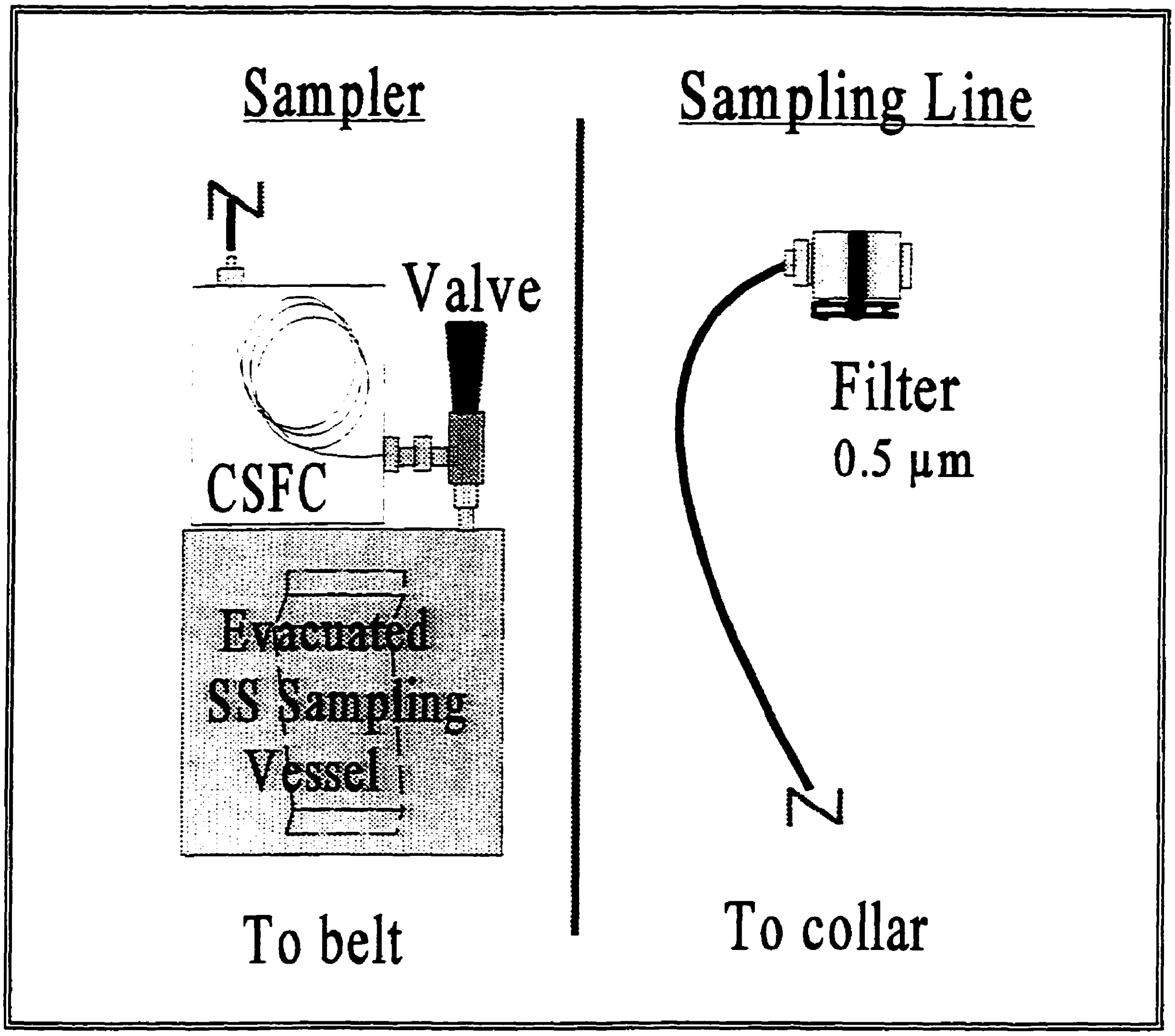


Figure 4.4: Diagram of a long-term passive personal sampler prototype incorporating the CSFC

This simple and low cost passive sampler configuration was shown to be effective and reliable during field studies. However, it can be optimized and even automated. The internal surfaces of the sample container can be treated with a process such as summa passivation or fused silica lining (Silcosteel, ®Restek) to minimize active sites. This improvement may be important if the sampling device is to be used to measure very low concentrations found in environmental exposure assessment's studies. Nonetheless, a surface treatment may not be required if the sampler is only used for industrial hygiene surveys where exposure limits are significantly higher than environmental background levels. In such instances, an aluminum or Teflon container could be used with the added advantage of reducing the sampler's weight.

The size of the container should be as small as possible. The minimum volume required for the analysis must be considered. In this design, the relative error arising from the summation of the sampling train's dead volumes is increased as the size of the sample container is reduced. To overcome this limitation, Snider (1977) proposed some modifications. First, he suggested the installation of a second valve on the container for gas evacuation and injection procedures. Also, he proposed that a septum port be welded on the container to facilitate syringe sample collection for GC injection. Finally, the flow controlling assembly, in his design, was enclosed in the container. This later improvement certainly will decrease the errors from dead volumes but the system is no longer versatile: the integrated sampling time cannot be modified with this sampler. Otherwise, the other additions could be considered (other valve and septum port), but they significantly increase the sampling device's fabrication cost.

Personal passive samplers could be automated if they were equipped with battery operated solenoid valves and timers. The device could then be programmed to stop after the selected sampling period. A pressure transducer to monitor internal pressures could also improve the design by allowing the verification of the container status. If these electronic parts were added, efforts in miniaturization would have to be considered to ensure the portability of the sampler. However, such considerations are beyond the objectives of this research project and automation was not considered for the assembly of prototypes.

The operation of the personal sampler involved the same procedures used for the stationary sampler. Because of its simplicity, the device can be operated by the worker at the beginning and at the end of his/her work shift. If the flow controller is properly designed, the personal sampler can be used on consecutive work shifts to collect a sample which will represent the average exposure over a full work week (5 days) or any other period.

The most important aspect of the design is the selection of appropriate capillary geometries to allow new strategies to be achieved with extended sampling periods. Whether a stationary sampler or a personal sampler is used, their basic operating principle relies on the selection of a length of capillary tubing of a given internal diameter. To design the flow controllers, a mathematical model was derived based on known equations and on simplifying assumptions.

The assembly of flow controllers and long-term passive samplers has been described. The next section is dedicated to a more theoretical aspect of the design: the relationship between geometrical parameters and integrated sampling times.

4.1.2-Model development

The gas flow in a tube subjected to a pressure differential at steady state can be calculated using known equations. However, these relationships cannot be applied to a passive sampling process based on the use of a CSFC, where the container's internal pressure is always increasing with time. For this scenario, the challenge was to incorporate, in a mathematical model, a time dimension that would relate the geometry of the system to the time period during which a constant flow rate is achieved.

The mathematical model was developed on the basis of two fundamental equations that were modified and adapted to incorporate a long-term sampling process. The first relationship is based on fluid mechanics: the Hagen-Poiseuille equation. The other relationship is based on gas kinetics: the ideal gas law.

To understand the significance of the Hagen-Poiseuille equation, the steps and assumptions that lead to this fluid dynamic relationship are explained in what follows. The relationship applies to a laminar flow of Newtonian fluids in circular tubes. Its development, based on physical variables, begins with a momentum balance which uses a volume element: a cylindrical shell (see figure 4.5). The momentum balance which occurs when components due to friction, compressibility, pressure and gravity are at equilibrium, is stated as:

$$(2\pi rL\tau_{rz})\big|_{r}-(2\pi rL\tau_{rz})\big|_{r+\Delta r}+(2\pi\Delta r v_z)(\rho v_z)\big|_{z=0}-(2\pi\Delta r v_z)(\rho v_z)\big|_{z=L}+2\pi\Delta r(P_o-P_L)=0 \quad \text{(eq.4.1)}$$

The variables used in this expression are defined in the list of notations. When the fluid is assumed to be incompressible (i.e. $v_z\big|_{z=0} = v_z\big|_{z=L}$), only the friction and the pressure component forces are considered and the terms for the variation of longitudinal velocity (v_z) cancel. Then, at the limit as Δr goes to zero, one gets:

$$\lim_{\Delta r\to 0}=\left\{\frac{(r\tau_{rz})\big|_{r+\Delta r}-(r\tau_{rz})\big|_{r}}{\Delta r}\right\}=\left\{\frac{P_0-P_L}{L}\right\}r \quad \text{(eq.4.2)}$$

This expression can be written as:

$$\frac{d}{dr}(r\tau_{rz})=\left\{\frac{P_0-P_L}{L}\right\}r \quad \text{(eq.4.3)}$$

To integrate equation 4.3, the appropriate boundary conditions (at r = 0, the shear stress $\{\tau_{rz}\}$ is not infinite) are selected to obtain the following:

$$\tau_{rz} = \left\{ \frac{P_0 - P_L}{2L} \right\} r \qquad \text{(eq.4.4)}$$

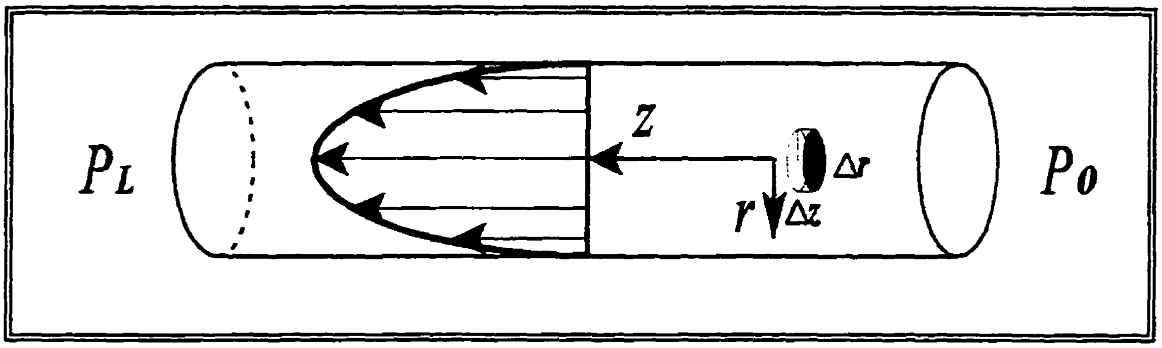


Figure 4.5: Cylindrical coordinates, volume element and velocity profile for a laminar flow of Newtonian fluid in pipes ($P_L < P_0$)

Then, using Newton's law of viscosity for this case:

$$\tau_{rz} = -\mu \frac{dv_z}{dr} \qquad \text{(eq.4.5)}$$

Equation 4.4 and Newton's equation were combined to obtain a differential equation for velocity (v_z) which is related to the fluid's viscosity (μ), the pressure gradient across the pipe (P_0-P_L) and the geometry of the pipe (L: length, r: radius). This gives the following expression:

$$\frac{dv_z}{dr} = -\left\{ \frac{P_0 - P_L}{2\mu L} \right\} r \qquad \text{(eq.4.6)}$$

The integration of equation 4.6, using a boundary condition where the velocity is null at the fluid-solid interface (i.e. $v_z = 0$ at $r = R$) results in a velocity distribution relationship:

$$v_z=\frac{(P_0-P_L)}{4\mu L}r^2([1-(\frac{r}{R})^2)] \qquad \text{(eq.4.7)}$$

This expression indicates that the velocity distribution for the laminar flow of incompressible fluids is parabolic, as shown in figure 4.5. From this expression, the equation for the average velocity is defined as:

$$<v_z>=\frac{\int_0^{2\pi}\int_0^{R} v_z r dr d\theta}{\int_0^{2\pi}\int_0^{R} r dr d\theta}=\frac{(P_0-P_L)R^2}{8\mu L} \qquad \text{(eq.4.8)}$$

The volumetric flow rate, which is the product of the cross-sectional area of the cylinder (πR^2) and the average velocity defined in eq.4.8 is then obtained. This leads to the rather famous expression which was called the Hagen-Poiseuille law in honor of the two scientists who derived it around 1840:

$$Q=\frac{\pi(P_0-P_L)R^4}{8\mu L} \qquad \text{(eq.4.9)}$$

When a laminar flow of a Newtonian fluid is established, the volumetric flow rate between the inlets of a pipe is related to the pressure gradient, the viscosity of the fluid and the pipe dimensions (radius and length).

Assumptions associated with this equation include the facts that the tube should be long enough, so that end effects can be neglected. This relationship only applies to laminar flow (Reynold number less than 2100) of Newtonian fluids in isothermal conditions. The fluid should behave like a continuum and this assumption is theoretically not valid for very dilute gases or very narrow capillary tubes where the molecular mean free path can be higher than the tube diameter, and where a slip flow or free molecular flow regimes may be established. Finally, since the Hagen-Poiseuille equation is valid under steady-state conditions, the flow should be time independent.

The mathematical equations obtained from a momentum balance (from eq.4.1 to eq.4.9) were developed by Hagen and Poiseuille and described elsewhere (Bird et al., 1960). To characterize the behavior of a passive ambient air sampler using a CSFC, other assumptions were made. First, the volumetric flow rate and the internal sample container pressure should both be a function of time: the sampling time. Second, in this process, P_0 is equal to atmospheric pressure (P_{atm}) and the internal pressure of the vessel is time dependent and defined as $P(t)$. Finally, even if some variables are time dependent, the process can be characterized as being pseudo steady-state. Based on this hypothesis, the Hagen-Poiseuille relationship was modified as follows:

$$Q(t)=\frac{\pi(P_{atm}-P(t))R^4}{8\mu L} \qquad \text{(eq.4.10)}$$

This expression also assumes that air viscosity between vacuum and ambient pressure remains constant. Hagen and Poiseuille had to assume that fluid density is constant, which is certainly not the case when one considers gas compressibility. Equation 4.10 is one of the initial expressions used to develop a mathematical model for the CSFC design. However, this equation cannot be solved. A second relationship was postulated to obtain the set of equations required to characterize the relationship between sampling time and the geometry of the system (length and internal diameter of the capillary column, and size of the evacuated sample container).

To characterize the behavior of a CSFC, a fundamental relationship based on the kinetic theory of gases, the ideal gas law, was also used:

$$PV=n\mathbb{R}T \qquad \text{(eq.4.11)}$$

Many gas matrices including air, normally behave like perfect gases under specified conditions, and this relationship between pressure, volume, molar concentration and temperature is well established. This equation was modified by considering two variables which are a function of sampling time: the internal sample container pressure $\{P(t)\}$ and the molar content $\{n(t)\}$-the amount of gas inside the sample container. As the sample container is being filled over time, the internal pressure $\{P(t)\}$ and the number of mole $\{n(t)\}$ rise proportionally with sampling time. Based on this fact, a new expression was derived as:

$$P(t)=\frac{n(t)\mathbb{R}T}{V_s} \qquad \text{(eq.4.12)}$$

where V_s is defined as the sample container volume. The objective was to obtain an expression which would associate on a time basis the molar content inside the vessel $\{n(t)\}$ and the flow rate delivered by the inlet restriction $\{Q(t)\}$. The first step was to relate the flow rate to the sampled volume $\{V(t)\}$:

$$V(t)=\int_0^t Q(t)dt \qquad \text{(eq.4.13)}$$

Within the operating range of the passive sampler, the flow rate is kept constant because of critical flow conditions. As observed with critical orifices used on evacuated vessels, the volumetric flow rate remains reasonably constant during the time required to fill approximately half of the sampler. Therefore, in part of the process, the sampled volume can be expressed as:

$$V(t)=Q(t)t \qquad \text{(eq.4.14)}$$

This sampled volume $\{V(t)\}$ is related to the molar content. By using the molar volume at standard temperature and pressure ($\overline{V}$), another physical property of gas, the following equation was obtained:

$$n(t)=\frac{V(t)}{\overline{V}}=\frac{Q(t)t}{\overline{V}} \qquad \text{(eq.4.15)}$$

When eq.4.15 is substituted in equation 4.12, a relationship is obtained for the variation of pressure in the sample container as a function of the volumetric flow rate controlled by the capillary:

$$P(t)=\frac{\mathbb{R}TQ(t)t}{V_s\overline{V}} \qquad \text{(eq.4.16)}$$

The latter relationship is used to derive the mathematical model developed to predict the geometry of a capillary column required by the design of the flow controller. The ideal gas law was adapted to reflect the time variations of physical parameters involved in the transfer of a gas into an evacuated sample container.

The model was derived by combining equation 4.10 and equation 4.16 in which one of the two unknowns was eliminated $\{P(t)\}$ to obtain a single expression for the volumetric flow rate $\{Q(t)\}$. This relationship incorporates two constants (K_1, K_2) used to simplify the equation as follows:

$$Q(t)=\frac{K_1}{1+K_2t} \qquad \text{(eq.4.17)}$$

where the constants K_1 (in m^3/s) and K_2 (in s^{-1}) are defined as:

$$K_1=\frac{\pi P_{atm}R^4}{8\mu L} \qquad \text{(eq.4.18)}$$

$$K_2=\frac{\pi \mathbb{R} T R^4}{8\mu L V_s \overline{V}} \qquad \text{(eq.4.19)}$$

Again, using the same two equations (eq.4.10 and eq.4.16), the pressure variable $\{P(t)\}$ was obtained by eliminating the flow rate variable $\{Q(t)\}$. Two other constants were are also used (K_3, K_4) to simplify this expression:

$$P(t)=\frac{K_3 P_{atm} t}{K_4-K_3 t} \qquad \text{(eq.4.20)}$$

where the constants K_3 (in kg · m^3/s^2) and K_4 (in kg · m^3/s) are defined as:

$$K_3=\frac{\pi \mathbb{R} T R^4}{\overline{V}} \qquad \text{(eq.4.21)}$$

$$K_4=8\mu V_s L \qquad \text{(eq.4.22)}$$

These expressions for the variation of volumetric flow rate $\{Q(t)\}$ and internal pressure $\{P(t)\}$ with sampling time were not obtained to characterize the behavior of these variables. For example, the assumption made to modify the ideal gas law was that volumetric flow rate would be constant over a definite period of the process. This assumption was required and, as shown later, it is a good approximation. However, equation 4.17 represents a saturation process and according to this expression, the flow rate continuously decreases with time. This is an apparent contradiction. Nevertheless, these intermediate expressions are required to establish a relationship between the geometry of the passive sampling system and the integrated sampling period.

To resolve this problem, the flow rate expression (eq.4.17, eq.4.18 and eq.4.19) was integrated to determine the variation of sampled volume with sampling time:

$$V(t)=\int_0^t Q(t)dt=\int_0^t \frac{K_1}{1+K_2 t}dt \qquad \text{(eq.4.23)}$$

By solving this expression, a solution for the sampled volume as a function of time {*V(t)*} was obtained and again, two arbitrary constants (K_5, K_6) were defined. This relationship is stated as:

$$V(t)=K_5 \ln(1+\frac{K_6 R^4}{L}t) \qquad \text{(eq.4.24)}$$

where constants K_5 (in m^3) and K_6 (in $m^{-3} \cdot s^{-1}$) are given as:

$$K_5=\frac{P_{atm}V_s\overline{V}}{\mathbb{R}T} \qquad \text{(eq.4.25)}$$

$$K_6=\frac{\pi \mathbb{R}T}{8\mu V_s\overline{V}} \qquad \text{(eq.4.26)}$$

Finally, *V(t)* was defined as the final sampled volume (V_f) which equals 0.5 times the sampler's volume (V_s). This was done to answer the following question: If a capillary of known geometry acts as restriction to the entry of air into an evacuated container, how much time will be required to fill half of it? An expression relating the capillary length (*L*) as a function of total sampling time (t) was obtained. The internal radius of the capillary column (*R*) and the volume of the sampler were also considered. This final relationship includes two constants previously described and is stated as:

$$L=\frac{K_6R^4t}{(e^{\frac{V_f}{K_5}}-1)} \qquad \text{(eq.4.27)}$$

This theoretical result provides a basis for mathematical simulations used to approximate the capillary geometries required to achieve a selected sampling period with a given evacuated sample container. This mathematical model was not developed to characterize gas flow behavior inside a capillary but to perform calculations applied to the design of flow controllers which can be used to collect long-term integrated samples for VOC analysis. Many assumptions were made to arrive at this solution. The theoretical model derived will be critically assessed by comparing calculations obtained from computer simulations with experimental results.

4.2-Evaluating sampling time factors

The principle of long-term integrated sampling using an evacuated containter equipped with a capillary flow restriction is based on the physical relationship between the geometry of the capillary and the total sampling period during which a critical flow is established. This is also a function of the volume of the evacuated sample container used in the configuration. To study this relationship, two approaches were used. Simulations were performed with the mathematical model to show the influence of each dimensional parameter on the integrated sampling time. Experiments were also conducted to estimate the volumetric flow rate obtained from selected capillary geometries.

4.2.1-Simulation studies

Calculations were initially made using the Hagen-Poiseuille equation (eq.4.9) as a first approximation. This was initially done to verify if the available capillary column with relatively small internal diameters could be used to significantly reduce flow rates to increase sampling times. These simulations were performed before the mathematical model relationships were developed based on more advanced theoretical considerations (see section 4.1.2-). These calculations were based on the hypothesis that the pressure gradient between a complete vacuum and ambient pressure would remain constant during the whole process. It was also assumed that a laminar flow would be established, and that effects of fluid compressibility would be negligible.

The results of these calculations are presented in table 4.1. From the flow rate calculated using different capillary lengths (*L*) with small internal diameters (ID), the total sampling period was estimated in days for the situation where 500 ml of air was sampled using a 1-litre sample container.

Table 4.1: Estimation of sampling times (days) based on capillary geometries using the Hagen-Poiseuille equation: situations where a 500 ml air sample is collected with a 1-litre sample container using a CSFC

Column ID	**(*L*) Capillary column length** (m)								
(mm)	**0.1**	**0.25**	**0.5**	**0.75**	**1**	**2**	**5**	**10**	**30**
0.05	0.68	1.69	3.38	5.06	6.75	13.5	33.8	67.5	202
0.10	0.04	0.11	0.21	0.32	0.42	0.84	2.11	4.22	12.7
0.18	0.004	0.01	0.02	0.03	0.04	0.08	0.20	0.40	1.21
0.25	0.001	0.03	0.01	0.01	0.01	0.02	0.05	0.11	0.32

These results show that less than 25 cm of a capillary with an ID of 0.05 mm would be required to restrict the flow of air over a one day period. Moreover, based on theoretical and practical assumptions, the same capillary column having a 30-metre length would afford an extended sampling period of approximately 200 days. It can be seen that capillary columns with small internal diameters, theoretically, can give long integrated sampling times. Also, based on these assumptions, a column, 10 meters or less in length, 0.18 mm ID, would not offer more than a few hours of sampling time. This indicates that larger ID capillaries would not play an important role in the flow restriction required for long-term integrated sampling time. However, these data theoretically provide an underestimate of sampling intervals because the reduction of the pressure gradient over time is not considered in this steady state situation where a 1 atmosphere pressure gradient is assumed.

One of the assumptions made for these calculations is that a laminar flow is established. To verify this assumption, Reynolds numbers (*Re*) were calculated for these situations. This dimensionless number represents the ratio between kinetic and friction forces when the flow of a fluid such as ambient air is at steady state. *Re* numbers were calculated according to the following relationship:

$$Re=\frac{2R<v>\rho}{\mu} \qquad \text{(eq.4.28)}$$

The average velocities ($<v>$) were determined from calculated flow rate values using the Hagen-Poiseuille equation and the cross-sectional area of the capillaries. Air density (ρ) and viscosity (μ) at ambient temperature and pressure were used. The Reynolds numbers obtained based on this hypothetical situation are presented in table 4.2. Inside a pipe, flow is considered to be turbulent when this number exceeds 2100. Otherwise, a laminar flow can be assumed when lower Reynolds numbers are estimated. In such situations, the

Hagen-Poiseuille equation can be applied. It can be seen from table 4.2 that for every capillary dimension, the laminar flow assumption is respected.

Table 4.2: Estimation of Reynolds numbers based on capillary geometries using the Hagen-Poiseuille equation for a pressure gradient of 1 atmosphere

Column ID	**(*L*) Capillary column length** (m)								
(mm)	**0.1**	**0.25**	**0.5**	**0.75**	**1**	**2**	**5**	**10**	**30**
0.05	14	5.7	2.9	1.9	1.4	0.7	0.3	0.1	0.05
0.10	116	46.3	23.1	15.4	11.6	5.8	2.3	1.2	0.4
0.18	674	270	135	89.9	67.4	33.7	13.5	6.7	2.2
0.25	1807	723	361	241	181	90	36.1	18.1	6.0

These results indicate the possibility of extending sampling time using the CSFC. As previously mentioned, these calculations were made before the mathematical model was developed to combine gas kinetic and fluid mechanic phenomena (see section 4.1.2). However, simulations were also made using the mathematical model developed to determine the geometry of capillaries under non steady state behavior. The final relationships (eq. 4.25 to eq. 4.27), which consider the internal pressure variations with time when capillaries are used as flow controllers, were used to perform the calculations.

Figure 4.6 illustrates simulation results which attempt to clarify the relationship between capillary geometries and the integrated sampling time when a one litre sample container is used to collect a 500-ml ambient air sample. Three graphs are shown where the lengths of capillaries for various available ID are correlated with sampling periods measured in days, hours or minutes. Simulations were made to obtain long-term integrated sampling intervals with capillaries having internal diameters of 0.05 mm, 0.10 mm or 0.18 mm.

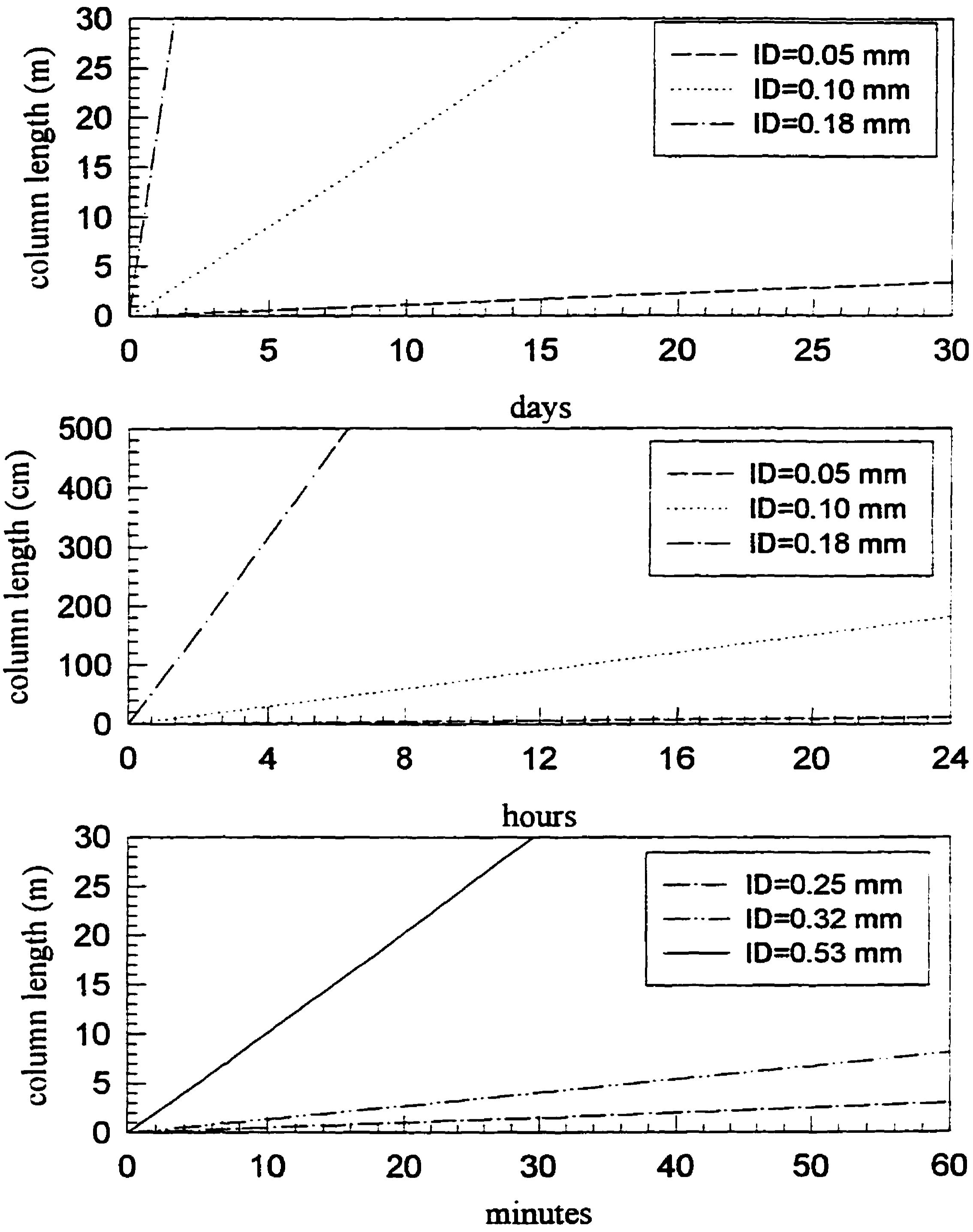


Figure 4.6: Integrated sampling time for capillary geometries calculated with the mathematical model: situations where 500 ml of ambient air is collected with a 1-litre sample container

Calculations were also made with larger internal capillary diameters (0.25 mm, 0.32 mm and 0.53 mm) to determine their effects on flow restriction. As expected, any given capillary length predicted by these simulations affects the sampling intervals to a greater extent than when derived from the Hagen-Poiseuille equation (table 4.1). For example, a 10 metres column with an ID of 0.10 mm was shown to offer a 4.22 day sampling period when the Hagen-Poiseuille equation was used. For the same situation where 500 ml of ambient air is collected in a one litre container, the mathematical model predicted an integrated sampling time of approximately 6 days.

This model was also applied to determine the potential effects of the sample container's volume on the length of a capillary required to achieve selected long-term sampling periods. A capillary with an ID of 0.05 mm was used for these simulations. The results are illustrated in figure 4.7. In this graph, the simulations showed that when the volume of the container is greater than 2 liters, less than 20 cm ($2.0e^{-1}$ m) of the capillary is required to achieve sampling periods which can exceed 24 hours. This relationship between these two parameters, which is based on the model, revealed an important fact. The length of the capillary tends toward zero as one increases the size of the sample container and/or reduces the sampling time. For example, consider a situation where six-liter (6 l) summa canisters are used to collect passive subpressurized air samples. To design CSFC units that allow sampling periods of 8, 24 or 40 hours, 0.6, 2.0 and 3.3 cm long capillaries having an internal diameter of 0.05 mm are needed respectively. A point is reached where the length of capillary required becomes so small that it may be physically difficult to assemble units. For such situations, the assembly would require a longer length of capillary having a larger cross-sectional area (ID) to achieve these target flow rates.

This part of the study was performed to predict the capillary geometries required for the different configurations of passive stationary and personal samplers which use flow controllers that, theoretically, can be designed for long-term integrated sampling.

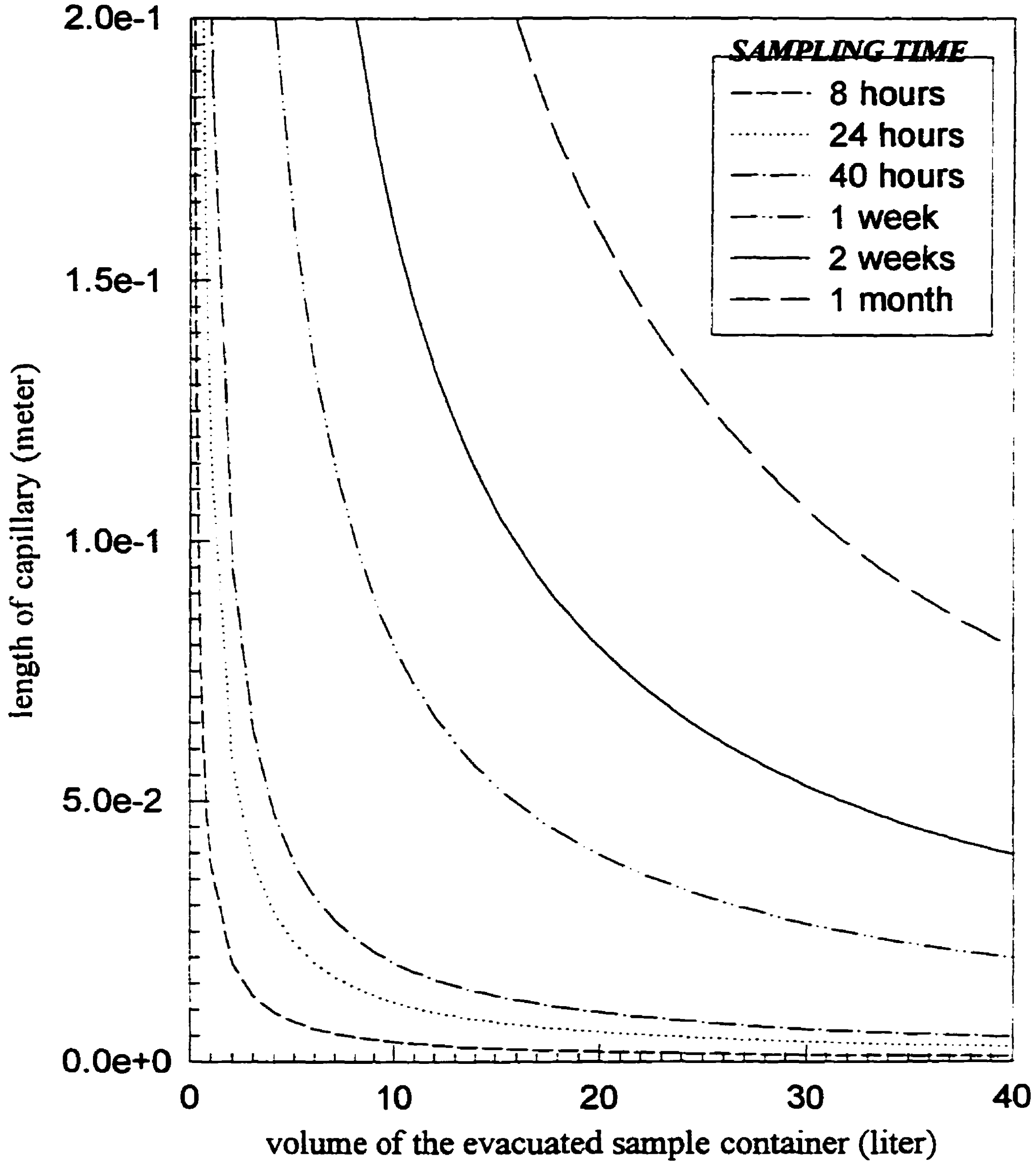


Figure 4.7: Effects of container sizes on the length of a 0.05 mm capillary column required to achieve selected integrated sampling intervals as predicted by the mathematical model developed to design CSFC units

The simulations made possible by the model developed earlier as demonstrated the capacity of selected capillary geometries to provide long intervals during which a constant flow rate of a gas sample can be delivered to any sample container sizes. These results provided the basis for experimental studies with passive sampler prototypes. Capillary column geometries were selected according to these theoretical calculations. Geometries were tested with various sample container sizes. The results obtained from laboratory experiments will now be compared with predictions from the mathematical model.

4.2.2-Experimental tests

Theoretically, based on the mathematical model derived in the preceding section, flow controllers can be designed to control and increase the sampling interval for ambient air and thus, improve a passive sampling methodology for gaseous contaminants such as VOCs. Accordingly, experiments were made with prototypes to evaluate flow rates. Model simulations were used to select the capillary geometry required for a selected integrated sampling period with a given evacuated container volume.

Two objectives were defined for these studies. Data were collected to determine flow rate values obtained from passive sampler prototypes. This was performed to characterize the operating range of flow controllers and to evaluate the validity of the long-term integrated sampling process. From compiled results of all configurations tested, the effects of capillary geometries on experimental flow rates afforded by the CSFC was established to provide appropriate design specifications. These results are now presented and compared with model predictions.

4.2.2.1-Flow rate

Volumetric flow rates were determined with a sampling train designed for stationary samplers using evacuated summa canisters. The first tests were conducted to achieve a 24-hour sampling interval using a one-liter container. Based on simulations, a capillary with an ID of 0.05 mm was selected to fulfill these criteria. Experiment results using a predicted length (0.115 meter) of a restriction capillary column are presented in figure 4.8. The sampled volumes (data points) are based on pressure readings taken during specified time intervals. Two different readings are reported: 1) those obtained from an electronic pressure transducer; 2) others taken from a simple mechanical pressure gauge (Bourdon type). These data were transformed into sampled volume using equation 3.1 (figure 4.8, left axis). The pressure time function computed from equations 4.20, 4.21 and 4.22 was used in a similar manner to calculate the predicted sampled volume.

Flow rate predictions from model simulations are also reported on this graph (figure 4.8, right axis). This curve was obtained from equations 4.17, 4.18 and 4.19. The model simulations were able to predict an appropriate capillary geometry. However, simulations did not entirely agree with experimental findings. The selected capillary column geometry allowed the collection of approximately 500 ml of ambient air over a 24-hour period. During this period, a linear relationship between sampled volume and time can be observed. However, the sampling rate decreases with time as the container continues to be filled after this 24-hour period. The model does not reproduce this phenomenon. In fact, as the sampling time increases, the curve obtained from experimental results tends to deviate from the one generated by the mathematical model. The equations were developed to estimate the capillary length required to obtain a predefined sampling time based on the sample container size selected. The model that predict the design specifications used the integration of the area under the predicted sampled volume curve as shown in the graph (Fig. 4.8).

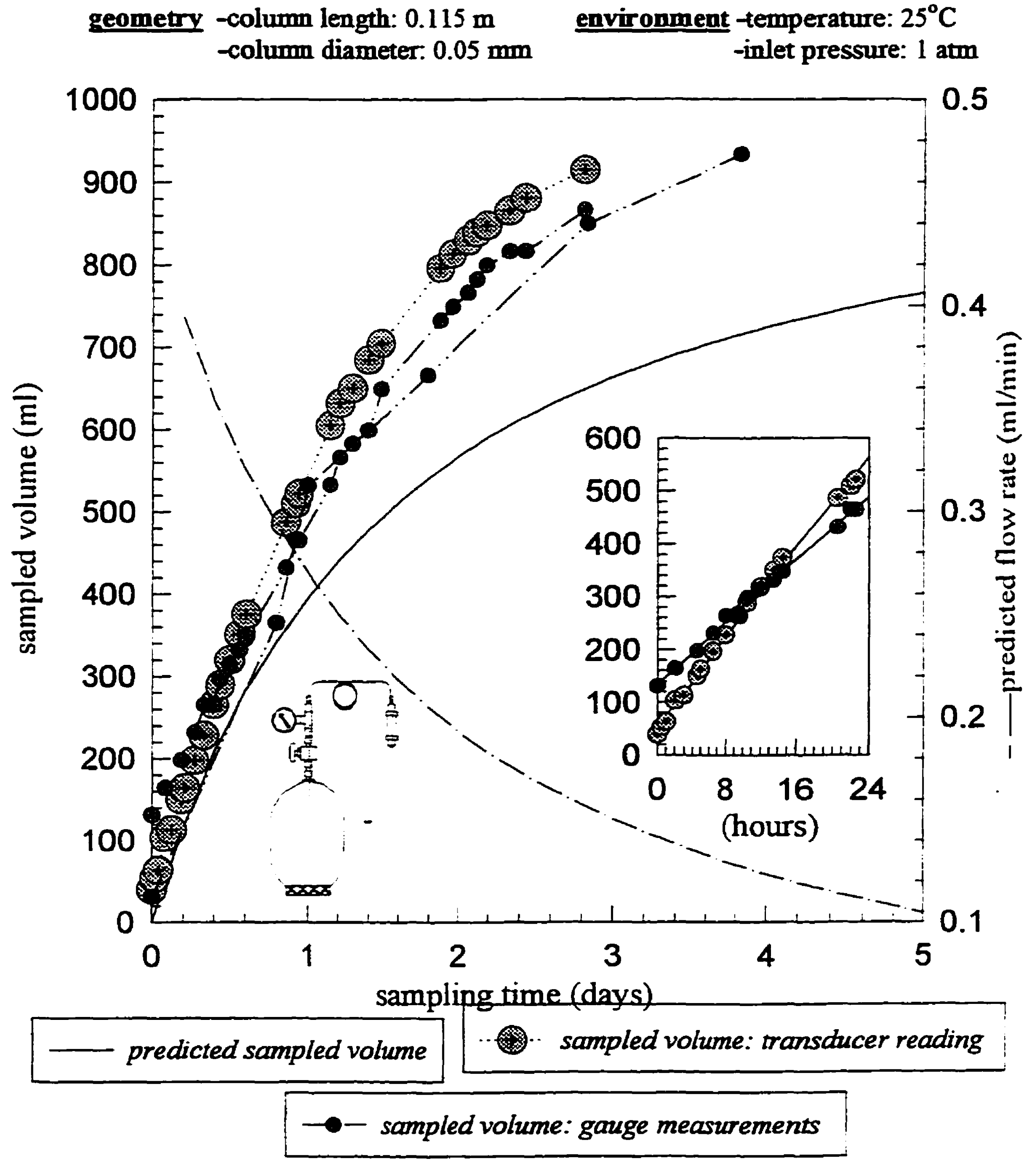


Figure 4.8: 24-hour sampling profile using a CSFC with a 1-litre sample container

Neither simulation curve for the flow rate and the sampled volume was able to characterize the true behaviour of the sampling process occurring under experimental conditions. Nonetheless, the theoretical calculations made on the basis of the model provided an appropriate estimation of the geometry required for this situation.

To approximate the sampling flow rate during the first 24 hours, the data obtained from the prototypes and the curve from the predictive model were linearized using least-square approximations. These results are illustrated in figure 4 9. They show that the CSFC can deliver a constant sampling flow rate (between 0.23 ml/min and 0.35 ml/min) to collect an integrated ambient air sample passively. In fact, the model predicted a saturation process and hence, a less constant flow rate than what is observed experimentally. The regression coefficients (r^2) were higher in experiments when compared with those obtained from the theoretical relationship. Both experimental factors were estimated at 0.997, whether measurements were recorded with an electronic pressure transducer or with a mechanical pressure gauge which is comparatively less accurate.

These experimental results illustrate the efficiency of the CSFC in effectively extending the sampling interval. The small flow rate variations observed between prototypes can be explained by differences in initial vacuum within evacuated samplers, or by calibration errors for the pressure measuring devices. Nevertheless, it appears that these variations have negligible effects on the linearity of the sampled volume measured experimentally during the passive sampling process. Moreover, these differences did not affect the prior characteristic of the controller which is to achieve a constant flow rate over the selected period. Even if the final volume collected during 24 hours was not exactly similar, units were able to provide gas samples that can similarly be handled for GC injection, detection and quantification. Such samples can represent long-term mean estimates of VOC concentrations.

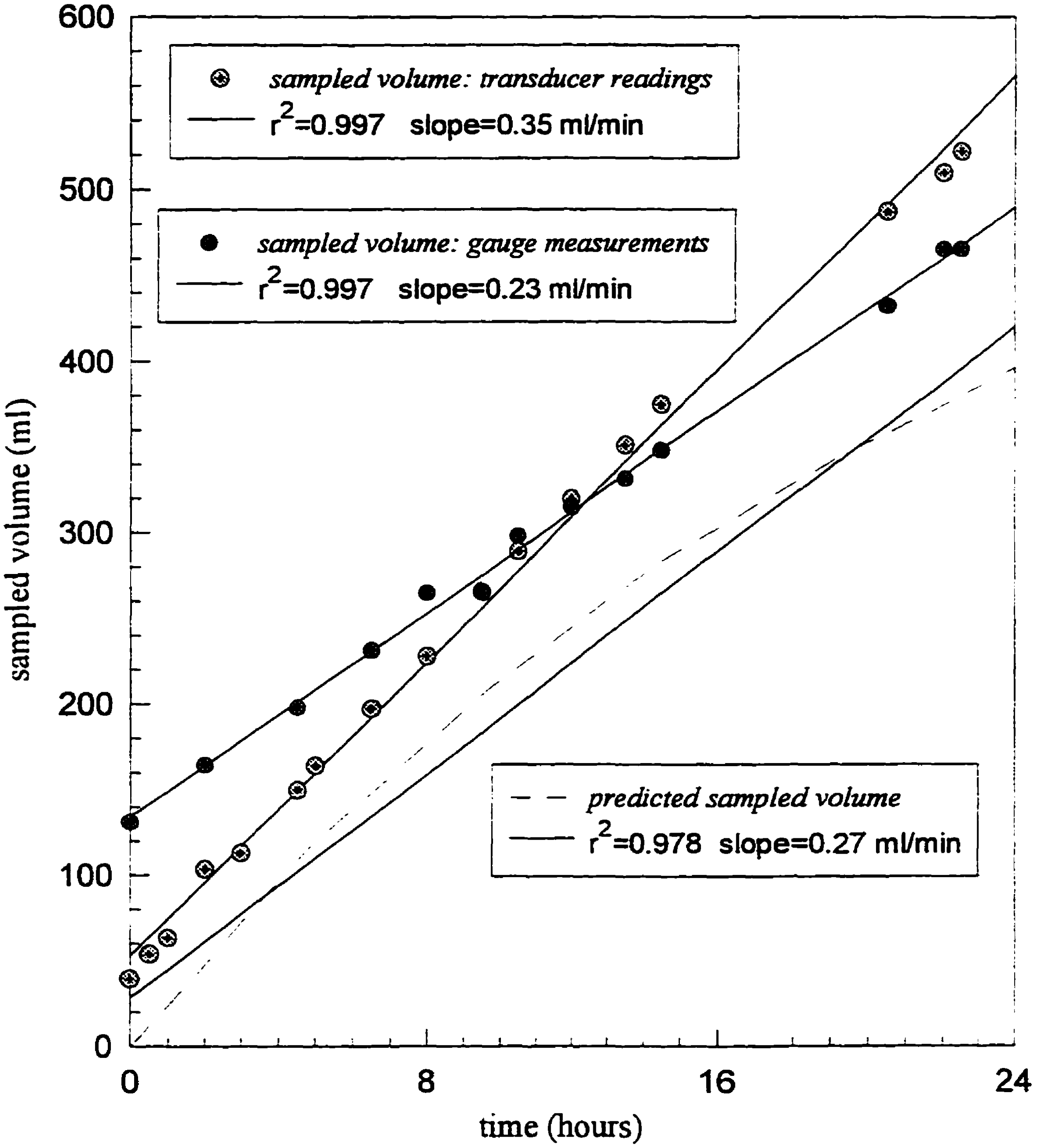


Figure 4.9: Linear approximation of flow rates using a 0.115 metre of a capillary column (ID=0.05 mm) with a 1-litre sample container

The length of capillary column selected for this application was rather small. Another experiment was made to achieve a longer duration (1 week) with a smaller size of container. This study was also conducted to investigate in more detail the effect of the final sampled volume on the constancy of the volumetric flow rate offered by the CSFC. This new experiment was made in the laboratory using a 500-ml summa canister, and data from a pressure transducer were obtained over more than three weeks. The flow controller was designed with 1.25 meters of fused silica capillary having an ID of 0.05 mm. These results are shown in Fig. 4.10.

Again, it can be seen that the model predictions closely approximated what was observed experimentally. Linear regressions were made when 40%, 50%, 60% or 70% of the sampler size was filled during the gas sample collection. Figure 4.10 shows that when more than 60% to 65% of the vessel is filled with a gas sample, the pressure gradient is not sufficient to deliver a constant sampling flow rate. Otherwise, when such low flow rates are achieved, the operating range of this mechanical controller can provide very broad integrated sampling times, in this case ranging from 7 to almost 14 days. Table 4.3 summarizes the results obtained from this analysis. Regression coefficients, which characterize the precision of the sampling rate, exceeded 99% during a large time interval. Volumetric flow rate was maintained at 0.018±0.001 ml/min over a long integrated sampling period. By analogy, if a six-litre canister was used with this flow controller, a sampling interval ranging between three to six months could be achieved.

This particular passive sampler configuration which requires a CSFC designed with 1.25 metres of a capillary having an internal diameter of 0.05 mm was developed for a specific application. These prototypes were used to monitor the air quality inside the Mir Russian orbital station (see section 5.3.3.3-).

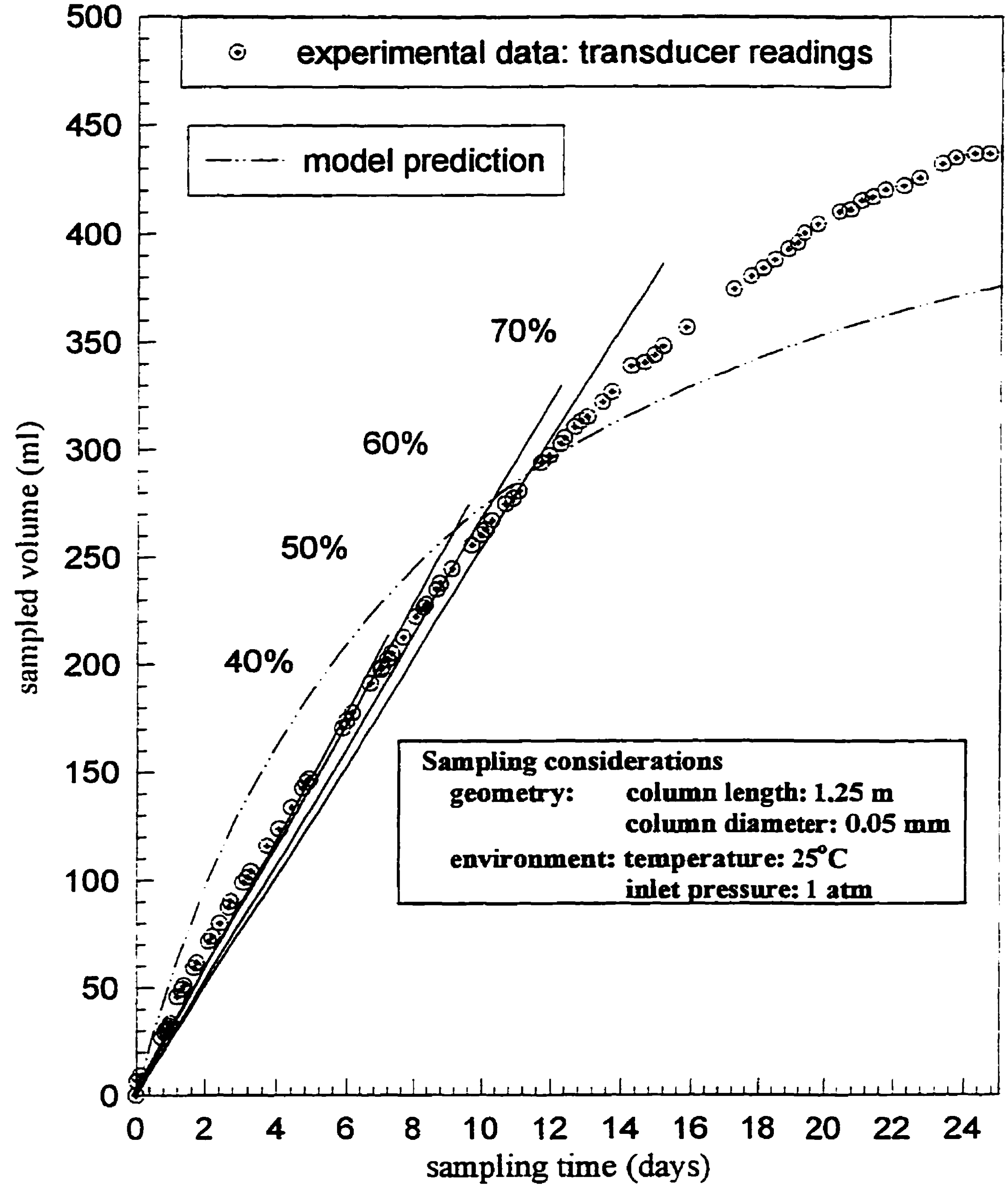


Figure 4.10: Effect of the final sampled volume on flow rate using a CSFC prototype and a 500-ml summa canister

Table 4.3: Regression analysis to estimate the effects of the final sampled volume on flow rate

Final sampled volume		**Integrated sample period**	**Volumetric sampling flow rate**	**Correlation coefficient (r^2)**
(ml)	(%)	(day)	(ml/min)	%
200	40	7	0.019	99.6
250	50	10	0.018	99.6
300	60	12	0.017	99.3
350	70	15	0.016	98.9

These experimental results have shown that the CSFC can be used to extend the sampling period when combined with an appropriate evacuated container. They also provided evidence that the mathematical model can adequately approximate the capillary geometries required to achieve long-term integrated passive sampling.

More importantly, these results demonstrate that a constant flow rate can be obtained over a portion of the process in which the operating range of the sampler is defined. However, this behaviour was predicted based on some theoretical aspects of a maximum discharge rate of gas in pipes. In such systems, the conditions at the end of a capillary can explain why the maximum flow rate is kept constant over a period of time. Mathematically, it was demonstrated that the velocity of the gas equals that of sound at the tube exit until a point is reached where a change of pressure will start to influence the flow rate (McCabe, W.L and J.C. Smith, 1956). During this initial phase, a pressure gradient reduction does not affect the flow because the gas is moving faster than a change of pressure can be carried back into the capillary. In other words, the flow rate is regulated by the sound pressure wave instead of the internal pressure of the container.

Based on these considerations, studies were conducted to establish the effects of capillary geometries on the low volumetric flow rates obtained experimentally with various passive sampler prototypes.

4.2.2.2-Effects of geometry

Similar studies using other capillary lengths having a 0.05 mm ID were performed. For each experiment, a linear relationship was always observed between the sampled volume and the time during which approximately 50% of the container volume was filled. Table 4.4 summarizes the flow rate results obtained from experimental studies conducted with specific prototype configurations. Each experiment identified by a letter in table 4.4 was conducted at ambient temperature and pressure except when indicated.

A general pattern can be observed. As the capillary column length (L) is increased, the experimental flow rate (Q_{exp}) decreases. This phenomenon does not depend on the volume of the sample container (V_s) used. However, this trend was not observed in one of the experiments (Exp. Id. i). In this test, the gas inlet was connected to a 6-litre summa canister pressurized to 5 psi with humid air. The volumetric flow rate is increased because the pressure gradient is significantly higher than when atmospheric gas is sampled. Similar conditions were used for experiment "e".

It should be noted that experiment "d" was performed by an external laboratory. A cooperative agreement was arrived at with the Boeing Analytical Services in Alabama for the verification of the long-term passive sampling device's performance. This collaboration provided further confirmation of the validity of the measurements.

The column lengths tested were initially selected from model simulations for their ability to achieve a predefined integrated sampling time based on evacuated container volumes.

Table 4.4: Experimental volumetric flow rates (Q_{exp}) obtained with 0.05 mm ID capillaries of various lengths (L)

Configuration of the sampler			Results		
Exp. Id.	V_s (ml)	L (m)	Q_{exp} (ml/min)	r^2 (%)	Pressure reading device
a	6000	0.019	0.92	99.6	gauge
b	1000	0.115	0.25	99.7	gauge
c	1000	0.189	0.14	99.0	gauge
d*	500	0.370	0.12	99.9	transducer
e**	1000	0.795	0.057	99.8	gauge
f	150	0.870	0.031	99.1	gauge
g	1000	1.00	0.023	99.4	gauge
h	500	1.25	0.018	99.6	transducer
i**	100	1.89	0.028	99.5	gauge

* Data collected by Boeing inc. (Manual, S., 1995)
** Test performed with a pressurized inlet

Sampling periods of 24 hours[1], 40 hours[2] and 7 days[3] were selected as long-term sampling objectives. The experimental results are illustrated and compared with the model prediction in figure 4.11. Based on a null hypothesis, the percentage difference between theoretical and experimental flow rate results is not statistically significant. The probability that observed variations within the studied range of capillary geometries could be due to chance is less than 10% (*student T-Test*, 95% confidence interval, one tail).

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[1] Exp. Id.: a, b

[2] Exp. Id.: c, d, f, i

[3] Exp. Id.: g, h

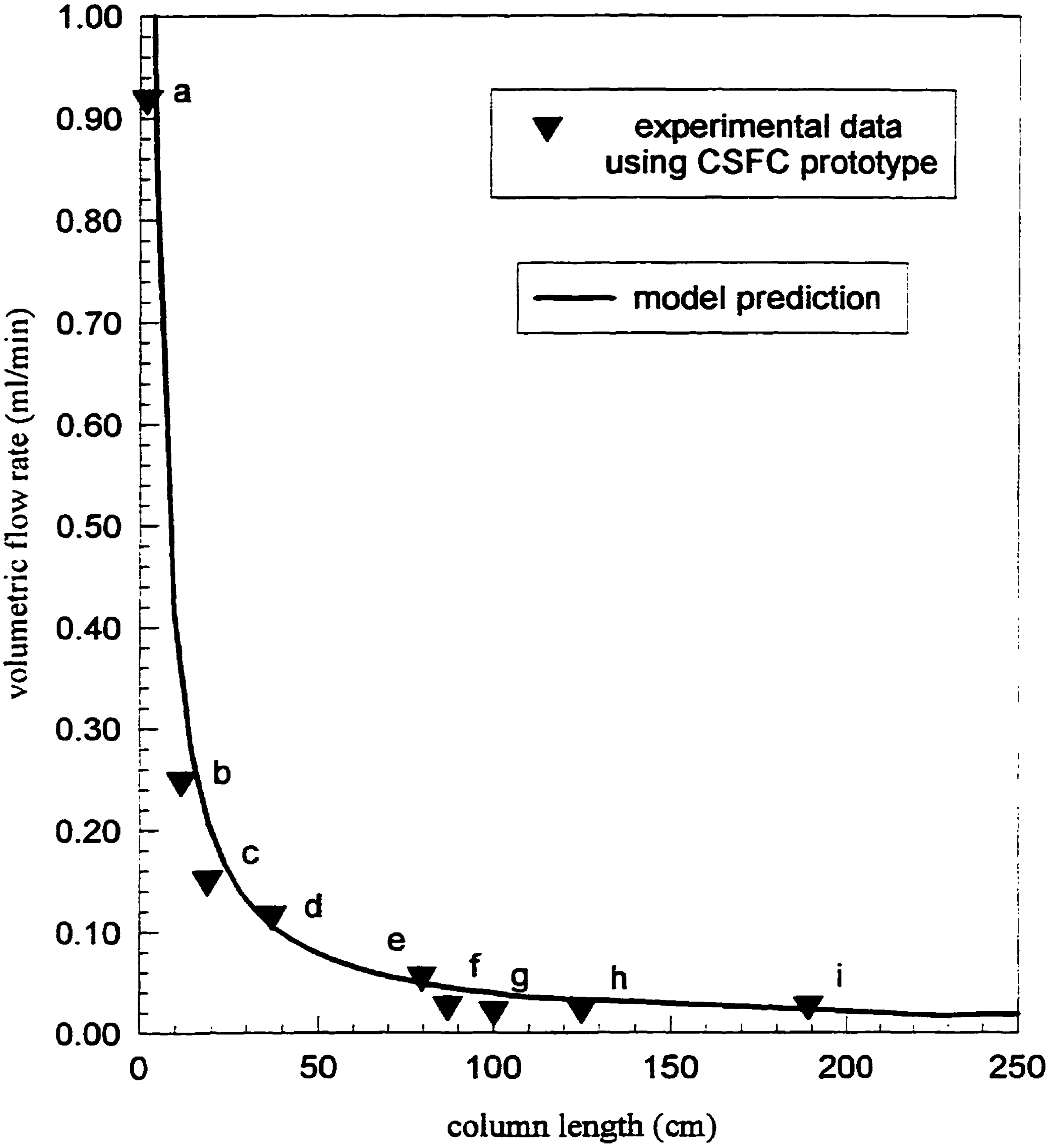

Figure 4.11: Comparison of experimental versus simulation results for the volumetric flow rate obtained with various 0.05 mm ID capillary lengths (see table 4.4 for nomenclature)

Generally, experimental results approximate rather well the relationship calculated using the model simulation. Except for annotated experiments (see table 4.4), most of the results fall below the predicted curve. From this graph, one can see that as the capillary length increases, the changes in flow rate diminish. A transition zone occurs between 10 cm and 50 cm. For short lengths (less than 10 cm), a marked influence is noted on the volumetric flow rate. In this part of the curve, the variations in capillary lengths have a severe effect on the flow. For this reason, less precise time integrations are obtained from the selection of such short lengths. In experiment "a" (table 4.4) where 1.9 cm was used based on model prediction to achieve a 24-hour sampling time with a 6-litre canister, the flow rate obtained experimentally was significantly different from the expected value (3 litres of gas sampled over 24 hours = 2.1 ml/min). With this configuration, an approximate 48-hour period was obtained instead. Configurations using short capillary lengths are less precise, and as mentioned earlier they are also more difficult to assemble.

One of the assumptions made to use the Hagen-Poiseuille equation was that the tube is long enough that end effects (sudden expansion) are neglected. This is probably not the case with short capillary length as indicated by experimental findings.

Other experiments were also conducted to study the effects of columns having a larger cross-sectional area. Flow rates obtained for specific samplers are presented in table 4.5. The design of the flow controller unit to obtain a 24-hour sampling time with a 6-litre summa canister incorporated a 0.10 mm ID capillary. Three different lengths of such a capillary were tested for this situation[4].

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[4] Exp. Id. j, k, l

These data were compared with the model prediction and illustrated in figure 4.12.

Table 4.5: Experimental volumetric flow rates (Q_{exp}) obtained with 0.10 mm ID capillaries of various lengths (L)

Geometry of the sampler			Results		
Exp. Id.	V_s (ml)	L (m)	Q_{exp} (ml/min)	r^2 (%)	Pressure reading device
j	1000	0.150	2.60	99.6	transducer
k	6000	0.180	1.82	99.9	transducer
l	6000	0.303	1.00	99.7	gauge
m	1000	1.12	0.37	99.7	transducer
n	1000	1.80	0.23	99.8	gauge
o	1000	2.61	0.17	99.6	gauge
p	500	10.0	0.046	99.5	gauge

Experimental sampling results from which flow rate values were obtained and compiled in tables 4.4 and 4.5 are presented in appendix 3. In figure 4.12, the results for an experiment where 10 metres of column was used (Exp. Id. p) does not appear on this graph but data can be found in appendix 3. All capillary lengths longer than one metre and having a 0.10 mm ID were randomly selected (Exp. Id. m, n, o, p). The exact length required to achieve a 24-hour sample with a 6-litre canister was estimated. Approximately 17.5 cm is required for this situation. For each data point illustrated in figure 4.12, the flow rate obtained experimentally was systematically lower than that calculated using the model. Percentage differences were statistically significant. The simulation overestimated the length required to achieve the selected time. This was also observed with capillaries having a 0.05 mm ID, but the effect is apparently much less severe.

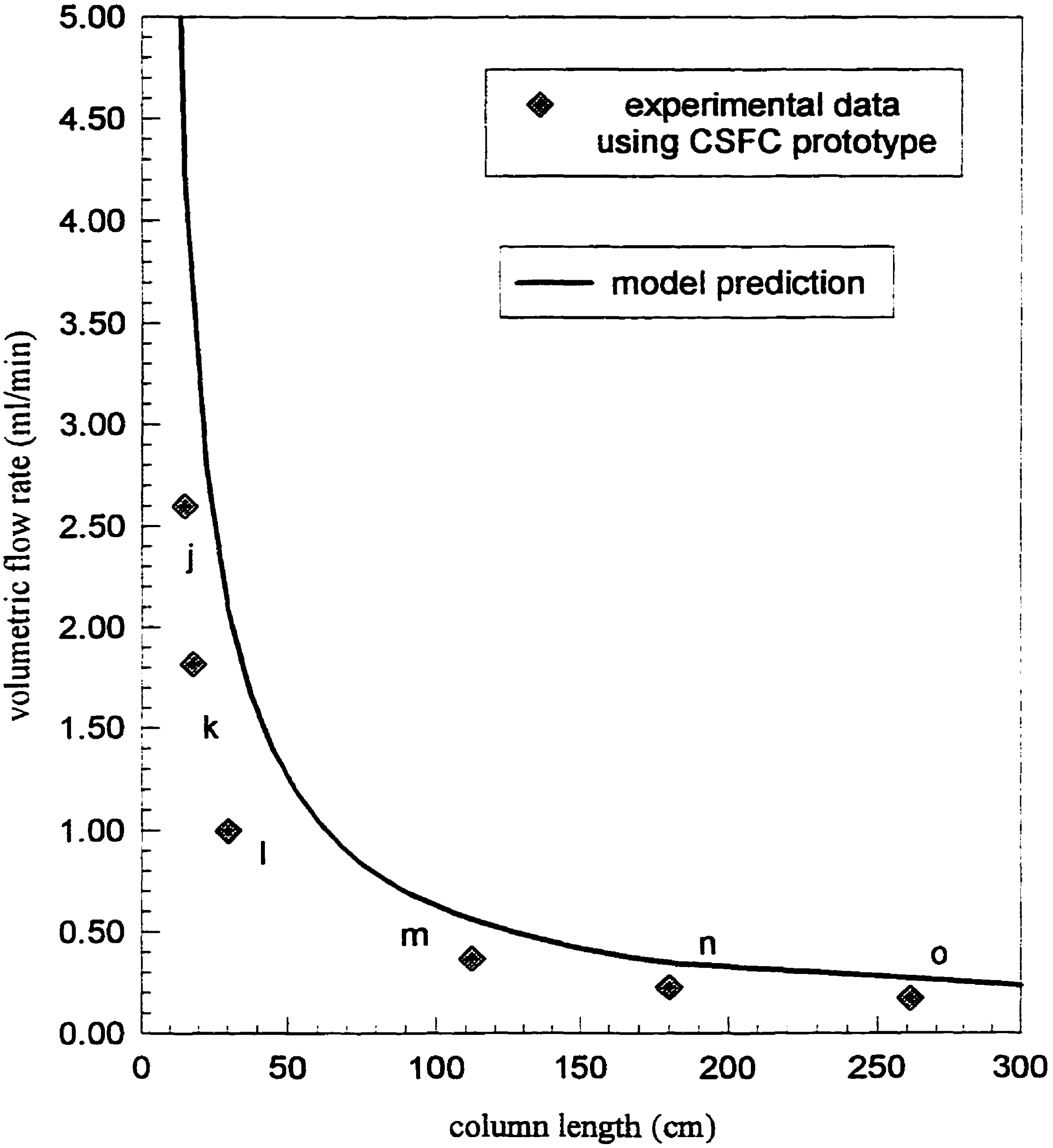

Figure 4.12: Comparison of experimental vs simulation results for the volumetric flow rate obtained with various 0.10 mm ID capillary lengths (see table 4.5 for nomenclature)

In an attempt to understand why a greater deviation from the model prediction is observed with larger capillary cross-sectional area, the capillary's ID was measured using electron microscopy. The hypothesis was that the true column's internal diameter would have been smaller than the one specified by the manufacturer. Figure 4.13 shows a photograph where the internal diameter of a 0.10 mm ID capillary is measured. From 10 different cross-section samples, the microscopy revealed that internal diameters were effectively 100 ± 5 μm.

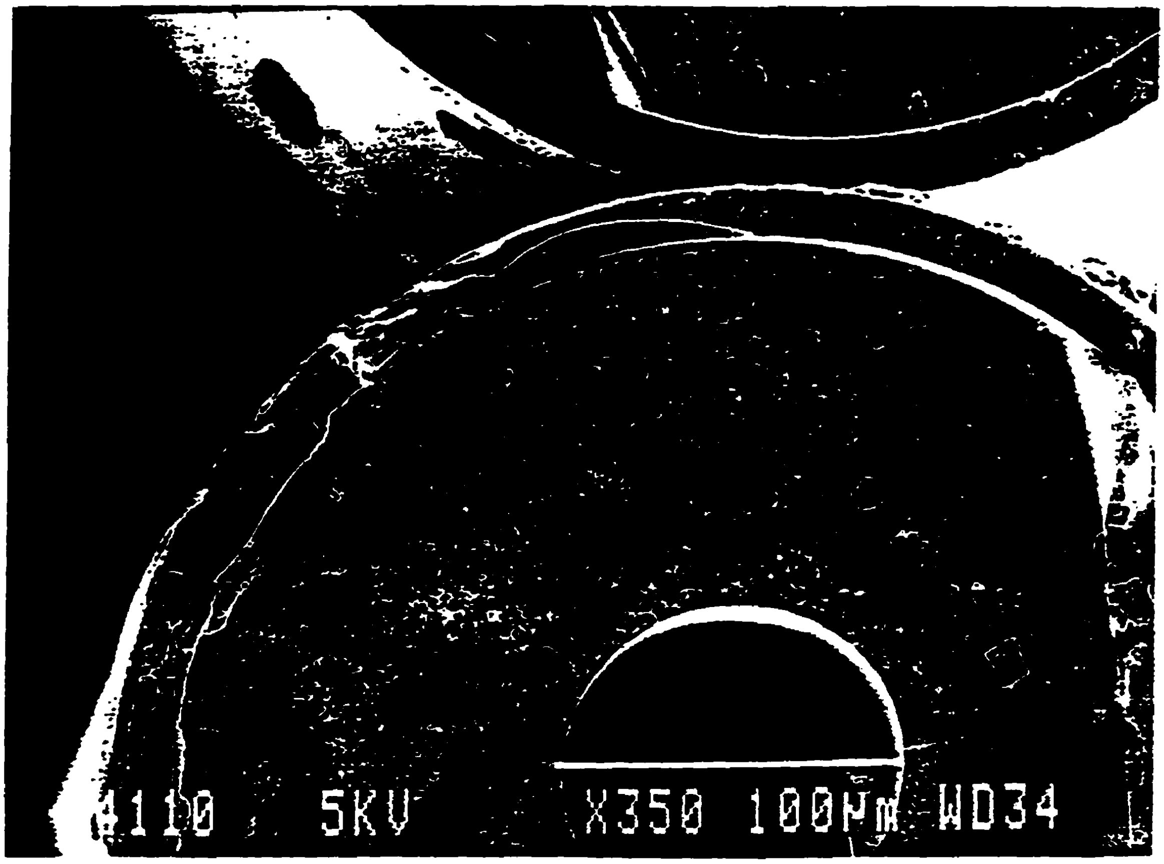

Figure 4.13: Photograph of a 0.10 mm ID capillary's cross-section obtained by electron microscopy

These results provided an insight into the capillary internal diameter's precision. However, they could not explain differences between mathematical model predictions and measured sampling dynamics. Otherwise, capillary lengths can be measured to a tolerance of approximately 2 mm. Such errors have a minimal effect on flow rate delivered by a CSFC.

4.2.3-Empirical model

To improve mathematical predictions, another approach was used to study the relationship between experimental and theoretical modelling results. For both capillaries (0.05 mm and 0.10 mm ID) tested, the flow rate is inversely proportional to the length of the column used. To establish the effects of capillary column geometries on the integrated sampling time, the inverse of the flow rate ($1/Q$) was plotted against the capillary length. These results are shown in figure 4.14.

For this analysis, only the data points obtained at ambient pressure were considered: experiments identified as d, e and i were rejected based on the fact that they were not performed under the same conditions. It has been demonstrated that a linear relationship exists between the capillary column length and the time when a maximum discharge rate is achieved due to the driving force of the vacuum. This phenomenon was predicted by the model (see figure 4.6). However, it appears from experimental findings that length effects are more important than expected. With the two capillary columns studied, the slopes obtained from experimental data were greater than the ones calculated using the model.

Figure 4.14 also confirms that evacuated sample container volume does not affect the sampling flow rate delivered by the CSFC. This parameter was considered in the mathematical model because it is part of the selected geometry of samplers, but the variable does not influence the maximum discharge rate. In fact, the selection of an appropriate volumetric flow rate depends on only two variables: the length and the ID of a capillary column.

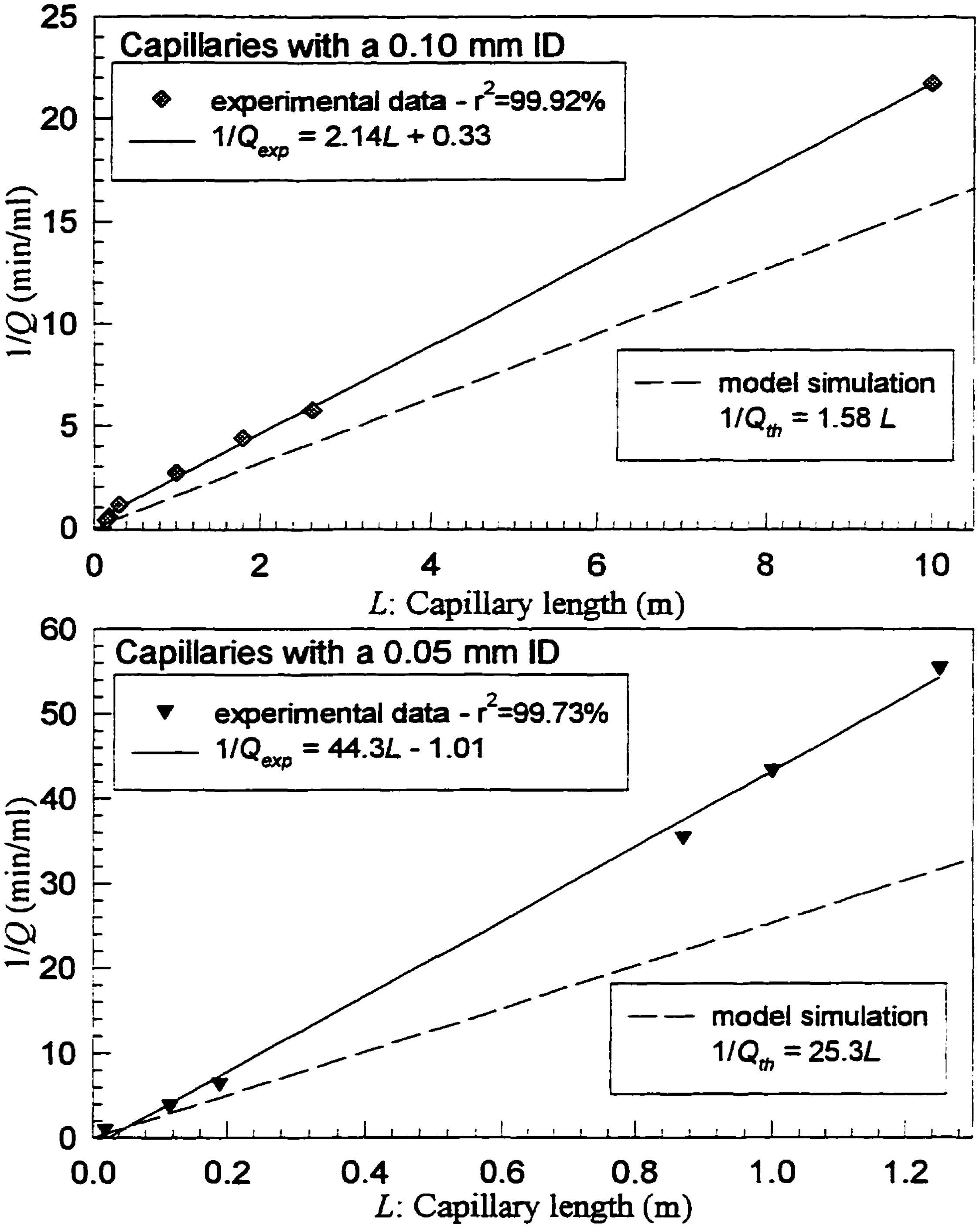

Figure 4.14: Relationship between the inverse flow rate and capillary lengths having a 0.10 mm and 0.05 mm ID: comparison of experimental and theoretical results

The results reported in figure 4.14 provide an opportunity to improve the prediction obtained from simulations. If the same column ID is used for the design of a CSFC, first order experimental relationships between $1/Q_{exp}$ and L can be applied. For the deactivated fused silica capillary having a 0.05 mm ID, this equation is stated as:

$$\frac{1}{Q_{\mathrm{exp}}}=44.3L-1.01 \qquad \text{(eq.4.29)}$$

Based on the correlation coefficient obtained, the capillary column with a 0.10 mm ID was shown to have a better fit for the same type of linear relationship and for a wider range of lengths. The equation obtained for such a capillary is as follows:

$$\frac{1}{Q_{\mathrm{exp}}}=2.14L+0.33 \qquad \text{(eq.4.30)}$$

These two relationships can provide precise estimates of capillary geometries required to design CSFC. Nevertheless, they do not offer the opportunity of predicting the design parameters for other capillary ID values. Fortunately, a more generalized expression can be derived and an empirical model was developed from experimental results.

When the slopes obtained from model simulations are compared, a ratio of 16 is obtained (25.3/1.58). This is explained by the fact that the capillary radius is at the fourth power in model equations. Doubling the ID for a selected capillary length theoretically results in a 16 fold (2^4) increase in the flow rate. From experimental results, the ratio between the slopes was found equal to 20.7 (44.3/2.14), suggesting that the capillary ID may have a different influence on the process than that predicted from theoretical considerations. Therefore, a new power for the radius was estimated at 4.37 by dividing the log value of the slope's ratio by the log value of the ID's ratio (log20.37/log2). From this calculation, an empirical model is proposed:

$$Q=K_{\exp}\frac{R^{4.37}}{L} \qquad \text{(eq.4.31)}$$

The value of the experimental constant (K_{exp}) was derived from the linear relationships illustrated in figure 4.14 (eq. 4.29 and eq. 4.30). When the flow rate (Q) is measured in ml/min, the radius (R) is determined in mm and the capillary length (L) is selected in meters, this constant equals $2.25*10^5$. Figure 4.15 compares the flow rate obtained from every experiment conducted using long-term passive sampler prototypes with their respective predicted values calculated using this new empirical relationship (eq. 4.31). The effects of capillary geometries on volumetric flow rates appear to be well characterized by this empirical equation which considers both capillary dimension variables (eq. 4.31). For the very low flow rates required to significantly increase the sampling period, the correlation is improved. It can be seen that for the six data points where the flow rate was below 0.2 ml/min, the regression coefficient was estimated at 97.9%. In this range, the ratio between the experimental flow rate and the predicted value was more than 99%. However, the proposed relationship was not exhaustively tested. Only two results were obtained at low flow rates using the capillary with the largest ID (0.10 mm). With higher flow rate values, the results are more scattered, probably because shorter capillary lengths were used.

This relationship only applies when a pressure gradient between one atmosphere and vacuum is used. Data could be collected to determine the influences of inlet pressure and absolute temperature on the experimental constant (K_{exp}) and on the power of the radius. This could eventually lead to a more general solution for the maximum discharge flow rate obtained from capillaries. However, these objectives are beyond the scope of this thesis.

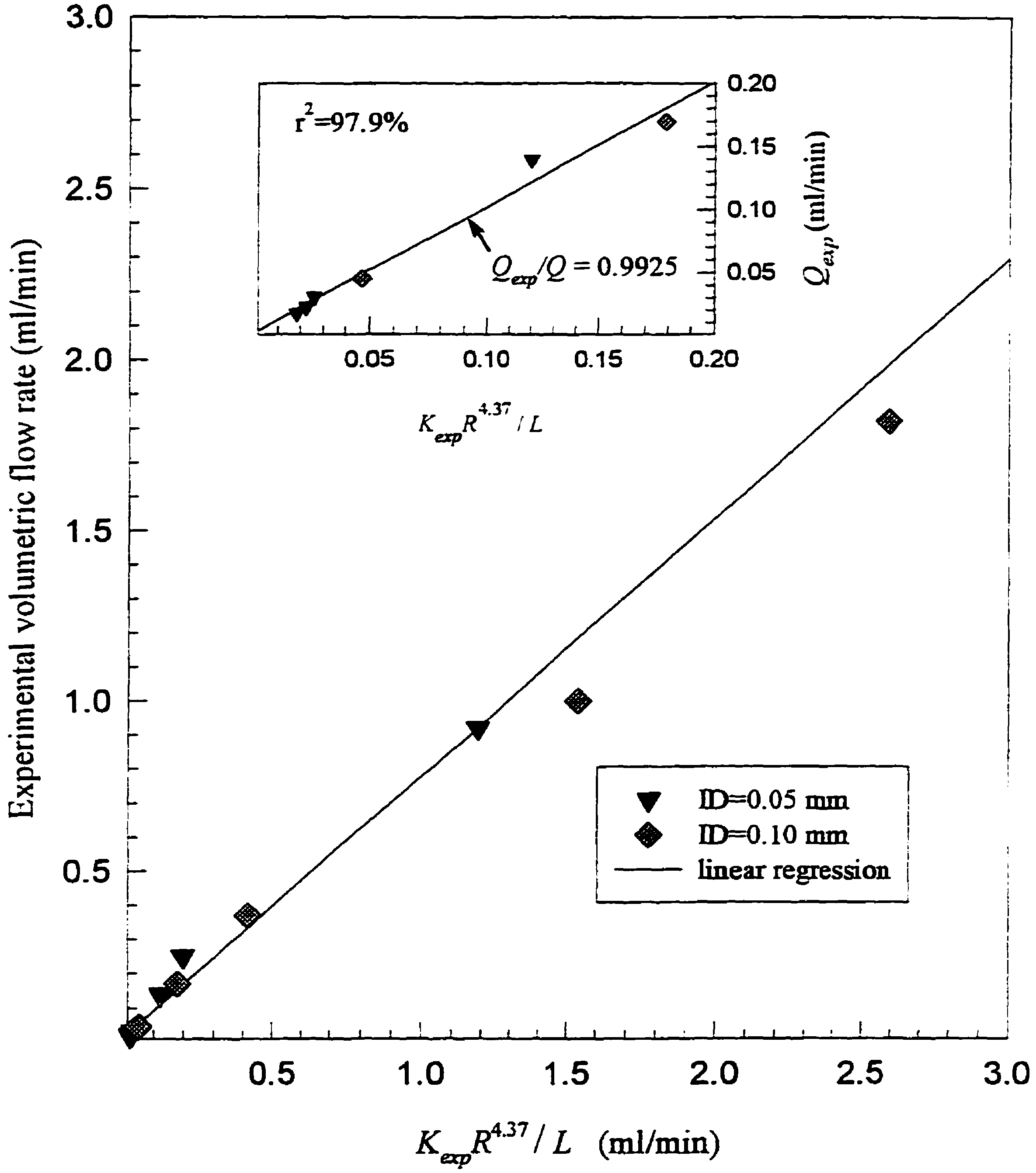

Figure 4.15: Comparison between predicted flow rates calculated using the empirical model with experimental results obtained using selected capillary geometries

The use of capillaries as flow controllers was proposed for other applications. Dewilde developed a flowmeter in which a capillary is used to achieve an accurate gas flow. In this device, the capillary is used to regulate, at steady-state, the flow from a pressurized gas source so it can be delivered at a constant rate (Dewilde, M.A., 1980). Also, Hildenbrandt proposed an emergency oxygen supply device in which a selected length of capillary is used as a regulator to provide sufficient gas discharges from a high-pressure cylinder. However, information was not provided as to the appropriate capillary geometry required for these applications (Hildenbrandt, A.J., 1971). In both cases, the process is under a much higher pressure gradient than that studied with the CSFC. Moreover, these systems are operated at steady-state conditions when compared with the long-term passive sampler in which the pressure gradient decreases with time. Selected capillary geometries were also proposed as means of controlling the flow rate for the collection of specified respirable aerosol fractions in a workplace environment (Clark. R.H and J.R. Nodelman, 1982). Ambient air particles are discriminated by sampling based on their aerodynamic diameters according to the flow rate which is used for their capture on a filtering medium. These authors have shown that capillaries can be applied for such purposes.

From results obtained, it has been demonstrated that a passive sampler using a CSFC can provide long-term sampling durations. However, neither the phenomenological model based on fluid mechanics and gas kinetics theories (eq. 4.17 to eq. 4.27) nor the empirical model based on experimental results (eq. 4.29 to 4.31) can provide clarifications of gas flow phenomena occurring within selected capillary lengths.

Many questions can be asked as to what is happening within the capillary during the process. When such low flow rate are achieved, what kind of velocity profile is established along the capillary length? What are the effects of some physical gas properties such as the viscosity (μ) and the fluid density (ρ) which are both functions of many parameters (i.e. temperature and pressure)? What types of flow is being established? Does a limit exist in the capillary geometry where the observed phenomena cannot be reproduced? It is not the purpose of this thesis to answer all these questions but some explanations can be found in the literature, principally in articles reporting on the flow of rarefied gas. An extensive review concerning this subject has been published (Steckelmacher, W., 1986).

The flow of gas inside a capillary at very low pressures can be characterized as a molecular flow. In this region, the tangential momentum of a molecule transferred to the wall of the pipe on collision does not influence the velocity distribution. The gas moves as individual molecules rather than as a continuous fluid and the velocity is constant over radial coordinates. Knudsen introduced a criteria for the molecular flow which is defined in terms of the mean free path in relation to the capillary dimension. This is known as the Knudsen number. This relationship was developed around 1908 based on initial concepts introduced by Clausius and Maxwell. Following Knudsen's work, others studied vacuum flow conditions inside capillary tubes (Lund, L.M. and A.S. Berman, 1966; Fujimoto, T. and M. Usami, 1984).

Aside from a molecular flow, the motion of gas can also be located in a region in which the regime is characterized as slip flow conditions. Within this specific range, it appears that the hypothesis, according to which the gas velocity at the solid interface (capillary surface) is assumed to be null, is not valid anymore. A correction factor is required to consider slip effects when the gas flow is mathematically determined from a pressure gradient in this intermediate region (Fryer, G.M., 1966). Otherwise, when the cross-sectional area of the capillary and the pressure gradient are sufficiently high, a streamline or viscous flow can be assumed. In this laminar flow region, the Hagen-Poiseuille equation provides a good approximation of the relationship between the geometry, the pressure gradient and the volumetric flow rate. A solution for the transition density profile was proposed by Abramson (1972). The variation of this property along the capillary does not influence the validity of the Hagen-Poiseuille equation in characterizing the macroscopic phenomenon. Other aspects of the physical process involved when selected capillary lengths are used to partially fill a gas sample container could be part of more fundamental studies.

This chapter has disclosed the most important results of this research project. A new long-term integrated passive sampler was proposed and a flow controller that can be designed to provide any sampling durations was characterized. In the next chapter, results from validation studies including field investigations are described. These studies were performed to show that a CSFC offers a precise and reliable instrument for the characterization of long-term mean gaseous airborne contaminant concentrations.

5-VALIDATION OF A LONG-TERM SAMPLER: RESULTS AND DISCUSSION

Airborne gaseous contaminants such as VOCs can be collected using a novel flow controller, the CSFC. This device can increase the integrated sampling intervals as part of a passive sampling technique where ambient air flow rates are controlled with selected capillary geometries. However, the effects of parameters such as temperature, humidity, diffusion and absorption are of concern when the precision of this sampling method is considered.

Validation studies were made to demonstrate the reliability of this new environmental sampler. Different approaches were used for these purposes. Theoretical studies were initially performed based on fundamental aspects of the process and existing physico-chemical relationships. Experimental studies were also made in the laboratory to verify the passive sampling device's reliability. Using CSFC prototypes, field demonstration studies were finally conducted in indoor and outdoor environments to confirm their applicability.

5.1-Theoretical approach

Physical factors which can potentially affect the constancy of the low flow rate delivered by the capillary controller, or which can interfere with gas chemistries can be estimated based on data found in the literature. The mathematical model developed to predict appropriate capillary geometries can also provide a useful tool to study the influence of some of these parameters. Results obtained to estimate the effects of temperature based on theoretical calculations are presented here. The influence of relative humidity on the sampling process will also be discussed. Finally, the contribution of gas diffusion to the separation of chemicals which move by convection inside the capillary column is also addressed.

5.1.1-Effects of temperature and humidity

The influence of temperature on the performance of the CSFC can be assessed by using the phenomenological model and the associated relationships that were derived (eq.4.17 to eq.4.27). These equations include a term for temperature (T). Calculations can be performed for any temperature value. It should be noted that every simulation presented in section 4.2.1 was made assuming the sampled gas was at 25°C. Certain variables in the model are influenced by temperature, notably the molar volume ($\overline{V}$) and the viscosity (μ) of air.

Assuming the inlet pressure is constant, the value of the molar volume can be calculated at different temperatures based on the ideal gas law. On the other hand, the effects of temperature on the viscosity of the fluid can be determined using Sutherland's formula (Bertin, J.J., 1987). For air, this equation is stated as:

$$\mu = 1.458 * 10^{-6} \frac{T^{1.5}}{T + 110.4} \qquad \text{(eq.5.1)}$$

To study the effects of temperature on the flow rate delivered by the CSFC, the molar volume and the viscosity were calculated for five different values of temperature which cover the range of potential sampling conditions. Ambient temperature from -30°C to 30°C were selected for this analysis because field studies are mostly conducted in such environments. The results of these calculations are presented in table 5.1.

Based on these data, the predicted sampled volumes over time were determined according to the model's relationships. Equations 4.24 to 4.26 were used to perform mathematical simulations. The situation where a 1000-ml sample container is utilized to collect a 40-hour passive integrated sample was used for these theoretical calculations.

Table 5.1: Values of molar volume ($\overline{V}$) and viscosity (μ) of air calculated at ambient pressure for different sampling temperatures

Temperature (T)	**Molar volume ($\overline{V}$)**	**Viscosity (μ)**
(°C)	**(l/mole)**	**(10^{-5} Poise)**
-30	19.9	1.56
-15	21.2	1.64
0	22.4	1.71
15	23.6	1.79
30	24.9	1.86

The results from model simulations are shown in figure 5.1. According to these theoretical data, a marked change in temperature does not significantly affect the integrated sampling periods achieved with the controller. As expected, the maximum discharge rate obtained from a capillary using an evacuated container increases with sampled air temperature. However, this effect appears to be very small. After 40 hours, the difference between the predicted final sampled volume under cold (-30°C: V_f=508 ml) and warm conditions (30°C: V_f=520 ml) was less than 2.5%. Based on these observations, it is anticipated that temperature variations occurring during operation should not significantly affect the sampling rate obtained with the novel flow controller.

For practical reasons, some parameters were assumed to remain constant during this analysis. For example, potential changes in the geometry of the restriction caused by thermal deformations were not considered. Mechanical properties of the flow controller's solid surfaces may vary with temperature. However, the internal diameter of fused silica tubing is less likely to be influenced by this phenomenon when compared with other

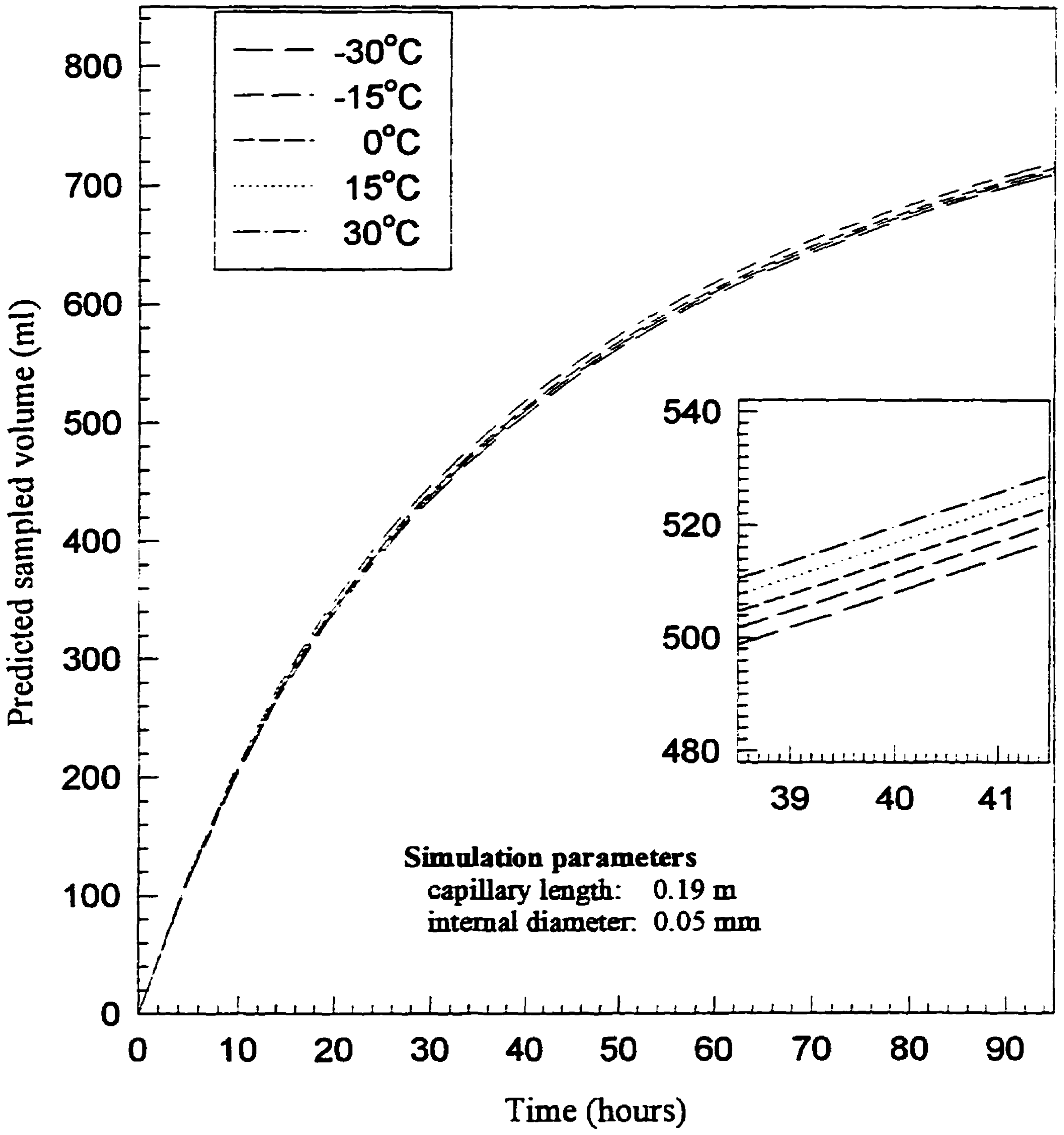

Figure 5.1: Predicted effects of temperature on the performance of a CSFC passive sampler according to model simulation

materials such as stainless steel. With capillaries, this temperature effect (expansion/compression) is shared on a large surface: the total length of the tubing. This impact is more important with critical orifices mainly because it is distributed at a point location. It should be mentioned that the most precise critical orifices used for low flow control are made of sapphire, a form of crystalline silica.

The effect of humidity on the sampling validity can also be discussed. The following questions were raised. Does the sampling flow rate change at different relative humidity levels? What is the contribution of such a factor to possible interferences with the gas sample? Theoretically, the maximum discharge flow rate obtained with specified tubing lengths should not be affected by atmospheric water content. Other factors like gas viscosity, temperature and initial pressure gradient are more relevant to fluid mechanic. These variables were included in the mathematical model. On the other hand, relative humidity is a characteristic of the atmosphere which reflects a concentration. The levels of various chemicals in ambient air including water, or contaminants such as VOCs, may change. However, theoretically, these variations should not modify the gas flow delivered by the controller.

For the validity of the long-term passive sampling process, there is another aspect to the presence of humidity: condensation. To prevent possible loss of organic chemicals by gas-liquid equilibrium transfer, water vapors should not condense in the system during operation. This phenomenon can occur if the gas is compressed or/and subjected to a temperature drop. However, with the CSFC, the sampled gas is maintained under a vacuum (decompression) during the whole process. Thus, condensation problems should not occur. Temperature fluctuations within sampled environments are unlikely to create water droplets within the controller and/or the sample container. As the gas travels through the capillary, pressure decreases. Temperature reductions should have a limited influence on water condensation even when nearly saturated ambient air samples are collected (ex.

relative humidity > 90%). It should be noted that, based on energy transport, the viscous transfer obtained from decompression will theoretically tend to reduce the temperature at the solid interface (i.e. the capillary). Nonetheless, this energy should be dispersed rapidly by conduction and/or convection to the surroundings. Based on these facts, it is expected that this effect will not contribute to the formation of a liquid phase within the flow controller.

Finally, airborne contaminant recovery rates and storage stabilities obtained from sample containers are optimized when high humidity atmospheres are sampled (Westerinen, A. and B.B Reisman, 1996). Moisture can fill active sites within a sampling system's solid wall surfaces and thus reduce the adsorption of VOCs and/or other gaseous contaminant. High humidity levels were never found to affect the precision and accuracy of measurements when evacuated sample containers were used to collect passive samples with mechanical flow controllers.

In conclusion, it is not anticipated that humidity levels will interfere with the sampling process. Also, temperature fluctuations should have a relatively small effect on the constancy of sampling rates delivered by the controller. These theoretical observations suggest that the long-term integrated sampling method can be reliable enough to be used under field conditions. Nevertheless, many assumptions were made and experiments should be conducted to conclusively characterize the effects of temperature and humidity on CSFC's performance.

5.1.2-Diffusional behavior

The use of appropriate geometry of capillaries to control the flow rate at such low values also raises a question concerning possible separation effects inside the tubing. Could physical separation of chemicals within the flow controller interfere with the gas sample's representativeness? This phenomenon is observed in chromatographic columns such as capillaries coated with a thin layer of a chemically bonded phase (stationary phase). The separation of chemicals inside a capillary column can be estimated using the Van Deemter equation (Van Deemter, J.J. et al., 1956). This relationship expresses the height equivalent to a theoretical plate (*HEPT*), an indication of separation efficiency, as a function of three factors that may influence the retention of molecules inside a column. This equation is written as:

$$HETP=A_E+\frac{B}{v_z}+Cv_z \qquad \text{(eq.5.2)}$$

where *HETP* is the height equivalent to a theoretical plate, A_E is the factor which represents the Eddy diffusion, B is the longitudinal molecular diffusion, C is the mass transfer coefficient in the stationary phase. With the CSFC, a plain capillary without internal packing or stationary phase is used. Therefore, factors A and C, being stationary phase related, can be neglected. The only factor which can influence separation is axial molecular diffusion. Based on Einstein's law of diffusion, equation 5.2 can be written as:

$$HETP=\frac{2D_z}{v_z} \qquad \text{(eq.5.3)}$$

where D_z is the diffusion coefficient for a binary mixture measured in m^2/s, and v_z is the average longitudinal velocity of molecules in m/s. Based on the capillary's cross-sectional area and simulation results for the volumetric flow rate, the average velocity was calculated for different lengths of 0.05 mm internal diameter capillary. As an example, the diffusion coefficient for a mixture of air and dichloroethylene (0.1 cm^2/s) was used, and values of *HETP* were computed as a function of capillary length. These results are illustrated in figure 5.2. A linear relationship between the height equivalent to theoretical plate and the capillary length is predicted. *HETP* values below 3 mm were calculated for tubing length shorter than 50 metres. Also in this figure, the average velocity of gas samples is shown to be higher than 10 cm/s when less than 3 metres of the capillary is used in the design of flow controllers.

Based on these data, it appears that high fluid velocities are achieved even if low flow rates are delivered. From this observation, the residence time of gas samples inside the flow controller can be estimated to be less than a few minutes. Considering time intervals of hours, days or weeks during which the CSFC is used, axial diffusion measured in minutes should not interfere with the process.

These theoretical data can also be expressed to show the relationship between the average velocity and *HETP*. This was done to compare the results with basic theory of separation for capillaries in a gas chromatograph. Figure 5.3 shows simulation results performed to study the validity of the capillary sampling flow controller. Chromatographic columns are often characterized by their number (*nb*) of theoretical plates. This number can be estimated using the column length divided by *HETP* *(nb=L/HETP)*. With this equation, calculations were performed and the number of theoretical plates was found to be independent of the capillary length. Using a 0.05 mm ID capillary, all lengths were shown to introduce approximately 16 750 theoretical plates of separation for a mixture of air and dichloroethylene. This is an interesting observation: the number of plates is not influenced by the capillary length required to provide a selected maximum discharge flow rate using an evacuated sample container. Normally, capillary columns usually longer than 15 meters are required in chromatography. They should have more than 200 000 plates to be efficient.

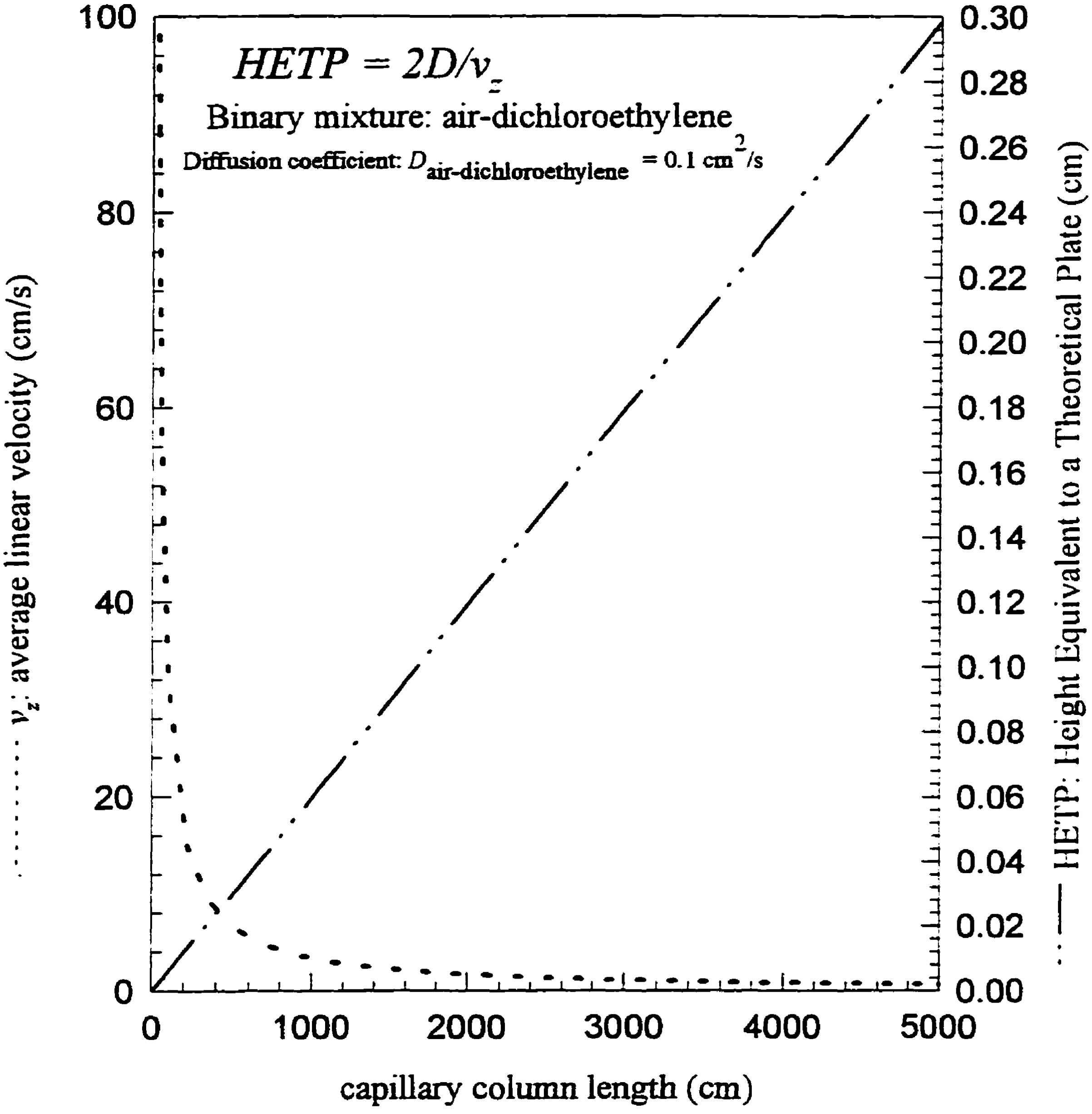

Figure 5.2: Theoretical relationship between the average gas velocity and *HETP* obtained from lengths of capillaries having a 0.05 mm internal diameter

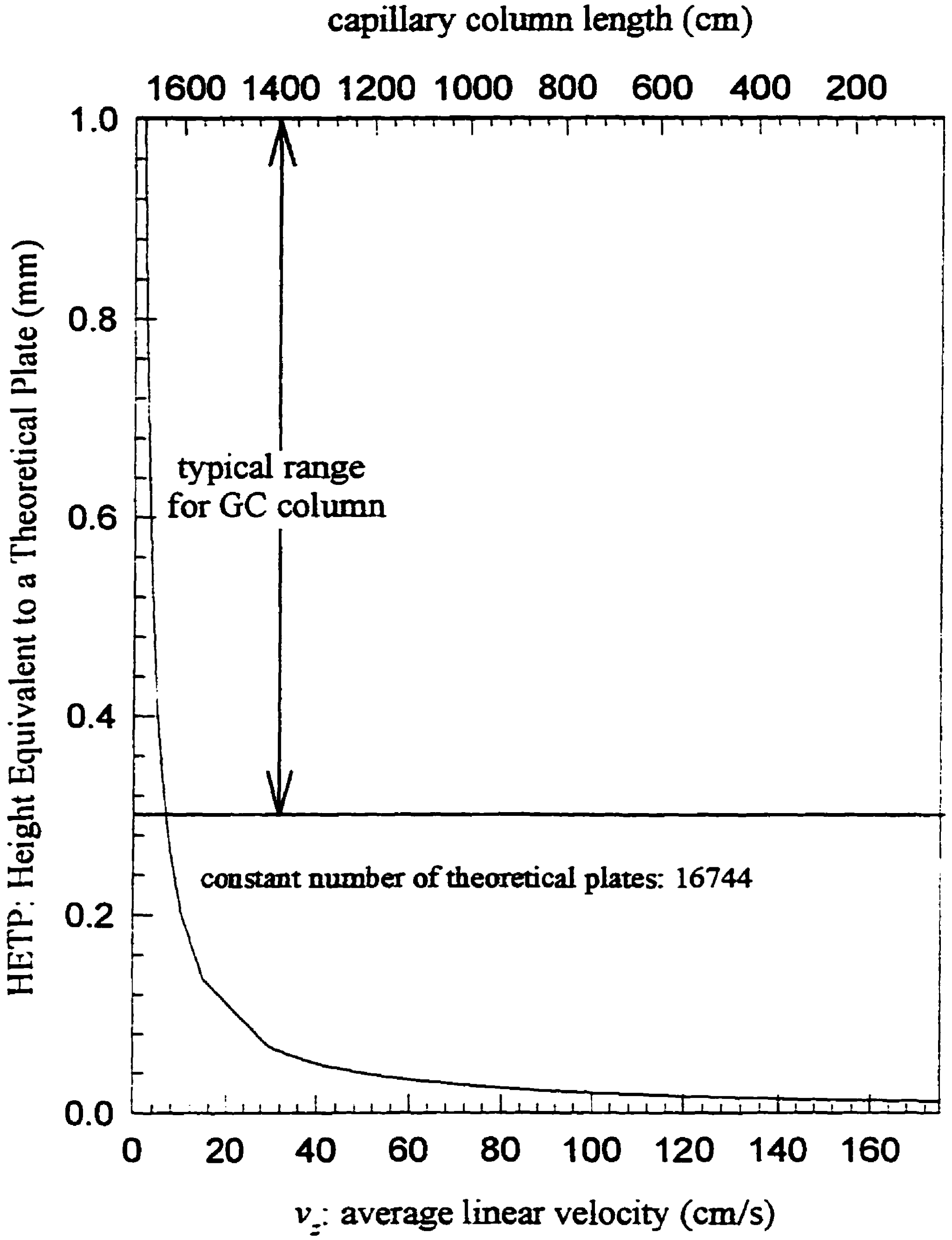

Figure 5.3: Relationship between *HETP* and the average linear velocity calculated from model equations based on capillary lengths having a 0.05 mm internal diameter

To achieve an appropriate separation, 30-, 60- and even 105-metre columns can be used (Fowlis, I.A., 1995). When capillaries are used for gas chromatography, it should be remembered that separation effects also come from mass transfer between the mobile and the stationary phases. Deactivated fused silica columns are non-coated thus, the mass transfer coefficient was ignored in theoretical calculations.

With the CSFC, much shorter capillary lengths are used to fulfil the appropriate flow rates. The estimated number of theoretical plates within the system is also much lower than what is required for chromatographic separation. From this analysis, it was shown that axial diffusion which can potentially interfere with gas chemistries will have a negligible effect on the validity of the sampling process. Nevertheless, experimental studies were conducted to confirm this observation (see section 5.2.3).

5.2-Experimental studies

Studies were performed in the laboratory to demonstrate the reliability of sampler prototypes and the validity of the results obtained with them. First, a trial was made to estimate the contribution of temperature variation on the sampling flow rate constancy. Secondly, experiments were conducted to determine the stability of sampled chemicals and evaluate recovery rates. Finally, diffusional behavior inside the capillary was characterized to verify if this factor is relevant when such low flow rate are used to collect gaseous ambient air contaminant like VOCs.

5.2.1-Temperature

Ambient temperature will theoretically affect the maximum discharge rate delivered by capillaries used to collect long-term, passive, subatmospheric gas samples into evacuated sample containers. Based on model relationships, calculations have shown that flow rate variations less than 2.5% can be expected from temperature variations ranging between -30°C to 30°C. However, this value is probably underestimated considering all the simplifying assumptions made to develop model equations. An experiment was performed to confirm that ambient air temperature fluctuations within extended sampling durations would not cause significant measurement problems.

For this purpose, a dynamic test was conducted over a period of 30 hours with a one-liter evacuated sample container equipped with an appropriately designed CSFC. Internal pressure was initially monitored with a transducer for 12 hours until approximately 200 ml of air was collected. During this phase of the experiment, the system was at ambient temperature (25°C). Then, the passive sampler was placed inside a freezer maintained at -25°C. After a 6-hour period, required to assure complete thermal equilibrium, internal pressure monitoring was continued for another 12 hours, until half the container was filled. Based on the linear relationship between sampled volume and time, the initial flow rate calculated at 25°C was 0.28 ml/min. At -25°C, the flow rate was estimated to be 0.26 ml/min showing a small reduction in the maximum discharge rate.

These experimental results have illustrated that temperature may have a more important effect on sampling flow rate than what was initially predicted from simulations. However, a less than 10% difference was observed for a temperature difference of 50°C. This value is considered to fall well within normal errors when compared with other sampling methods. However, the precision of this test could be improved.

5.2.2-Stability of chemicals

Physical factors such as adsorption may interfere with the sampling process by modifying the composition of the collected gases and vapors in the sample container. However, it has been shown that low VOC levels are stable in summa canisters for storage periods of up to one month (Brymer et al., 1996). Theoretically, the low flow through the capillary should not significantly affect the integrity of gaseous chemicals. However, it was felt that such assumptions should be verified by laboratory testing.

The objective of the study was to demonstrate that the CSFC can collect a representative gas sample. Experiments were performed using a flow controller designed with 0.5 meters of a capillary having a 0.05 mm ID. The device was installed on a 1000-ml evacuated summa canister. The gas entry was connected using Teflon tubing directly to a 6-liter container filled at approximately 5 psi above ambient pressure with a 40 VOC standard gas mixture each at 100±4 ppb(v). Figure 5.4 shows a schematic drawing of this experimental set-up.

At time zero, both cylinder valves were opened to initiate the long-term integrated sampling process. The dry nitrogen gas mixture was transferred through the CSFC. Approximately 500 ml was collected over a 60-hour period. The small pressure excess inside the larger vessel did not significantly affect the flow rate consistency. The sampling flow rate was estimated at 0.14 ml/min for this experiment.

At the end of the passive sampling period, the contents of both cylinders were analyzed using GC/MS. Figure 5.5 presents the chromatogram obtained for the subpressurized sample collected through the flow controller. This sample was diluted by a factor of 3 according to procedures described in section 3.1.2.2-.

The gas sample was injected into the analytical system at 15 ml/min for 18 minutes. The operating procedures used with the analytical system were described earlier (see section 3.2.1- and 3.2.2-).

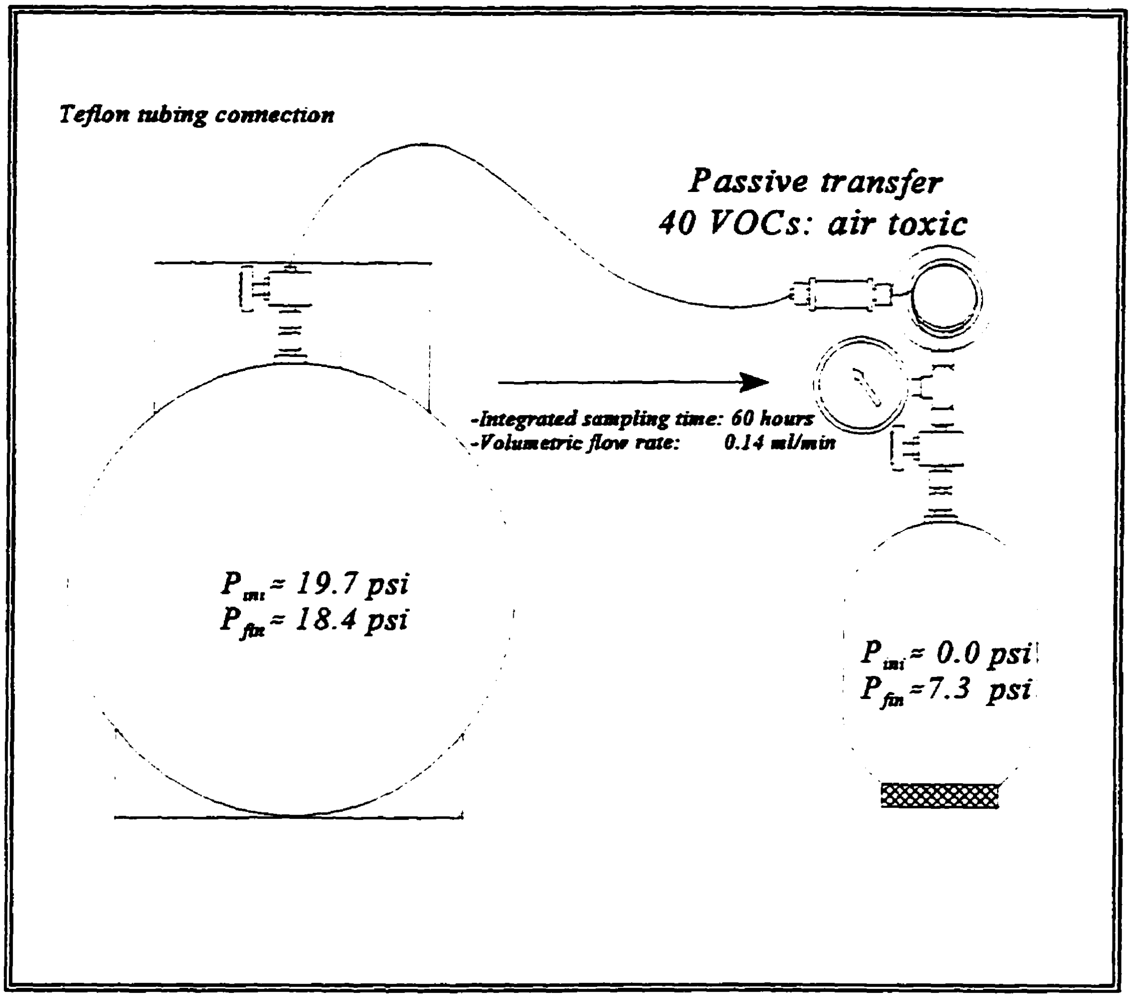

Figure 5.4: Experimental set up used to verify the stability of VOCs during long-term integrated sampling using the CSFC

Every chemical of this gas matrix was identified based on its retention time and mass spectra. This experiment was also conducted to show that the CSFC does not introduce any contamination into the gas chemistries. Loss of chemicals or appearance of artifacts could negate the sampling device's usefulness. A careful study of all signals obtained did not reveal any significant presence of other chemicals (artifacts). GC/MS analysis has shown no evidence of major interferences from such factors.

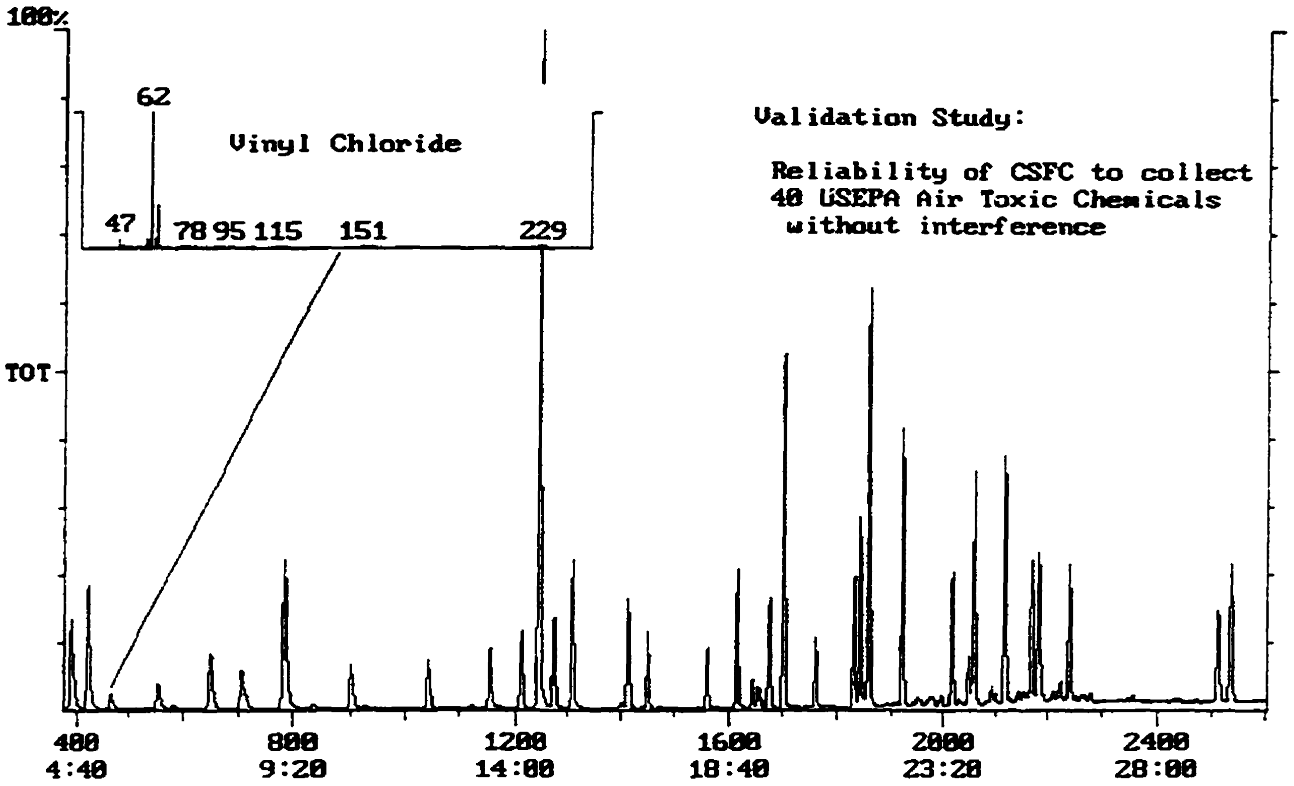

Figure 5.5: Chromatogram of 40 VOCs at 100 ppb(v) acquired from GC/MS analysis

The other container used in this experiment was also analyzed. In this case, a 90-ml gas aliquot was injected. The signals were converted to mass amount measured in ng using calibration procedures described in section 3.2.3-. Quantitative results from both samples were compared and figure 5.6 shows the relationship that was found between the levels of each VOC either delivered to the sampler, or collected over the long integrated period. Each data points corresponds to a single chemical.

Considering the procedural errors involved (long-term sampling, sample's dilution and analysis), the regression coefficient obtained from this comparison (r^2=91%) was satisfactory. However, certain shortcomings were noted.

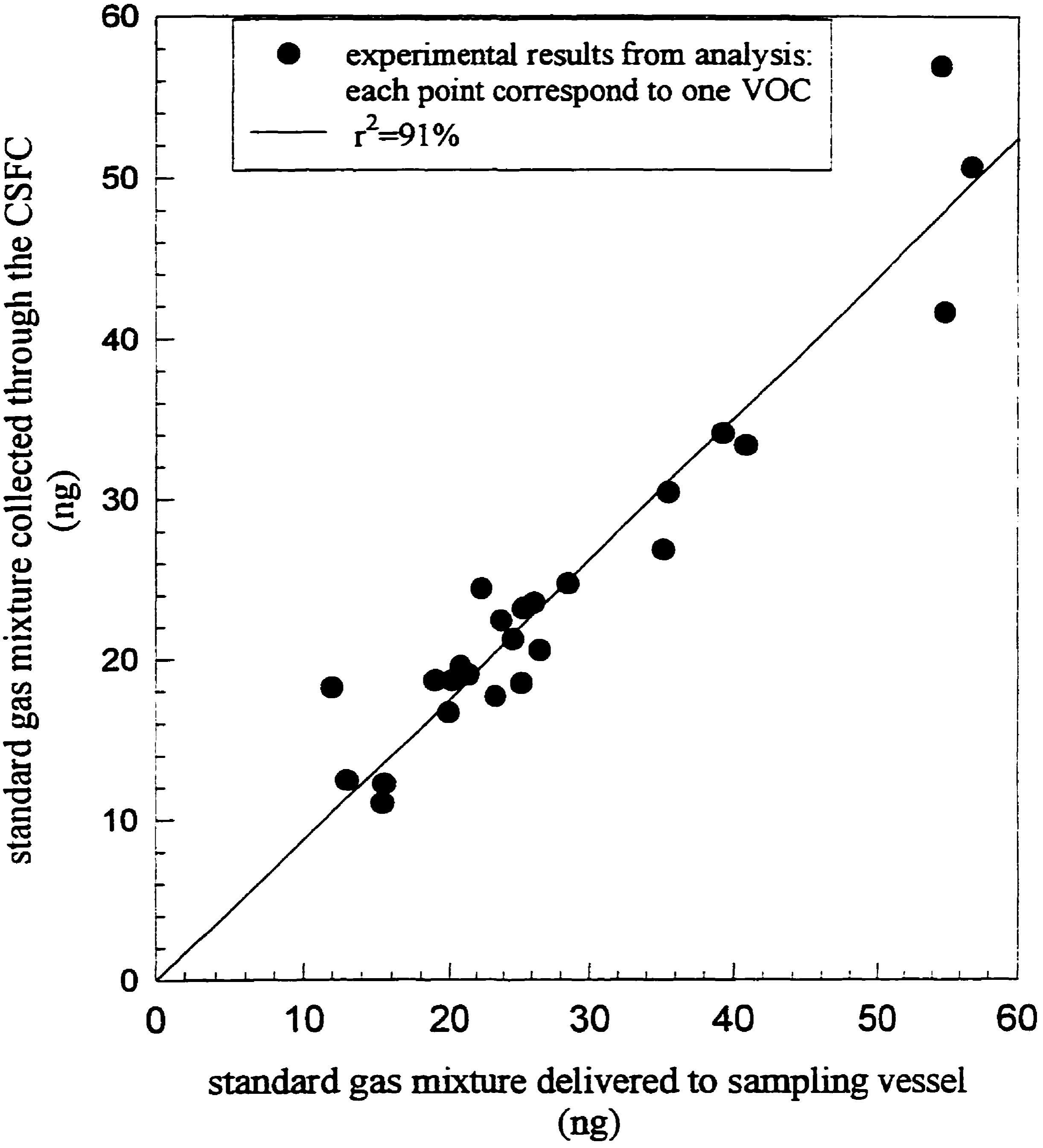

Figure 5.6: Estimation of the stability and recovery of VOCs following long-term integrated passive sampling of a dry standard mixture collected using the CSFC

First, the slope from this relationship was lower than the optimal value of one. This indicates a relatively small bias effect. The measured value (0.87) appears to show a slight reduction in recovery rate. Secondly, the results appeared to be more scattered as the calculated mass increased. It should be noted that these data points correspond to target VOCs having the highest molecular weight.

The calculations required to convert from volumetric to mass concentrations can explain this occurrence considering that all injected chemicals were at 100 ppb(v). High molecular weight VOCs are generally less volatile and more subject to adsorption (Young, D.M. and A.D. Crowell, 1962). As VOC molecular weights increase, their recovery rates tend to diminish.

These experimental results were validated by an external laboratory (see appendix 4-). To assess the transfer efficiency, bias effects were determined for 36 non-polar and 20 polar VOCs. This experiment was conducted using a CSFC designed to achieve 0.018 ml/min during seven days with a 500-ml summa canister. The same source of prepared standard was used for comparison. Based on analytical results, the recovery rates were determined.

The percent differences observed are summarized in table 1 and 2 (section 3.0 in appendix 4-). A negative deviation was observed. Again, for non-polar compounds, the high deviations were mainly observed for the largest molecular weight VOCs.

On average, the measured bias was less than 10 percent. With polar compounds, the average difference was higher: 13.7 percent with a range of 1.4 to 32.6 percent. Larger variations normally occur with polar organic compounds. As noted in this report (appendix 4-), the general trends observed were similar to those obtained with a simple standard's transfer from canister to canister.

These data partially confirm the CSFC's ability to provide a reliable sampling method. According to the results presented in this section, there is no evidence that the sampling train generates interferences or contributes to a significant bias due to adsorption. As mentioned earlier, all parts of the CSFC are made of materials (deactivated fused silica and stainless steel) known to minimize the presence of active sites. These static validation studies were able to demonstrate that the capillary sampling flow controller can effectively collect long-term integrated samples which reflect the atmosphere present at sampling locations.

5.2.3-Diffusional effects

The behavior of gas molecules traveling inside capillaries have raised questions concerning separation effects. Based on the sampling process, theoretical calculations predicted a constant number of theoretical plates for all selected lengths. On this basis, it was assumed that such factors would have no significant effect for 0.05 mm ID capillaries (see section 5.1.2-).

To confirm that diffusional effects will have, at most, a minor impact on the reliability and accuracy of the CSFC, an experiment was conducted in the laboratory using a GC/MS. The following procedures were used.

The chromatography column in the GC was replaced with a 1-metre length of a deactivated fused silica column with a 0.05 mm ID. This capillary was directly connected between the GC injection port and the MS ion trap maintained under vacuum. The GC back pressure was reduced to atmospheric pressure and the system was kept isothermal (30°C) to reproduce the conditions encountered in the field when a CSFC is used. A binary mixture of air and xylene was injected as a pulse to simulate the entry of a gas sample passing through the controller and collected in the sample container.

Figure 5.7 gives the chromatogram obtained from this experiment where, 1 μl of this mixture was injected in the system one minute after the detector and the acquisition were started. The mixture arrived at the detector over a time interval of less than 4 seconds. The mass spectra of air (m/e 28) was found to be predominant at the beginning of the signal when compared with the mass spectra of xylene (m/e 91) which was near the end of this peak.

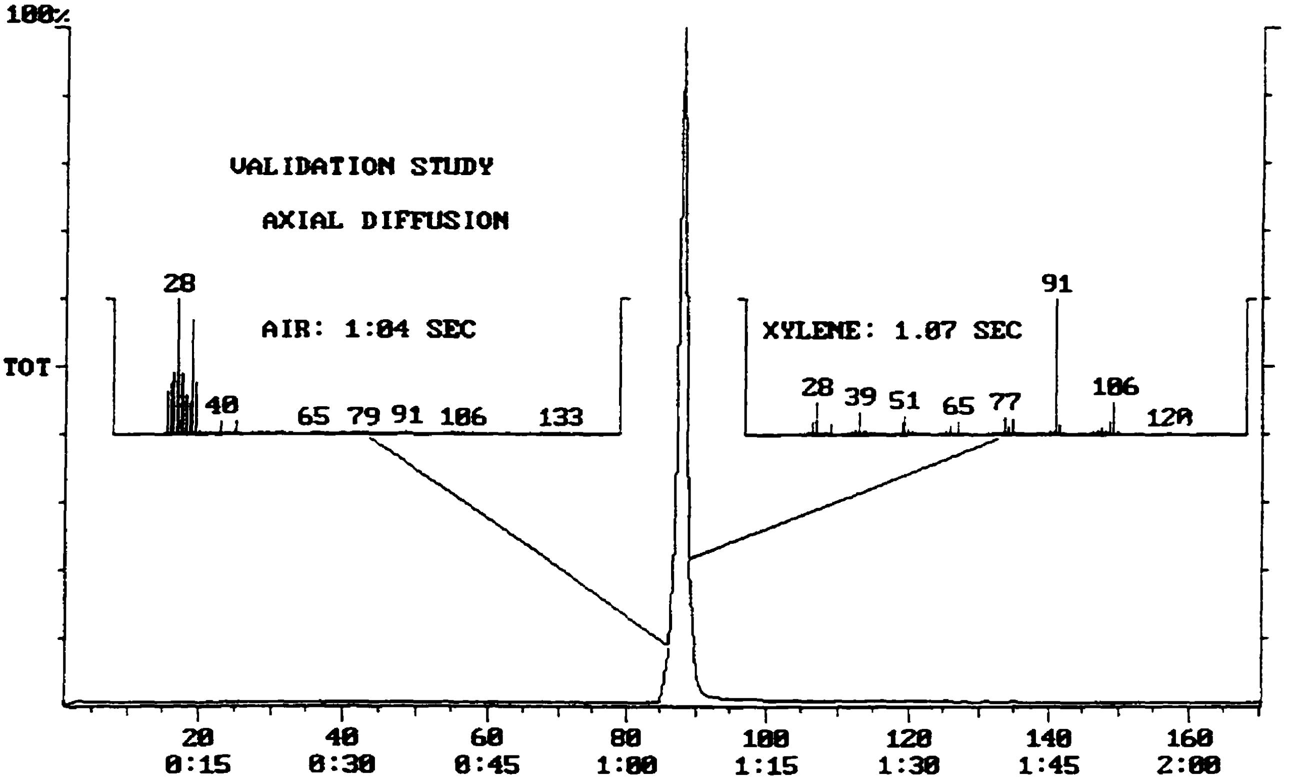

Figure 5.7: Chromatogram from an air-xylene gas mixture

As predicted from theoretical considerations using Van Deemter and Einstein relationships, a small separation was observed inside the capillary due to molecular diffusion. However, such a phenomenon occurred over a period of seconds. This separation effect cannot have any significant influence on the validity of samples taken using the CSFC where sampling durations are extended to minutes, hours, days or months.

From every theoretical and experimental validation study that was performed to date, the reliability and the applicability of the capillary sampling flow controller have been demonstrated. No evidence of major limitations or interferences was found. Based on these results, it was concluded that the passive sampling device could be used under field conditions. The last part of this section will present results from field demonstration studies.

5.3-Field studies

Long-term integrated passive samplers were used for field demonstration studies. These investigations were performed to provide further information about the novel sampling method's reliability. Another objective was to evaluate the CSFC's performance under field conditions, and to compare results obtained with those of other sampling methods. Field investigations were conducted in various environments to characterize indoor and/or outdoor VOCs. Other gaseous chemicals such as methane were also measured.

5.3.1-Workplace investigations

Workplace investigations were made using the novel passive sampler to provide quantitative and qualitative testing results. CSFC prototypes were designed to achieve the selected sampling times. In the first study, perchloroethylene exposure levels were measured in a dry cleaning facility. Results were compared with data obtained with sorbent based sampling methods. Second, long-term integrated samples collected in a wastewater treatment plant were characterized to establish mean VOC profiles. Finally, unknown airborne substances were identified inside pulp mill wastewater sludge treatment plants. For this situation, long-term integrated sampling was used to elucidate episodic events.

5.3.1.1-Dry cleaner

The field study at a dry cleaner had several objectives. Investigations were made to verify if prototypes could be used for personal sampling. Stationary and personal samples were also collected simultaneously using sorbent based methods to compare exposure results with more traditional sampling approaches.

A 3-employee dry-cleaning establishment using perchloroethylene as the process solvent was selected. Stationary samples were collected at two locations for five consecutive days during a workweek: A) near the dry-to-dry machine, B) near the front desk. Each day, a personal sample was also collected in the breathing zone of the worker in charge of the dry cleaning machines. Flow controllers were adjusted to represent the workshift duration: approximately a 7-hour sampling time. Two stationary samples were also collected during a complete workweek at selected locations. These two samplers were designed to achieve a 35-hour sampling period. Three prototypes were configured to fulfill these needs. Table 5.2 summarizes the design parameters used for the passive samplers tested during this field study.

Table 5.2: CSFC prototypes used at the dry cleaner: design considerations

Location	**Sampling time (hours)**	**Passive samplers**		
			CSFC	
		V_s	**Capillary length**	**Capillary ID**
		(ml)	(cm)	(mm)
A,B	7 (workshift)	1000	25	0.10
worker	7 (workshift)	150	20	0.05
A,B	35 (workweek)	6000	23	0.10

Workweek integrated samples covered the same time interval as daily workshift measurements to determine the cumulative mean exposure. Subpressurized gas containers were analysed by GC/MS according to procedures described in chapter 3.

Sorbent tubes and diffusive badges were used to monitor perchloroethylene workshift exposure simultaneously. The same three sampling sites (locations A and B, worker's breathing zone) were monitored each day using both devices. For the sampling method using sorbent tubes, flow rates were verified before and after daily surveys. Pumps were calibrated at approximately 100 ml/min. On their return from the field, sorbent materials from badge and tube samples were desorbed with carbon disulfide and analysed by GC/MS.

A total of 47 samples were collected. All 17 CSFC passive samples provided subpressurized gas samples below 0.6 atm. Investigation results are shown in figure 5.8. Perchloroethylene concentrations measured in ppm are compared according to sampling location and method. Sampling dates are identified from 1 to 5. These numbers represent consecutive survey dates distributed from Monday to Friday.

Variations observed between sampling locations can be explained by emission source proximity. The highest airborne concentrations were observed near the dry cleaning perchloroethylene machine with stationary samples collected at the back of the room (location A). On the other hand, lower levels were found near the front desk (location B). Intermediate values were measured for workers' TWA exposure. The air quality at fixed locations is influenced by environmental parameters (emission rates, ventilation efficiencies). In addition, responses from breathing zone sampling are also affected by a worker's personal habits. Results obtained for stationary locations were compared. When all the results were pooled, a statistical analysis (*student T-Test*) showed a significant difference between the sampling sites.

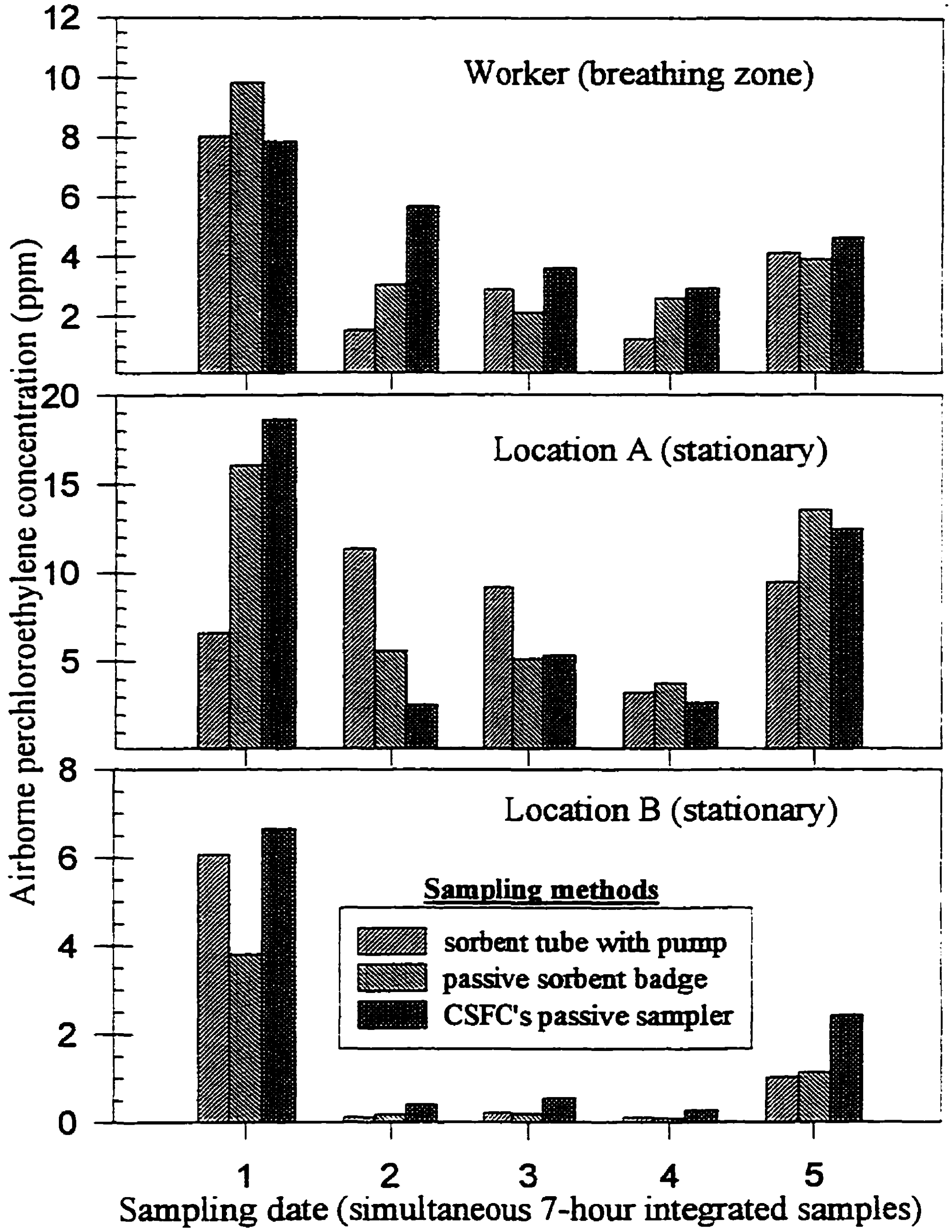

Figure 5.8: Perchloroethylene concentrations (ppm) obtained from consecutive daily measurements using 3 sampling approaches

Mean concentrations were 8.4 ppm for location A, and 1.5 ppm for location B. Assuming unequal variances, the probability that this difference could be due to chance was less than 0.1% (*student T-Test*: two tails, 95% confidence interval).

Airborne levels were also observed to vary within days. Concentrations generally appeared to be high on day 1, to diminish during the following days and to increase on day 5. Very low perchloroethylene levels were measured during three consecutive days near the front desk. For this week, variability was higher at this location. Temporal fluctuations can be related to production rates (amount of garments processed per day) in addition to other factors mentioned above. In general, long-term mean measurements should attenuate these fluctuations to provide a better estimate of central tendencies.

To compare results obtained with the three sampling methods, workweek averages were calculated based on locations. Table 5.3 presents arithmetic means determined for each situation. It should be mentioned that all measurements were below the threshold limit value for perchloroethylene exposure (25 ppm).

Table 5.3: Workweek averages calculated from five consecutive workshift measurements: airborne perchloroethylene concentration (ppm) in a dry cleaner

	Sampling methods		
Sampling locations	**Tube**	**Badge**	**CSFC**
Worker's breathing zone	3.6	4.3	4.9
Location A	8.0	8.8	8.3
Location B	1.5	1.1	2.1

Large within-day differences were often observed between the three methods. For example, on sampling day 1 and 2, measurements at location A provided data that varied significantly according to the method used (see figure 5.8). Such results cannot be explained. Nevertheless, for most comparative data, variations were within an acceptable range considering sampling and analytical errors. Interestingly, it appears that daily fluctuations between sampling methods were attenuated over time. As indicated in table 5.3, workweek concentrations agreed closely at each sampling location. Although this comparison is based on few samples, differences between sorbent based methods were not more significant than those obtained with the passive sampler prototypes.

Experiments were made with CSFC prototypes to extend sampling periods. It was assumed that it would be possible to collect a unique long-term integrated sample instead of five consecutive daily measurements to estimate mean exposure concentrations. Such a strategy would be worthwhile if it could provide the same information as that obtained using conventional sampling methods.

Comparisons were made between the results obtained from two long-term samples collected at stationary locations, and the mean levels calculated from five consecutive daily workshift measurements. For location B, 2.1 ppm of perchloroethylene was measured with the 35-hour integrated sample. This corresponds exactly to the calculated average obtained (see table 5.3) from highly fluctuating concentrations: the highest value was 6.6 ppm (on day 1),the lowest value was 0.3 ppm (on day 4).

For location B, the prototype was non functional (gas leak) during the first survey day. The sampler was brought back to the laboratory to be repaired. The flow controller was readjusted to cover the remaining sampling days (from day 3 to day 5: 21 hours). These field results provided a comparison between three daily measurements respectively, 5.4, 2.7 and 12.4 ppm for an arithmetic average of 6.8 ppm. Again, the long-term integrated sample collected during the same time interval approximated these consecutive measurements. 6.9 ppm of perchloroethylene were found within the sample container. The complete study was reported elsewhere (Racicot G., 1996).

To conclude, prototypes were shown to be reliable under field conditions and successful in providing long-term exposure estimates. Also, this study demonstrated that evacuated containers equipped with a CFSC can provide an alternative for conducting personal monitoring. Prototype results can compare with those obtained with other sampling methods. Although more studies should be conducted to confirm these findings, no significant differences were observed between the sampling approaches.

This field investigation was conducted in a workplace where only one VOC contributes to exposure. To further verify their performance, prototypes were also tested in a working environment that has complex VOC mixtures.

5.3.1.2-Wastewater treatment plant

Several VOCs are potentially released by municipal wastewater. Many chemicals are discharged in the collection systems (sewers) from sources such as industries, commercial facilities, public institutions and residential households. VOCs can be transferred from liquid to gaseous phases, mainly when high water turbulence occurs. These fluctuating phenomena increased airborne VOC concentrations and can be potentially hazardous to exposed workers (Quigley, C.J. and R.L. Corsi, 1995). An investigation was conducted to identify and quantify the mean VOC levels inside a facility that processes approximately 250 m^3 of wastewater per day. This plant was designed to enclose all operations in a single building to prevent odour nuisances to its immediate surroundings. This physico-chemical treatment plant has two independent ventilation systems. One supplies air to the control station, laboratory and administration section. The other provides pollutant removal in each room of the process (pretreatment, primary settling, sludge dewatering and incineration). This facility employs approximately 55 persons.

Long-term integrated samples were collected inside the plant. Prototypes were configured to offer a 7-day sampling period. The CSFC's were designed to meet the flow rate requirement (0.3 ml/min) to be used with 6-litre summa canisters. The flow controllers were equipped with 11 cm length, 0.05 mm ID capillary. Stationary samples were collected at three locations. Two samples were collected in rooms where organic contaminants are more apt to be released into the atmosphere. For comparison, the third sample was collected inside the administration section.

The prototypes provided subpressurized samples during the selected sampling time. At the end of the sampling period, all of the containers' internal pressure was below 0.6 atm. Thus, it was assumed that based on previous experiments and maximum discharge theory, a constant low flow rate was maintained to provide integrated measurements. Samples were pressurized to be analysed by GC/MS. VOCs were identified and quantified according to procedures described in section 3.2.3-.

Figure 5.9 shows the chromatogram obtained from a field sample. Many signals (peaks) corresponding to various VOCs were observed. On this figure, the mass spectra of trichloroethylene is illustrated. Quantification results from the three samples are presented in table 5.4. Approximately 30 VOCs were positively identified and quantified. These results represent the mean average concentration for a one-week period. The levels inside the administration section are significantly lower that those observed near process equipment. The independent ventilation system that serves this part of the building was shown to be efficient. Total VOCs were higher near the settling tanks and pretreatment equipment, mainly due to the presence of dichloromethane, chloroform, 1,1,1-trichloroethane, trichloroethylene and toluene among others.

Table 5.4: VOC results from long-term integrated passive samples collected with CSFC prototypes in a wastewater treatment plant

VOCs	Location		
Concentration (ug/m3)	**Administration**	**Settling tanks**	**Pretreatment**
Dichlorofluoromethane	1.6	1.2	0
Chloromethane	0	0	0
Vinyl chloride	0	0.5	0.2
1,1-Dichloroethene	0	0	0.1
Dichloromethane	2.3	16	30
trans-1,2-Dichloroethene	0	0	0
1,1-Dichloroethane	0	0.6	0.4
2,2-Dichloropropane	0	0	0
Bromochloromethane	0	0	0
Chloroform	0	24	12
1,1,1-Trichloroethane	0	17	16
Carbon tetrachloride	0.1	0.5	0
Benzene	0	3.2	4.0
Trichloroethene	0	10	7.2
1,2-Dichloropropane	0	0	0
Dibromomethane	0	0	0
Bromodichloromethane	0	4.1	2.0
trans-1,3-Dichloropropene	0	0	0
Toluene	0	33	14
cis-1,3-Dichloropropene	0	0	0
1,1,2-Trichloroethane	0.1	0.6	62
1,3-Dichloropropane	0	0	0
Dibromochloromethane	0	0.6	0.4
1,2-Dibromoethane	0	0	0
Tetrachloroethene	0	0	0
Chlorobenzene	0	0	0
1,1,1,2-Tetrachloroethene	0	0	0
Ethylbenzene	0	2.0	1.8
m,p-Xylene	0	3.4	3.5
Styrene	0.1	0	0
o-Xylene	1.1	3.2	3.0
Bromoform	0	0	0
Isopropylbenzene	0	0	0.4
1,1,2,2-Tetrachloroethene	0	0	0
1,2,3-Trichloropropane	0	0	0
Bromobenzene	0	0	0
4-chlorobenzene	0	1.5	1.2
1,3,5-Trimethylbenzene	1.0	1.9	2.0
2-chlorotoluene	0	0	0
ter-Butylbenzene	0	2.4	2.0
n-Propylbenzene	0	3.3	4.0
1,2,4-Trimethylbenzene	0	0.6	0
4-Isopropyltoluene	0.1	2.5	2.0
1,3-Dichlorobenzene	0.2	1.7	0.7
1,4-Dichlorobenzene	0.2	1.7	0.8
n-Butylbenzene	0	0.3	0.5
1,2-Dichlorobenzene	0	0.4	0.8
1,2-Dibromo-3-chloropropene	0	0	0
1,2,4-Trichlorobenzene	0	0	0
Hexachlorobutadiene	0	0	0.3
Naphthalene	0	0.2	0.1
Total	6.7	136.3	172.0

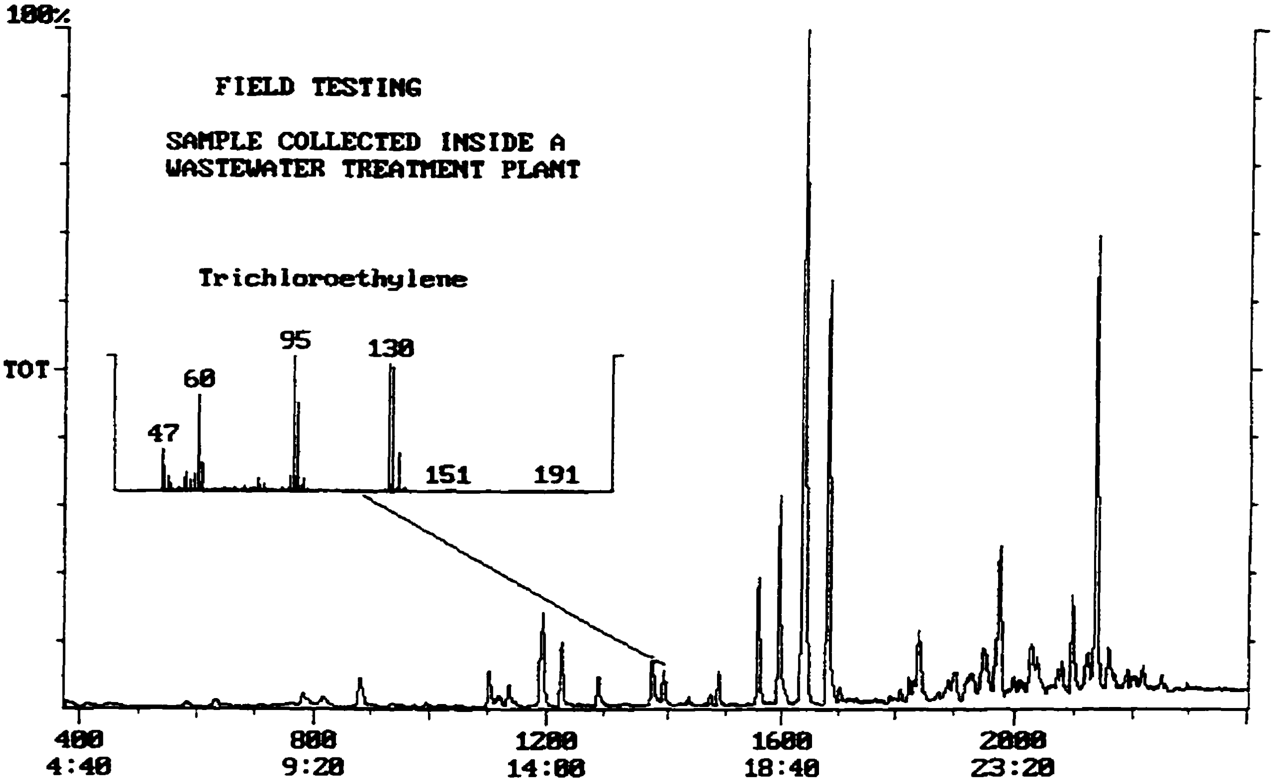

Figure 5.9: Chromatogram from the GC/MS analysis of a long-term integrated passive sample collected in a municipal wastewater treatment plant

However, measured concentrations were largely below threshold values for which exposure to such chemicals has known chronic or acute health effects. The ventilation system that supplies air to the treatment plant was designed to dilute carbon dioxide and H_2S. These two gaseous contaminants are emitted during the process. Although few samples were collected, it appears that ventilation was also able to keep VOCs at a safe level.

This field demonstration study shows that long-term integrated passive samplers can be used to characterize complex VOC mixtures. In such workplaces, the nature and the amount of VOCs depend on what is discharged into the sewer. Temporal variations can be fairly important. Thus, extended sampling periods reduce the number of samples required to estimate mean exposure profiles.

5.3.1.3-Pulp mill wastewater sludge treatment plants

This field study was conducted inside workplaces where sludge from pulp mill wastewater treatment plants is handled. Workers in charge of shovelling compost piles complained about occasional pungent nauseating odours. During these episodic events, they suffered various health outcomes (nausea, vomiting, headache). The study objective was to identify chemicals potentially responsible for such effects.

Episodic emissions are difficult to characterize using conventional sampling approaches. Considering sampling time limitations, industrial hygienists must be prepared to intervene when events occur. Logistically, this may require considerable effort with available equipment. A strategy using long-term passive sampling with CSFC sampler prototypes was proposed as a mean of collecting offending substances.

Prototypes were designed to sample ambient air during a continuous two-week period. Samples were collected simultaneously at two different plants. During this period, workers were asked to note events when strong emissions were perceived. Figure 5.10 gives a gas sample chromatogram obtained from a qualitative GC/MS analysis.

A cluster of peaks is observed between scan numbers 1900 and 2300[1]. As indicated in this figure, the predominant mass ion is 93.

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[1] Top x-axis nomenclature for GC/MS's figure are scan numbers (the bottom line is chromatogram's retention times)

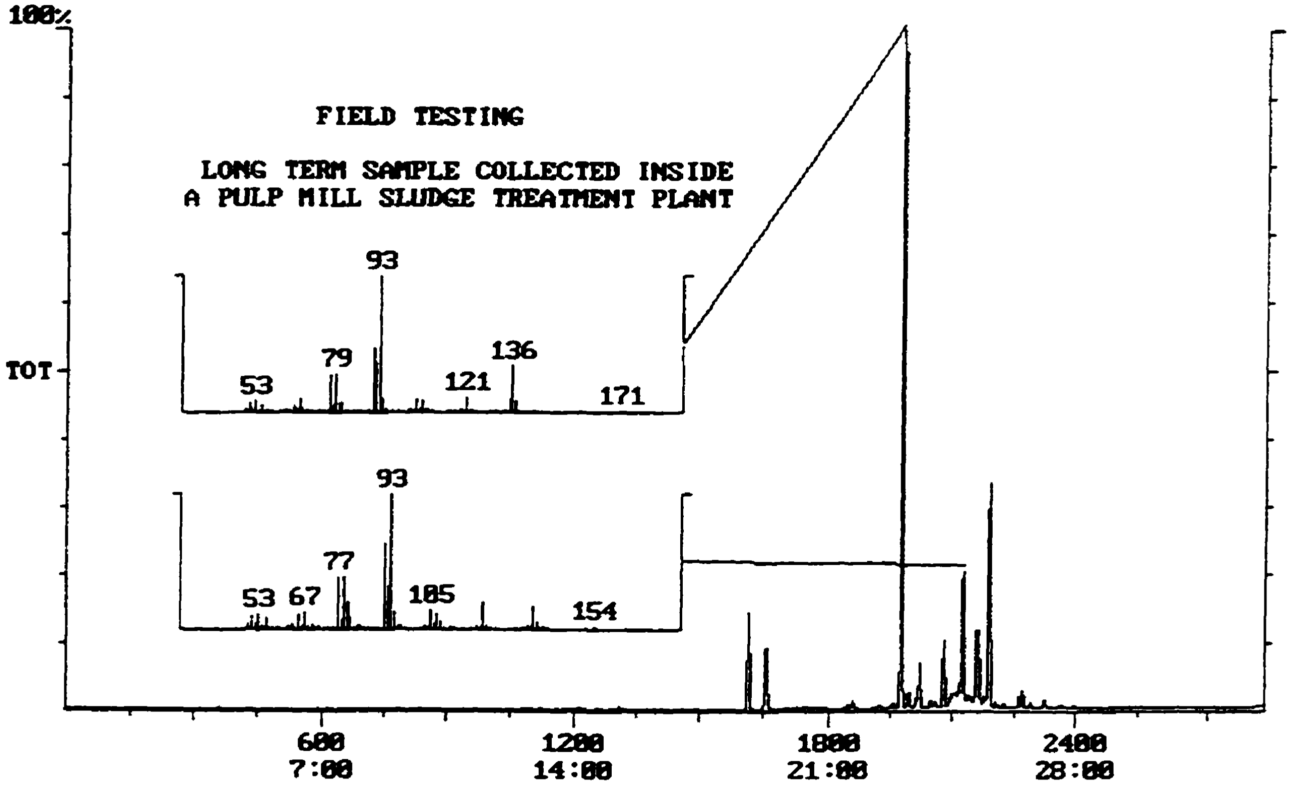

Figure 5.10: Chromatogram from the GC/MS analysis of a long-term integrated passive sample collected inside a pulp mill wastewater sludge treatment plant

Air samples from both plants had the same chromatogram pattern. Sludge samples were also collected and analysed. For this analysis, approximately 0.5 g of wet sludge was transferred to purge vials. 5 ml of distilled water was added to the vials. They were installed on the P&T autosampler (see figure 3.4). Sludge volatile organics were purged into the sorbent trap with 40 ml/min of nitrogen over an 11-minute period. Analytes were then thermally desorbed into the GC/MS, separated and detected using conditions similar to those used for gas samples.

Similar peaks were observed during the qualitative analysis of the sludge. Using a mass spectra library search[2], these signals were matched with chemicals having trimethyl, and bicyclic alkene functional groups, and they were tentatively identified as borneol derivatives. These compounds probably belong to the family of essential oils originating from woods and leaves. Their presence in ambient air may be the cause of health problems among workers handling sludge. Biogenic borneol type chemicals such as camphor, carene, alpha-pinene are odorous products. Borneol has a peculiar peppery odour and may cause nausea, vomiting, mental confusion and convulsions (The Merck Index, 1989).

Eucalyptus oil was also analysed by GC/MS to confirm the nature of predominant signals obtained from those samples. For this analysis, 10 μl of oil mixed in a purge vial with 5 ml of distilled water was injected using procedures similar to those used for sludge sample analysis. Four peaks were found between scan 1900 and 2300. The mass spectra from these signals matched those observed for ambient air and sludge samples. Retention times were nearly identical for two of these signals.

These results suggest that a mixture of essential oils is released in these pulp mill sludge treatment plants. Airborne concentrations can occasionally reach a toxic level. This field demonstration study shows that a strategy using long-term integrated passive sampling is a valuable alternative for the collection of airborne chemicals which are emitted during episodic events. In fact, this device is the only one available to conduct such studies.

Three field studies conducted in different workplaces provided further evidence of the reliability and advantages of using a CSFC with evacuated sample containers. Passive sampling periods can be adapted to meet any study objective. Quantitative and qualitative field test results demonstrated that this approach extend sampling periods for the collection

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[2] Based on the mass spectra obtained for a peak, the software compares signals with a bank that contains more than 60 000 different cracking patterns of chemicals.

of airborne VOCs in workplaces to establish their mean concentrations. This novel sampling approach was also shown to be applicable to personal monitoring.

5.3.2-Environmental survey

Investigations were also performed to collect outdoor ambient air samples. This field demonstration was conducted in the vicinity of a sanitary landfill site. The study objective was to verify that background VOC levels as well as methane concentration can be determined from long-term samples collected with the prototypes.

5.3.2.1-Landfill biogas

Sanitary landfill sites may pose an environmental and health hazard because toxic effluents are emitted in the form of leachates that can seriously compromise the integrity of groundwaters, and a complex mixture of toxic vapors and gases (biogas) that pollute the air. Montreal's main municipal solid waste landfill site is of particular concern. It is considered the third largest site in North America. The total landfill area is approximately 750 000 m^2. Since 1968, more than 36 million tons of domestic and commercial refuse has been buried there. According to projections, it will remain open for another 10-15 years until its complete capacity is reached. Finally, it is estimated that approximately 100 000 persons live within 2 km of this site.

In landfill sites, biogas is produced by the anaerobic degradation of organic materials. Approximately 99% of biogas is composed of methane and carbon dioxide in equimolar proportion. The residual fraction consists in low levels of several VOCs, hydrogen sulfide and mercaptans (U.S.EPA, 1991).

Epidemiological and toxicological data suggest that individuals chronically exposed to low biogas levels may experience a number of health outcomes, including low perceived health status, non-specific signs and symptoms, and respiratory ailments. Cross sectional studies have been carried out near landfills in New York and Hamilton (Hertzman, C. et al, 1987; Schultz, S., 1982). Although exposure situations, study designs and response rates were different, there were similarities in results: statistically significant increases (with respect to unexposed populations) were observed for the prevalence of respiratory symptoms, cough, ear, nose and throat problems, and for headache and mood. Moreover, previous retrospective epidemiological investigations among persons living in the vicinity of the Montreal's landfill have shown increased risk with proximity to the site (Goulet, L. et al., 1995; Goldberg, M.S. et al., 1995). However, these studies were not correlated with exposure measurements. The contribution of fugitive biogas emissions on indoor/outdoor air quality was poorly defined.

A research project was conducted to determine the distribution of air pollutants around the landfill site. One of the objectives was to demonstrate the feasibility of obtaining exposure results while conducting a cross sectional epidemiology study designed to compare non-specific respiratory problems between persons living in exposed and unexposed areas. Initially, methane and VOCs were measured as potential emission tracers using two different sampling approaches. VOCs were collected over a five-day period with sorbent passive badges. At the same locations, methane was also sampled, but over shorter periods using pumps and sampling bags. Indoor/outdoor measurements were taken during two seasons at randomly selected residences distributed within a two km radius of the site.

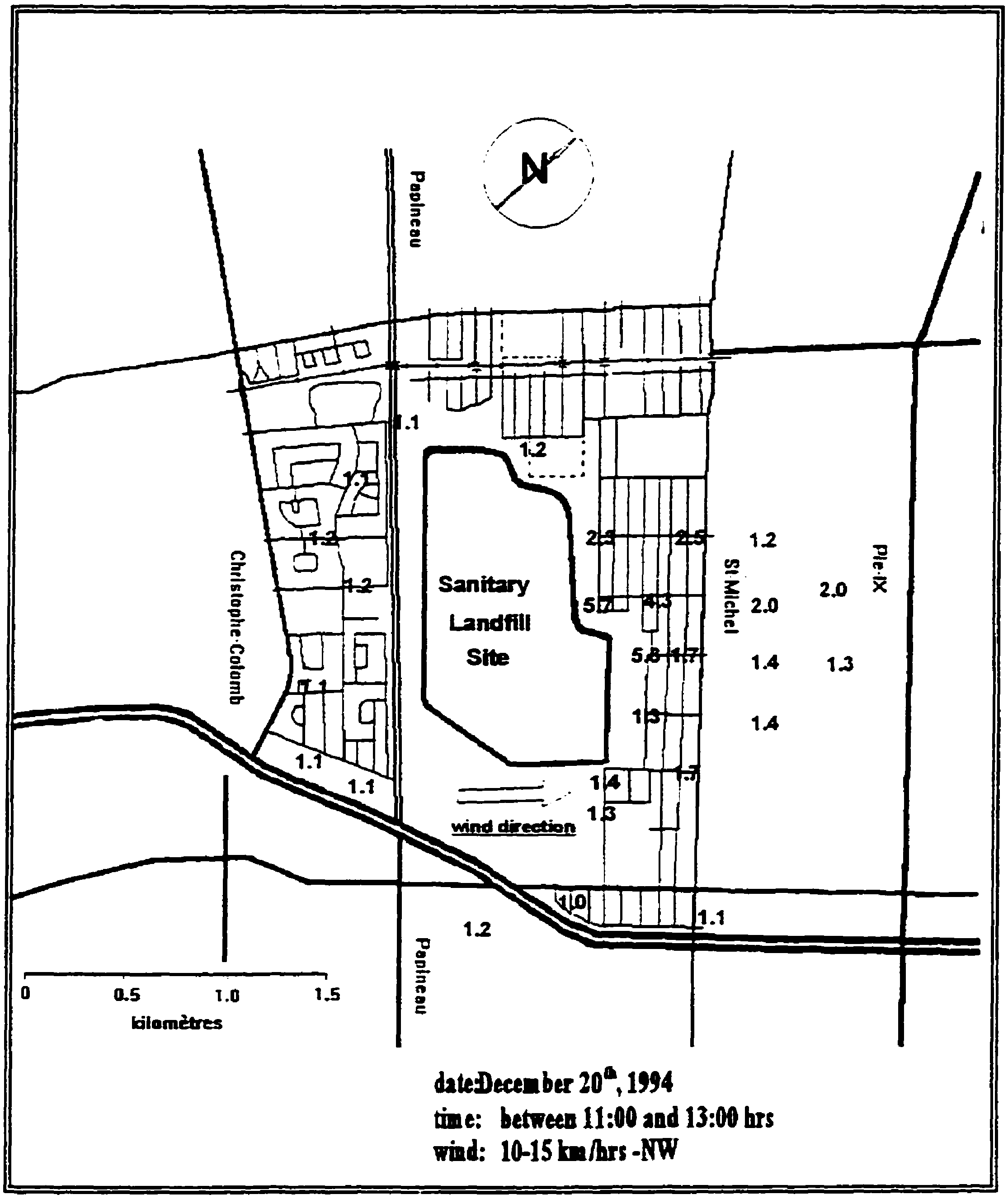
Based on these results, any correlation was found between distance from the site and neither airborne methane nor VOC levels. Exposed/unexposed populations could not be identified from the data. Nevertheless, general trends were observed. For VOCs, mean indoor concentrations were significantly higher than outdoor levels, and in both cases the distribution appeared to be very large. From 26 measurements, geometric mean (GM) of outdoor concentrations calculated for total VOCs equalled 19.8 $\mu g/m^3$, and the geometric standard deviation (GSD) was 4.1. Similar variability was found for indoor total VOC concentrations (GSD=4.7) but the mean level was higher (GM 77.3 $\mu g/m^3$). Based on a *student T-Test* (null hypothesis assuming unequal variances: comparison for a 95% confidence interval using one tail), the difference was significant ($p_{value} < 2.5\%$).

Even though the reliability of sorbent badges can be questioned, it appears from results that landfill biogas emissions contribute less to VOC exposure than average indoor air contaminations. Furthermore, methane results for samples collected inside and outside residences did not indicate the presence of biogas. Both indoor/outdoor methane measurements were near background levels (between 1 and 2 ppm).

To verify the hypothesis that methane can be used as a biogas emission tracer, other investigations were performed. Short-term upwind/downwind methane measurements were conducted to evaluate spatial atmospheric biogas dispersion profiles (see figure 5.11). Sampling bags were simultaneously collected on opposite sides of the landfill site during 10-minute periods. Bag samples were analysed by GC/FID according to procedures described in section 3.2.4-.

Upwind measurements were near background levels. However, downwind measurements were higher, principally in the immediate vicinity of the landfill. As expected, concentrations decreased as the distance increased. The highest measured concentration was 5.8 ppm. It should be mentioned that impressive biogas collection and destruction technologies have been installed on this landfill site to control emissions.

Nevertheless, the results in figure 5.11 show that methane can be used as a biogas tracer. Unfortunately, available sampling approaches would not extend sampling period to attenuate temporal fluctuations due to meteorological changes.



date:December 20th, 1994
time: between 11:00 and 13:00 hrs
wind: 10-15 km/hrs -NW

Figure 5.11: Upwind downwind methane concentrations (ppm) around Montreal's landfill site

This is probably why the presence of biogas could not be detected in methane samples collected near and in households. These studies were briefly described to point out inherent difficulties with sampling methods initially used for this research project. Later, CSFC passive samplers were proposed as a mean of overcoming these limitations. A demonstration study was performed to show that prototypes are reliable for the collection of outdoor air samples from which methane and VOCs can be quantified.

Seven prototypes designed to sample during a 7-day period were distributed around the site. Outdoor sampling was conducted at 21 selected sites during three consecutive weeks. Sorbent badges were also collected at the same locations during similar time intervals. For methane, a geometric mean concentration of 3 ppm was found (GSD=1.6). The highest value (11.4 ppm) was obtained at a site located at less than 150 meters from the site. Background levels were systematically measured at sites located more than 500 meters from the landfill. Based on this field study, it appears that the CSFC passive sampler can be used to determine average outdoor air methane concentrations.

For VOCs, GC/MS signals obtained from prototypes provided a more complete profile when compared with chromatograms from badge analysis. Highly volatile chemicals are not obscured by the desorbing solvent (CS_2). Figure 5.12 shows the chromatogram of a long-term integrated passive sample collected outdoors near this landfill site. The benzene peak with its mass spectra is also illustrated.

Prototype and badge results were compared based on pooled distributions of total VOCs. For the prototypes, the GM is 21.7 $\mu g/m^3$. This average is higher than that obtained based on outdoor badge sample analysis (i.e. 13.1 $\mu g/m^3$). This may be explained by the fact that with badges, toluene was not reported due to an analytical contamination. Interestingly, the variability within prototype measurements was lower. The GSD was found to be 1.9 whereas it was 2.3 with badge measurements.

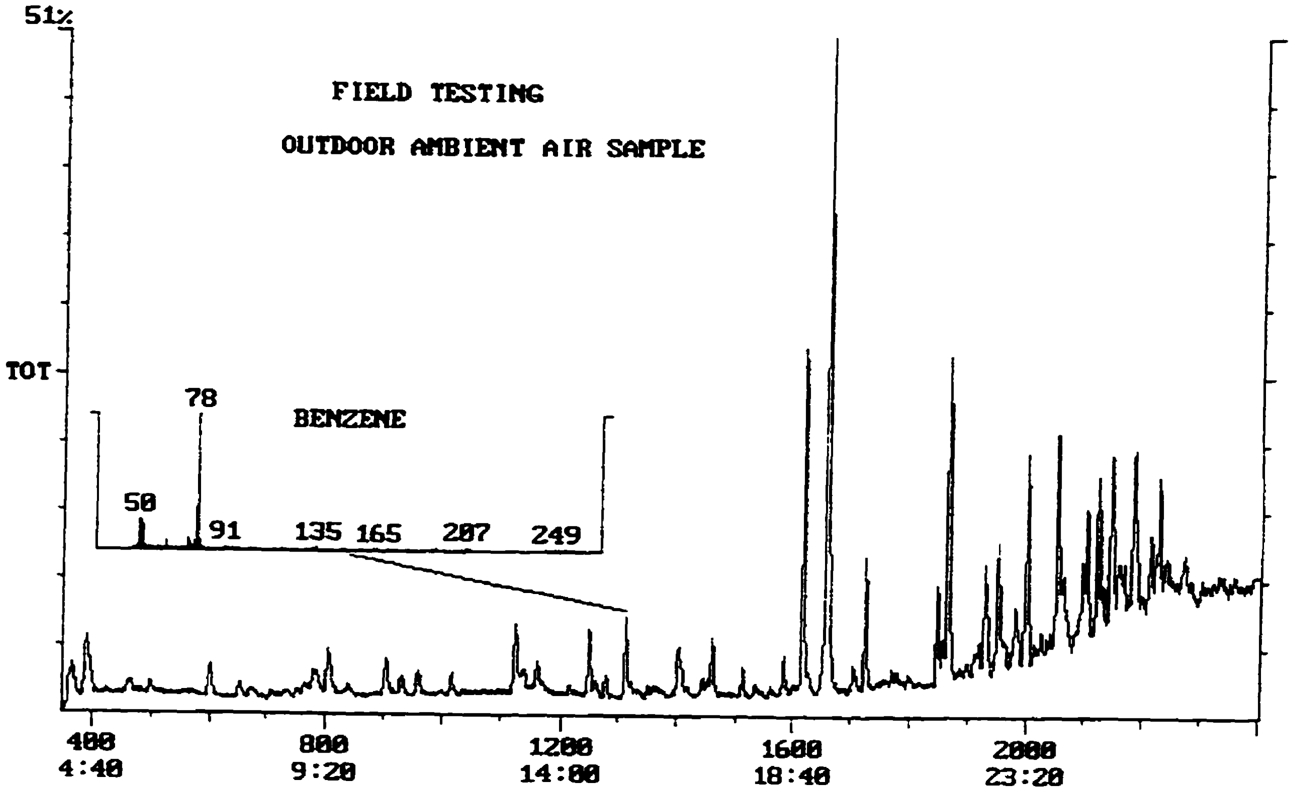


Figure 5.12: Chromatogram from the GC/MS analysis of a long-term integrated passive sample collected outdoor around a landfill site

Complete results from this environmental monitoring research near the Montreal's landfill site were reported elsewhere (Goldberg, M.S. et al., 1996). To conclude, it appears that CSFC prototypes are suitable for outdoor ambient air investigations. Compared with sorbent badges, this sampling approach offers the opportunity to analyse other gaseous contaminants such as methane. Furthermore, when extended sampling intervals are used, convective low flow rates may be more precise and reliable than diffusive uptake rates. To study the influence of biogas on air quality, this new approach can provide the results that can potentially define exposed/unexposed areas more easily.

5.3.3-Indoor air quality

Other field surveys were performed to evaluate indoor air quality. Studies were conducted in private residences and office buildings. Prototypes were used aboard the Russian Mir orbital station to characterize VOCs and other gaseous pollutants.

5.3.3.1-Residences

In private residences, VOCs are potentially hazardous and their presence in indoor air is of concern mainly because chronic exposure can result in adverse health effects. However, some residents may also develop a chemical sensitivity where a single VOC can be responsible for asthma and/or nonspecific symptoms such as headaches, nausea, fatigue, memory loss, etc (Miller, C.S., 1996). These individuals may react after a short-term exposure below the recognized substance's threshold limit level. Because emissions can be highly variable with time, it is difficult to assess their nature. Prototypes were used to collect long-term passive samples to characterize unpredictable and episodic events, to identify the source(s) and to determine the mean contaminant level. Two case studies are reported.

In the first case, three persons complained of occasional solvent odours and various respiratory problems. Over the past two years, they had experienced other nonspecific symptoms mainly when peak levels were perceived. An ambient air investigation was conducted and three passive samples were collected over a continuous three-week period. GC/MS analysis revealed the presence of an abnormally high mean concentration of perchloroethylene in the bedroom (175 ppb). It was later found that the presence of dry-cleaned garments was probably responsible for the exposure and symptoms (outgassing of this solvent over time after processing).

The second case involves a person living in a retirement home whose complaints and symptoms were similar. Here, naphthalene (220 ppb) was measured using two-week integrated passive samples, and the presence of moth balls in the bathroom adjacent to her apartment was identified as the emission source. A strategy using long-term sampling was able to capture the episodic events and identify the offending VOC which probably was the cause of the chemical sensitivity.

5.3.3.2-Office buildings

Investigations were performed in two office buildings. Prototypes were used to collect simultaneous ambient air samples on different floors during a five-day period (from Monday morning to Friday afternoon). Five samples were collected inside each building. The office towers were selected because of their similar characteristics (locations, number of floors and ventilation systems). However, one building is of recent construction, and this parameter was used for comparison purposes. Outdoor ambient air samples were also collected on the roofs to estimate the air quality at the ventilation intake.

A total of 12 long-term integrated passive samples were collected during this field demonstration study. Samples were analysed by GC/MS to quantify more than 50 VOCs. Total VOCs and toluene concentrations provided the most marked differences. Table 5.5 presents comparative results based on building construction dates.

Outdoor mean levels were very similar. Thus, indoor level variations cannot be explained by the quality of the outdoor air which enters the ventilation system. Measured indoor toluene and total VOC concentrations were observed to be higher inside the more recent building. Based on only five measurements, average toluene levels were significantly different (*student T-Test* assuming unequal variances, 95% confidence interval, one tails: p_{value}=8.7%).

Table 5.5: Toluene and total VOC concentrations obtained from the analysis of long-term integrated passive samples collected in two office buildings

Airborne concentration (μg/m³) in office buildings					
Recent construction			**Old construction**		
Floor	Toluene	Total VOCs	Floor	Toluene	Total VOCs
1st	296	343	*1st*	29	174
14th	100	145	*10th*	26	139
15th	25	76	*11th*	7	36
19th	750	818	*19th*	10	77
22th	39	88	*28th*	15	98
mean	242	294	*mean*	17	105
Roof	8	44	*Roof*	8	48

Building materials (carpets and furniture) are more likely to outgas in recently constructed buildings (Hodgson, A.T. and J.M. Daysey, 1989). This provides a plausible explanation for the findings. Highest toluene concentrations were found on the 19th floor of the newer building. Figure 5.13 gives the chromatogram obtained from the analysis of this long-term integrated sample. Toluene mass spectra (91 mu being the predominant ion) is also illustrated on this figure. The toluene peak was found to be more predominant than any other signal acquired from this long-term integrated passive sample. There were significant differences in the building's air quality based on its construction date. Extended sampling period results can theoretically require less observations compared with sampling methods using shorter sampling intervals. Complete results from this field investigation were reported elsewhere (Lal, S., 1996, Cragg, S., 1996).

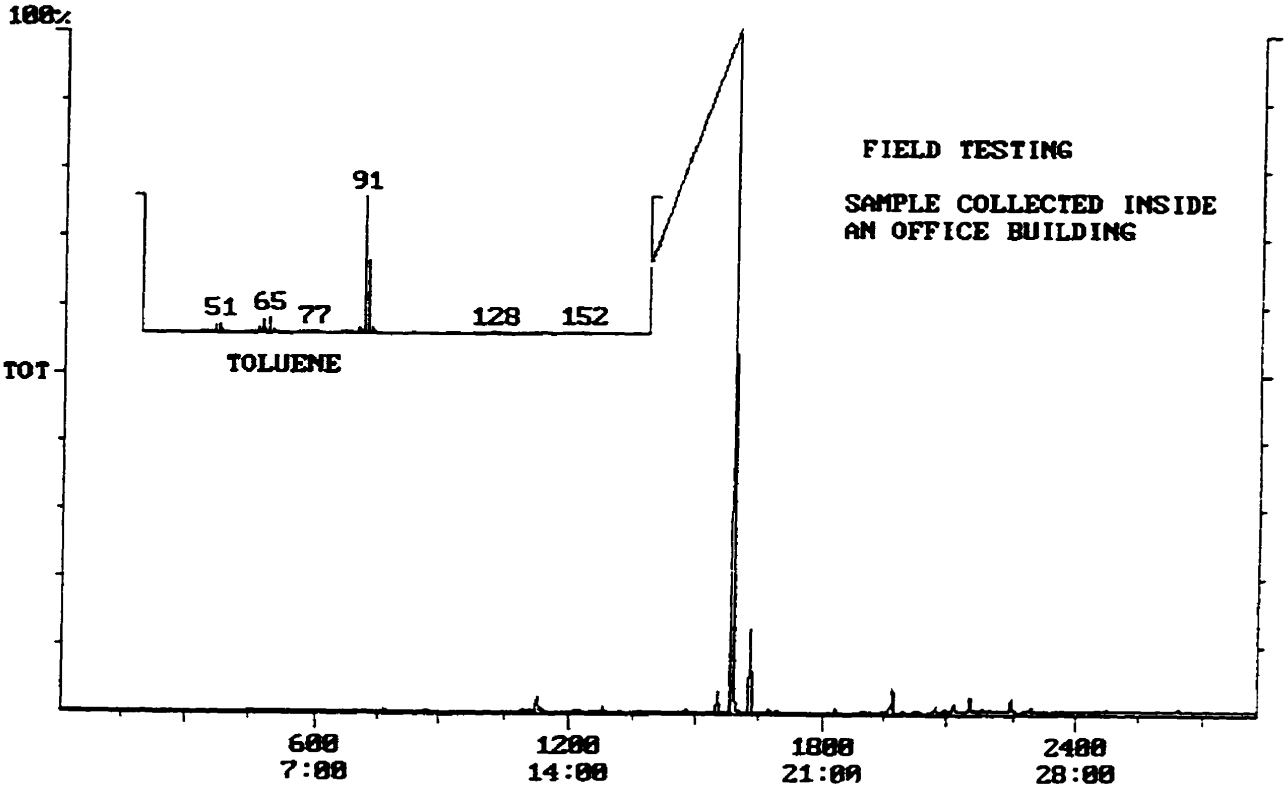


Figure 5.13: Chromatogram of a long-term integrated passive sample collected at the 19th floor of an office building

This demonstration study complemented the validation process which shows that the newly developed sampling method provides a viable alternative for the collection of VOCs.

4.4.3.3-Orbital station

The CSFC was used aboard the orbital station Mir as a first trial made by the US (NASA) and Russian space agencies to evaluate this novel sampler. Ten prototypes designed to achieve a 7-day sampling time using 500-ml canisters were assembled and initially tested. Based on successful laboratory results (see appendix-4), four of these units were launched into space during Soyuz mission TM-23, the 21st of February 1996. They were used inside the Mir station to collect air samples before and after docking with the Priroda module (Kubasov, V.N., 1996). Samples returned from space six months later in Challenger's mission STS 79. Each prototype provided a valid long-term integrated sample, and vacuum pressure below 0.6 atm was measured. They were successfully analysed in Boeing's laboratory to quantify target VOCs as well as other gaseous components such as CO_2, CO, N_2, O_2 and CH_4.

Recently, exposure limits for target airborne contaminants were defined for spacecraft atmospheres (James, J.T. and D.E. Gardner, 1996). The authors defined maximum allowable concentrations which are a function of exposure periods (1 hour, 24 hours, 7 days, 30 days or 180 days). It was recognized that health risks from chronic exposure are better defined based on long-term mean measurements. The sampling technology developed during this research project was selected to be part of a space experiment because the new device was found to be reliable. Other advantages include the fact that it is simple to operate, inexpensive, and more importantly, it can provide extended sampling period.

Field demonstration studies provided evidence that passive samplers using the CSFC offer an improved approach for the collection of VOCs and other airborne gaseous pollutants. With evacuated sample containers, selected capillary geometries were shown to allow long-term integrated measurements and to provide reliable results.

6-CONCLUSIONS

6.1-General

This research has focussed on the use of capillaries as flow controllers that provide a passive sampling method able to achieve long-term integrated sampling periods. Selected capillary geometries are used to control constant low convective air flow rates delivered by maximum discharges due to a pressure gradient established between an evacuated sample container and the atmosphere. Four general conclusions can be drawn from this research:

1. Any sampling time can be achieved by the selection of an appropriate capillary geometry (length and internal diameter) used to design the flow controller (CSFC).

2. Capillary geometries can be determined from mathematical equations based on theoretical and empirical models to arrive at the sampling time requirements.

3. Validation studies have shown that long-term integrated ambient air samples collected with summa canisters for the analysis of gaseous pollutants such as VOCs are not altered by the flow controller (CSFC).

4. Field investigations conducted with prototypes confirmed that long-term passive samplers equipped with the flow controller can provide a simple, versatile and reliable alternative to characterize airborne VOCs in indoor and outdoor environments.

In essence, capillaries can be used to control and, principally, to extend sampling time. This research has culminated in the development of a flow controlling device that effectively opens a host of new possibilities in the realm of sampling strategies. Thus, passive samplers equipped with this novel flow controller can most certainly play a role in the understanding of the relationship between airborne VOCs and their health and/or environmental effects.

6.2-Summary of findings

This research went beyond the objectives stated initially. The main results obtained for the design, development and validation of the novel long-term integrated passive sampler are now summarized.

6.2.1-Capillary Sampling Flow Controller

The most important aspect of this research concerns the development of a flow controller based on selected capillary geometries. Relationships between sampling time and capillary geometries were determined to allow the design of long-term integrated passive samplers. Based on theoretical considerations, a mathematical model, derived from fluid mechanic and gas kinetic laws, was obtained to predict the capillary length required to provide a selected sampling period considering other dimensional and physical parameters (see equations 4.17 to 4.27). The Hagen-Poiseuille and ideal gas equations were modified to include a temporal dimension (see equations 4.10 and 4.16) that could characterize the sampling process.

Predictions based on theoretical calculations demonstrated that capillaries having 0.05 and 0.10 mm ID can potentially reduce sampling flow rate, thus increasing sampling time. Experimentally, sampling flow rates between 0.018 and 0.92 ml/min were observed when less than 2 metres of a capillary having a 0.05 mm ID was used. These results compared surprisingly well with model predictions and percentage differences between simulation and experimental results were not statistically significant. Unfortunately, the theoretical model was not as precise for the capillary having a 0.10 mm ID. Experimental flow rates between 0.046 and 2.6 ml/min were obtained when up to 10 metres of this capillary was used. Model predictions for these predefined lengths systematically overestimated the sampling flow rate. Based on measurements by electron microscopy, this observation could not be explained by the precision of internal diameters. It could be due to many other parameters considering simplifying assumptions used for the model development. Explanation for the occurrence of this phenomenon was judged to be beyond the objectives of this research.

Nonetheless, experimental results obtained by testing various lengths of both capillaries provided an opportunity to improve mathematical predictions. The length was found to be inversely proportional to the maximum discharge sampling flow rate. This was predicted based on the theoretical model. However, correlations obtained experimentally for the inverse flow rate versus capillary length were different than those obtained on a theoretical basis. The internal diameter was shown to have a greater effect than initially predicted. Based on experimental results obtained with an initial pressure gradient of 1 atmosphere, an empirical model was derived as a generalized solution that can account for the observed phenomena (see equations 4.29 to 4.31).

The low flow rate (Q) required to achieve a specific long-term integrated sampling time is dictated by the volume of evacuated containers used to collect a subpressurize passive sample. Capillary geometry can be calculated to meet the design specifications of a flow controller. The mathematical equations that were derived provide a most valuable tool to design passive sampler flow controllers that can achieve any predetermined sampling time.

It should be remembered that other currently available flow controllers (critical orifices) cannot reduce sampling flow rates below 2 ml/min. Consequently, whole air passive sampling methods were limited, at best, to a 24-hour sampling interval. Experiments were mainly performed to achieve low flow rates to extended sampling periods. However, capillaries could also be used to obtain shorter sampling times. Apart from ambient air, such flow controllers could also serve to monitor gases within process equipment to establish their performance.

From these findings, a new passive sampler is proposed. It can be configured for stationary sampling and personal monitoring. The novel flow controller (CSFC) is the key part that allows extended integrated sampling times. Although it is very simple, the approach used is completely original. These passive samplers may create a revolution in the fields of industrial hygiene and environment. New strategies can be implemented to characterize VOCs and other gaseous airborne pollutants. The concept could also provide new fundamental knowledge in fluid mechanic, gas kinetic and applied physic. However, many questions still need to be answered. For instance, what is happening inside a capillary when such low gas flow rates are delivered by maximum discharge into an evacuated container?

6.2.2-Validation studies

The concept of using capillaries to control flow rates and extend sampling times was successful. However, more studies were performed to demonstrate that the use of such flow controllers is a valid alternative for the collection of ambient air samples to characterize airborne VOCs. Three approaches were used to evaluate the reliability of long-term samplers. Theoretical, experimental and field demonstration studies were conducted.

From simulations using a theoretical model, the temperature effects on flow rate constancy were estimated for a predefined capillary geometry. Based on this approach, less than a

2.5% flow rate variation was calculated for a 60°C temperature difference. The longitudinal molecular diffusional effects were also determined theoretically. As an example, an air-dichloroethylene binary mixture was used to assess potential separation inside the capillary column. The height equivalent to a theoretical plate (*HETP*) was calculated from average gas velocities within lengths of a 0.05 mm ID capillary using Van Deemter's equation. The estimated number of theoretical plates were found to be independent of capillary length used to design flow controllers. Results obtained based on theoretical considerations indicate that separation effects from longitudinal molecular diffusion should have no impact on the long-term sample's representativeness.

Laboratory studies were performed to verify conclusions drawn from theoretical findings. For temperature, less than a 10% difference in sampling flow rates was observed for a 50°C variation. Experimentally, the temperature changes appeared to have more a important effect than shown initially by the results of mathematical calculations. However, these potential errors are still below an acceptable level. Experiments also confirmed that diffusional effects does not affect the sample's validity. An air-xylene mixture was injected as a pulse into the GC/MS modified to reproduced conditions within CSFC samplers. Signals obtained did not reveal a significant separation of gaseous chemical that could affect the reliability of long-term samples. Furthermore, experimental studies were conducted to verify the stability of ambient air VOCs transferred at low flow rates to a summa canister. Recovery rates were determined and results showed that the flow controller does not significantly alter the chemical composition of sampled gas. It was concluded based on theoretical and experimental studies that long-term passive samplers with evacuated containers using selected capillary geometries as flow controllers can be a reliable approach for the collection of gaseous airborne pollutants such as VOCs.

Based on these facts, field investigations were conducted to further demonstrate the applicability of sampler prototypes. Studies were performed inside workplaces and in other outdoor or indoor environments. Prototypes were used to characterize perchloroethylene exposure in a dry-cleaning establishment. For this case study, comparisons with other sampling methods (sorbent tubes and badges) showed that passive samplers equipped with the CSFC were as reliable to determine mean breathing zone and/or stationary concentrations. In fact, if one considers the possibility of overloading and breakthrough, and the effect of temperature and humidity on sorbent-based methods, it can be concluded that the novel sampler is more reliable. Prototypes were also successfully used to determine VOCs levels over long sampling periods: inside a wastewater treatment plant to characterize large contamination profiles, and in two pulp mill sludge wastewater treatment plants to identify episodic emission events. For outdoor ambient air studies, CSFC samplers were shown to provide a better alternative to the usual methods to characterize the potential influence of landfill site's biogas, mainly because methane and VOC's concentrations can be determined from the same long-term samples over extended sampling periods. Indoor air quality studies were also conducted. Inside residences, long-term sampling strategies were able to identify substances responsible for cases of chemical sensitivities. These studies further confirmed the unmatchable ability of such a sampling device to investigate episodic events. Inside office buildings, long-term integrated samples could result in statistically significant differences between VOC levels between more recent and older constructions. CSFC prototypes were also used inside the Mir orbital station, and they were able to provide valid results on air quality inside such a confined space.

These field demonstration studies have shown that long-term sampling is a worthwhile alternative to define and characterize source emissions, ventilation efficiencies, to identify episodic events and to quantify mean exposure or background levels. Theoretical, experimental and field validation studies were able to provide evidence that the novel samplers provide a simple, versatile and reliable passive sampling method to characterize indoor or outdoor VOCs. The proposed concept should directly benefit professionals involved in field monitoring. Indirectly, results from long-term integrated sampling should also help toxicologist, epidemiologist and physician who attempt to establish a relationship between exposure and health outcomes.

6.3-Suggestions for further studies

Further developments on the use of selected capillary geometries to control maximum discharge flow rates can be anticipated. Fundamental and applied studies are now proposed.

6.3.1-Fundamental research

Fundamental aspects of gas kinetic and fluid mechanic should be studied based on the use of capillaries to provide a constant flow rate. The following research topics are proposed:

- to study the behaviour of certain parameters such as air viscosity and density profiles between a vacuum and ambient pressure: that could help to establish a more precise theoretical relationship between sampling flow rate and capillary geometries,
- to determine relationships that would better characterize the velocity profile inside capillaries used for long-term integrated sampling with the novel flow controller (CSFC),
- to verify how model relationships that predict maximum discharge flow rates apply to other sampling conditions found in process monitoring: for instance, pressurized gas sources (other than ambient air),
- to elucidate what type of flow (molecular, slip or streamline) is being established as a function of capillary geometries,
- to explore limits in geometries (capillaries having longer lengths, smaller or multiple cross sections, sample containers having smaller sizes) where observed phenomena may not apply.

6.3.2-Applied research

Sampling methods based on the use of a CSFC would require further research to better characterize performances obtained with this passive sampling approach. The following research projects are proposed:

- to extend testing with capillaries having larger cross sectional areas to control shorter sampling times (verify if model relationships also apply),
- to develop CSFC passive samplers to monitor VOCs to evaluate process equipment efficiencies,
- to improve experimental sampling configurations by using an interface that could connect pressure probes to computers,
- to use a Pirani pressure gauge that could more precisely measure initial vacuums,
- to perform recovery rate studies with a larger group of VOCs: for example, polar VOCs, essential oils and mercaptans,
- to use controlled low flow rates offered by maximum discharge to preconcentrate more reactive VOCs onto sorbent materials;
- to conduct other comparisons with recognized sampling techniques;
- to conduct further field investigations.

6.4-Contribution to knowledge

This study has made theoretical and practical contributions to the field of industrial hygiene and environmental sciences. Health and engineering professionals will benefit from the longer integrated sampling periods now possible when airborne VOCs are sampled. Contributions are defined as follows:

- Flow controllers designed with selected capillary geometries that offer low sampling flow rates.

- Mathematical models that predict capillary geometries required to achieve maximum discharge rates with evacuated containers.

- A passive sampling process that can extend sampling periods and theoretically provide any sampling time.

- Passive samplers that are reliable and simple to operate, that can be configured to perform either stationary or personal sampling, and that can be used as part of new field strategies.

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APPENDIX-1: Patent manuscript

US Patent Application, Serial No. 08/646,073

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CAPILLARY SAMPLING FLOW CONTROLLER

ABSTRACT OF THE DISCLOSURE

A capillary sampling flow controller provides an improvement in the process of sampling or monitoring for the analysis of air and gas chemistries; a constant flow rate is used to introduce a specific volume of gas into a vessel or through a trapping media over the selected sampling period. The improvement employs calculated geometry of the capillaries employed to deliver the gas sample to the evacuated vessel. It can also include a pressure reading device installed between the vessel and the capillary, and a filter at the inlet. The length of capillary with available internal diameters is estimated mathematically and confirmed experimentally to achieve any sampling time using any size sampler. The flow rate obtained from the controller is constant over its operating range and is designed to meet a specific sampling duration to obtain long-term integrated samples. The sampling process becomes completely passive, precise, reliable and simple to operate.

BACKGROUND OF THE INVENTION

i) Field of the Invention

This invention relates to the collection of gases or ambient air samples. More specifically, the invention relates to a novel flow controller wherein calculated dimensions of a capillary tube are used to introduce a constant flow of sample into any size of pre-evacuated sampling vessel. Any flow rate is theoretically possible and hence, choices of average sampling time can be selected. The time integration property of this new flow controller is a major attribute. It can contribute in extending sampling duration to obtain more relevant data on the mean levels of contaminants. Also, it can be used to collect grab samples and short term sampling can efficiently be controlled. It provides benefits in air quality studies and process control monitoring.

ii) Description of Prior Art

In air quality monitoring, the sampling methodology is a critical step where many requirements must be fulfilled to assure reliability and to optimize precision prior to the laboratory analytical determination. For many target chemicals, regulations are applied in the workplace to mitigate potential health hazards from inhalation. Again, many chemicals are also regulated in the environment considering their local or global effects. For an industrial hygienist or an environmentalist, active methods of ambient air sampling are mostly used such as sampling pumps and sorbent tubes, to characterize the risk and/or to verify compliance.

At present, active sampling devices consist of cumbersome and expensive equipment that can efficiently collect at best only 24-hour integrated samples. With these existing methodologies, the sampling duration is limited by technological considerations for the achievement of low and precise flow rate. Sample size is also reduced when the investment in equipment required for an extensive field study is considered.

In the case of gaseous contaminants such as organic vapors, all present sampling methodologies have an upper integrative time boundary. According to the sampling principles applied in workplace monitoring employing sorbent cartridges, it is still difficult to adequately characterize the nature of mean exposures. Such methods require that enough air be collected at a definite flow rate to assure the validity of laboratory analysis (adequate amount of trapped analytes vs analytical limits of detection).

In order to simplify the sampling procedures and lower the cost of air quality studies, passive techniques have been developed but they lack either precision or versatility. For the measurement of volatile organic compounds in air, a sampling procedure has been developed recently by the U.S. Environmental Protective Agency using a pre-evacuated stainless steel vessel or Summa (Trade Mark) canister as a whole air sampler. With this new sampling procedure integrated subpressurized samples can be collected passively using critical orifices as an inlet mechanical flow controller. This type of flow controller acts as a point restriction for the entry of air or gas sample, and the low flow rates obtained are principally a function of the orifice size. However, the average sampling time cannot exceed a few hours because of physical limitations of the orifice size.

In the development of an overall strategy of sample collection, temporal and spatial considerations are of prime importance. It is necessary to adopt sampling strategies which recognize the inherent statistical nature of assessing air quality. Considering the environmental variability observed in ambient air levels, combined with the chronic or the carcinogenic effects associated with exposure to some chemicals, long-term average concentration provides meaningful information in terms of risk analysis.

Toxicologically, it has been suggested that sampling duration should be adapted to represent the human uptake, distribution and elimination kinetics of these harmful substances so that exposure measurements can be related to the total body burden. For many of the toxic chemicals such as volatile organic chemicals (VOCs), rates of elimination support the use of longer sampling time. Long term integrated sampling can provide a better estimate of the absorbed dose, and correlations between exposure assessment and health effects can be improved.

Statistically, it has been shown that standard deviations calculated for airborne contaminants data collected in one location, or for a class of workers, will be a function of averaging times. The distribution of mean long term integrated measurements has a smaller variance. When comparing workers mean exposure, this observation is very important in testing for compliance. It means that less data would be required to observe statistically significant differences based on legal standards or threshold limit values (TLVs) defined for the workplace. This effect of averaging time on the distribution of air quality measurements also has the same mathematical importance in data handling when environmental levels need to be established to determine global trends.

Based on a legal standpoint, definitions are also in favor of increasing the sampling duration worldwide. For environmental protection, many guidelines are defined as mean levels not to be exceeded over periods of weeks, months or a year. In a workplace, the limits established by the American Conference of Governmental Industrial Hygienists (ACGIH) correspond to normal 8-hour workday and a 40-hour workweek. Under many regulations, arguments support the application of devices which could evaluate airborne contaminants over an extended period of time.

The use of long term monitoring has been justified according to toxicological, statistical and legal criteria. For the benefit of air quality studies, it was shown that actual methodologies should be improved to overcome present drawbacks. Better sampling methods can also find application in solving engineering problems.

In process control, it is sometimes necessary to perform routine monitoring when direct on-line readings systems are not available. Indirect collection of process gases or emissions at the source is then required. For these purposes, the present methodologies have the same sampling time limitations as those found in air quality monitoring. For example, in fluctuating processes such as organic vapors biofilters and scrubbers, it is only possible to estimate the global performance of these gas treatment technologies with a repeated number of short time (hours) samples taken over a significant period (months) of operation. The overall yield is difficult to define. Long term sampling at the inlet and outlet of such technologies can improve the estimation of performance.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a sampling assembly for the time integrated passive collection of a gas or ambient air.

It is a further object of this invention to provide a process of time integrated sampling of a gas.

It is a still further object of this invention to provide a sampling flow controller for time integrated flow of gas or ambient air.

In accordance with one aspect of the invention there is provided a sampling assembly for the time integrated passive collection of a gas or ambient air comprising a sample vessel having a negative atmosphere, said vessel having a gas inlet and being operatively connected to a sampling flow controller comprising an elongated capillary tube having an inlet port and an outlet port with a gas flow passage therebetween, said outlet port communicating with the vessel, said capillary tube having a length and an internal diameter selected such as to provide flow control of gas or ambient air at said gas inlet of the vessel.

In accordance with another aspect of the invention there is provided a process of time integrated sampling for the analysis of a gas comprising the steps of: introducing a gas sample at a substantially constant flow rate into an evacuated vessel along an elongated capillary tube having an inlet port and an outlet port with a flow passage therebetween, including selecting said capillary tube to be of a specified length and internal diameter to provide flow control at said outlet port and a predetermined sampling duration.

In accordance with another aspect of the invention there is provided a sampling flow controller for time integrated flow of gas or ambient air during collection comprising, in combination: an elongated capillary tube having an inlet port and an outlet port with a gas flow passage therebetween, means for communicating said outlet port with a sample vessel adapted to be held under a negative pressure, and a filter operatively connected to said inlet port for prevention of entry of particulate matter into said flow passage, said capillary tube having a length and an internal diameter selected such as to provide flow control of gas or ambient air at said outlet port.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention principally addresses problems of versatility in time integration sampling that are encountered when monitoring ambient air and gas.

The invention thus relates to an improvement in the process of time integrated sampling or monitoring for the analysis of air and gas chemistries. In the process the gas sample is introduced at a substantially constant sampling flow rate into an evacuated vessel, for example, using a critical orifice, or in a trapping media.

The improvement in said steps relates to the use of a substantially constant flow rate using the driving force of an evacuated vessel connected to a capillary tube of a specified geometry, acting as an inlet controller; providing any desired sampling duration by the selection of appropriate geometry (length and internal diameter) of the capillary tube. The selection of the geometry of the capillary tube for sampling duration and evacuated vessel size is developed from calculations using mathematical equations based on a phenomenological model.

The sampling flow controller comprises a designed inlet geometry of capillary tube which is connected to an evacuated vessel. Suitably a pressure measuring or reading device is installed between the evacuated vessel and the capillary. The sampling flow controller suitably has a filter installed at the inlet port of the capillary tube. This filter is operatively connected at the inlet port and prevents entry of particulate matter into the flow passage. The capillary sampling flow controller may also suitably include a trapping material inside a holding material connected between the capillary tube and the evacuated vessel. The sampling flow controller may conveniently have a wider internal diameter at the outlet port connected at the gas inlet of the vessel.

Samples collected with the capillary sampling flow controller can be analyzed for various air contaminants to provide mean levels over the selected integrated time.

More especially the geometry of the capillary tube is such that wherein the length and internal diameter are selected in accordance with the relationship

$$L=\frac{K_6 R^4 t}{(e^{\frac{V_f}{K_5}}-1)}$$

wherein

L is the length of the capillary in meters,

R is the internal radius of the capillary in meters,

V_f final sample volume in cubic meters,

t is the time in seconds, and

K_5 and K_6 are constants for the system in which

$$K_5=\frac{P_{atm} V_s \overline{V}}{\mathbb{R}T}$$

and

$$K_6 = \frac{\pi \mathbb{R} T}{8 \mu V_s \bar{V}}$$

wherein

P_{atm} is atmospheric pressure (Pa)
$\bar{V}$ is the molar volume (m^3/mole)
$\mathbb{R}$ is the gas constant (N.m/mol.k).
T is the temperature (°K), and
V_s is the volume of the vessel.

Thus the length and internal diameter of the capillary tube are selected employing mathematical equations derived from a phenomenological model.

In particular embodiments the volume of the sampling vessel will typically be from 50 ml to 50,000 ml, the capillary tube will have a length ranging from 5 cm to 500 cm and the related internal diameter of the capillary tube ranges from 0.05 mm to 0.53 mm, but small diameter tubes may be employed provided the required relationship with the length is observed.

In one particular embodiment the capillary tube is enclosed within a protective housing which may contain protective packing material which absorbs vibrations and prevents breakage of the tube during transportation or handling.

In a further particular embodiment the assembly is formed as a portable unit design to be mounted on a support, accessing a garment of a person. In such case the assembly includes mounting elements for mounting the vessel on a support which is adapted to be worn by a person, for example, a belt or shoulder harness. The vessel is then of a size and weight suitable for being carried from place to place by the person while mounted on the support. Such portable unit also includes mounting elements for mounting the inlet port of the tube adjacent the breathing zone of the person, i.e., the atmosphere adjacent the nose and mouth of the person. The inlet port might, for example, be mounted at the collar of a garment worn by the person, or from headgear worn by the person.

BRIEF DESCRIPTION OF THE DRAWINGS

Having thus generally described the nature of the invention, reference will be made to the accompanying drawings, showing by way of illustration, a preferred embodiment thereof, and in which:

Fig. 1 is a schematic view of an embodiment of the present invention;

Fig. 2 is a schematic view of an embodiment of the present invention used for stationary sampling;

Fig. 3 is a schematic view of an embodiment of the present invention used for personal sampling;

Figs. 4a, 4b and 4c are graphs showing predicted design parameters of capillary flow based on present embodiment;

Fig. 5 is a graph showing a prediction of capillary length for long term sampling;

Fig. 6 is a graph showing the results from experiments using a selected length of capillary;

Fig. 7 is a graph showing a linear approximation over a 24-hour period of sampling by the present invention;

Fig. 8 is a graph showing the relationship between the length of capillary and the passive sampling flow rates delivered by the present invention;

Fig. 9 is a graph showing experimental results where linear regressions were made to study the influence of final sampled volume on the flow rate given by the present invention;

Fig. 10 is a schematic view of a laboratory system used to analyze gas samples collected using the present invention;

Fig. 11 is a schematic view of laboratory devices required prior to the analysis of gas samples;

Fig. 12 is a schematic view of a laboratory system used to condition the sampling vessel tested with the present embodiment;

Fig. 13 is a graph showing the relationship between the levels of air pollutants delivered and collected using the invention;

Fig. 14 is a view of a chromatogram obtained from the analysis of a gas standard mixture taken using the present invention;

Fig. 15 is a graph showing the theoretical effect of molecular diffusion on the separation of chemicals and the validity of sampling using the present invention;

Fig. 16 is another graph showing the theoretical behavior of the present invention concerning the separation of chemicals;

Fig. 17 is a view of a chromatogram obtained from an experiment on molecular diffusion which demonstrates the efficacy of the invention, and

Fig. 18 is a view of a chromatogram obtained from the analysis of a field sample taken using the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS WITH REFERENCE TO THE DRAWINGS

The sampling vessel can be made of any material able to support a high vacuum, for example, deactivated fused silica, stainless steel, aluminum, glass, Teflon (Trade Mark), metallic alloys and polymeric materials and can be of various sizes or shapes. The improvement of the invention comprises a capillary sampling flow controller (CSFC) assembled with specific dimensions in length and internal diameter of the capillary tube to deliver the appropriate flow rate during a designated period of time.

The CSFC is a sampling train basically made of two components: a pressure gauge or transducer to monitor and control the time integrative sampling process and more importantly, a capillary tube of appropriate dimensions. An inlet filter prevents the entry of particulate matter.

Fig. 1 illustrates a time integrated passive ambient air sampler assembly using the CSFC.

With reference to Fig. 1 a sampling assembly 10 includes a sampling vessel 12 and a sample flow controller 14. Sample flow controller 14 includes an elongate capillary tube 16, a pressure gauge 18 and a filter 20.

Vessel 12 has an interior reservoir 22 and a needle valve 24.

A Summa canister (available from Graseby-Anderson, Atlanta, U.S.A.) is a stainless steel vessel in which the internal surfaces have been passivated employing an electro polishing step with chemical deactivation to produce a surface which is chemically inert.

In particular, vessel 12 may be a 1 liter Summa passivated canister with a ¼stainless steel needle valve (with Swagelok® fittings). The pressure gauge 18 is connected on-line between the sampling vessel 12 and the capillary tube 16 using appropriate leak free fittings. The capillary tube 16 such as a deactivated fused silica column, is connected between the pressure gauge 18 and the filter 20 with Swagelok® connectors and graphite-vespel ferules. In a particular embodiment filter 20 consists of a stainless steel frit of 0.5 μm porosity inside a body with ¼ or 1/8 Swagelok® connectors.

Capillary tube 16 has an inlet port at which filter 20 is connected and an outlet port communicating with a gas inlet of vessel 12. An elongate flow passage extends between the inlet port and the outlet port.

In a particular embodiment, the capillary tube 16 is a deactivated fused silica column of 0.4 mm outside diameter and pressure gauge 18 is capable of monitoring gas pressure from -30 Hg to 30 psi.

Fig. 2 illustrates the capillary sampling flow controller as a stand-alone unit 30. Unit 30 comprises a sample flow controller 32 with a connection element 42 for connection to a sampling vessel.

Sample flow controller 32 includes an elongate capillary tube 34, a pressure gauge 36 and a filter 38.

Elongate capillary tube 34 is housed in a protecting shield 40.

A fitting 44 interconnects pressure gauge 36, connection element 42 and fitting 46 which connects to a fitting 50 at the outlet port of tube 34. Fitting 48 connects filter 38 at the inlet port of tube 34.

In one embodiment fitting 48 is a 0.25" Swagelok; fitting 46 is a 0.0625 to 0.25" Swagelok reducer; fitting 44 is 0.25-0.25 Swagelok union; fitting 50 is a 0.125"-0.4 mm graphite-vespel ferrule; filter 38 is as for filter 20 in Fig. 1; tube 34 is a deactivated fused silica tube; shield 40 is a cylindrical enclosure 50 mm outside diameter; and pressure gauge 36 is a bourdon tube device 0.25" NPT -30" Hg to 30 psi. Here, the appropriate geometry of capillary tube 34 is enclosed in the protecting shield 40. This shield 40 is attached on the Swagelok® reducer fittings which join the capillary tube 34 between the filter 38 and the appropriate connection to the pressure gauge 36 or to the evacuated vessel. The protecting shield 40 can be machined from stainless steel and welded to the fittings. This protective shield or casing 40 can then be filled with any packing materials that will absorb vibrations and prevent the capillary tube from breaking during transportation or handling. The capillary tube 34 can also be incorporated into a plastic material using epoxy, polyacrylic or other polymeric resins. This latter type of protecting shield is cast using resin transfer molding directly on the capillary tube 34 and fittings which are installed in an appropriate mold.

Fig. 3 shows a schematic configuration of a portable personal sampler for gaseous contaminant using the CSFC.

With further reference to Fig. 3 a portable sampling device 60 includes a sampling vessel 62 and a sample flow controller 64.

Sample flow controller 64 includes an elongate capillary tube 66, and a sampling line 67. A filter 68 is connected to an inlet port of sampling line 67, and sampling line 67 has an outlet port connected to an inlet port of tube 66; tube 66 is housed in a protective housing 70.

Vessel 62 has mounting clips 72 (schematically shown) to mount vessel 62 on a belt worn by a person and filter 68 has mounting clips 74 (schematically shown) to mount filter 68 on the collar of a garment worn by the person.

Basically, this sampling device 60 is similar to those Shown in Figs. 1 and 2. However, the evacuated vessel 62 is small enough (less than 200 ml) to be carried on a belt worn by a person. This sampling train does not include a pressure gauge because of size limitations but may include a pressure indicator/sensor. The inlet filter 68 is attached to the person's collar to collect breathing zone air samples. The sampling line 67 preferably made of Teflon (Trade Mark) tubing (OD 1/16", ID 0.3mm) connects the sampler maintained at the belt to the filter 68 attached near the breathing zone. The CSFC is designed with the appropriate length of tube 66, for example, a deactivated fused silica tubing having an internal diameter less than 0.3mm. Tube 66 is enclosed inside protecting housing 70 or shield 70. Capillary tubes of 0.05mm, 0.10mm and 0.18mm internal diameter are commercially available and offer the selection of any sampling time. Multi capillary tubing is also available and may be used alternatively. The design of CSFC applied either for personal monitoring or stationary sampling is always based on the same principles. The configuration of samplers can be adapted to meet specific requirements.

Once assembled, the passive sampling unit made with the CFSC connected to an evacuated sampling vessel has to be tested for leaks. For that purpose, a cap is installed on the entry of air in the system, i.e. the filter. By opening the valve, the pressure gauge should read the low pressure inside the vessel and if the system is airtight, this vacuum will be maintained. An overnight check using this procedure is recommended. More sophisticated procedures can also be implemented using sensitive gas detectors when the sampling train is pressurized in close-circuit. This can provide a faster verification and certification of the sampling system.

With this invention, the pressure gradient between ambient air or process gases and the evacuated sampling vessel, acts as the driving force. Because motion can be controlled with the appropriate geometry of inlet restrictive capillary column, the system delivers a precise air sampling flow rate and hence, time integrated air samples can be collected. Sampling becomes completely passive, independent of any power requirement. The monitoring of air quality or process gases using this invention becomes fairly simple. The only operation steps consist in opening the valve (manually or automatically) at the beginning of the sampling period and closing it after the selected duration. To obtain a constant flow rate over the integrated sampling period, desirably the vessel should only be filled to approximately 40% to 60-65% of its total volume. If this is exceeded, the flow rate starts to decrease, the driving force being insufficient. Compared to systems employing the critical orifice inlet restriction, the capillary sampling flow controller can cover any time periods desired, and it can provide a much lower flow rate. Instead of being a point restriction, it offers a fully characterized line restriction.

RESULTS

The volumetric flow rate between the inlets of a pipe is related to the pressure gradient, the viscosity of the fluid and the pipe dimensions when a laminar flow of a Newtonian fluid is established. Also, many gas matrices including air normally behave as a perfect gas, and relationships between pressure, volume, molar concentration and temperature are well established in these situations. In order to characterize and predict the passive sampling process obtained with the CSFC prototype, a phenomenological model was developed after stating simplifying assumptions. It was developed from two different known equations that were modified and adapted to correlate the long term sampling process that is observed with the CSFC. The first relationship is based on fluid mechanics: the Hagen-Poiseuille equation. The other relationship is based on a fundamental gas kinetic equation: the ideal gas law. To present the mathematical model developed to design a CSFC, a description of how these two relationships were used and which hypothesis were stated is given here:

The Hagen-Poiseuille relationship applies to a laminar flow of fluids in circular tubes. The development starts with a momentum balance using a volume element: a cylindrical shell. The momentum balance where forces from friction + compressibility + pressure and gravity = 0 was stated as:

$$(2\pi rL\tau_{rz})\big|_{r}-(2\pi rL\tau_{rz})\big|_{r+\Delta r}+(2\pi\Delta r v_z)(\rho v_z)\big|_{z=0}-(2\pi\Delta r v_z)(\rho v_z)\big|_{z=L}+2\pi\Delta r(P_o-P_L)=0 \quad (1)$$

The fluid can be assumed to be incompressible (i.e. the velocity is constant over the length of the tube), only the friction and the pressure component forces are considered. Then, taking the limit as Δr goes to zero, this gives:

$$\lim_{\Delta r\to 0}\left\{\frac{(r\tau_{rz})\big|_{r+\Delta r}-(r\tau_{rz})\big|_{r}}{\Delta r}\right\}=\left\{\frac{P_0-P_L}{L}\right\}r \quad (2)$$

This expression can be written as:

$$\frac{d}{dr}(r\tau_{rz})=\left\{\frac{P_0-P_L}{L}\right\}r \quad (3)$$

In order to integrate the equation, the

appropriate boundary conditions (at r=0, the shear stress is not to be infinite) were stated to obtain this solution:

$$\tau_{rz}=\left\{\frac{P_0-P_L}{2L}\right\}r \tag{4}$$

Then, use the Newton law of viscosity for this situation:

$$\tau_{rz}=-\mu\frac{dv_z}{dr} \tag{5}$$

Combining the equation (4) and the Newton law, this gives the following differential equation for the velocity:

$$\frac{dv_z}{dr}=-\left\{\frac{P_0-P_L}{2\mu L}\right\}r \tag{6}$$

The integration, using another boundary condition where the velocity is null at the fluid-solid interface (i.e. $v_z=0$ at r=R) will result in the velocity distribution which gives:

$$v_z = \frac{(P_0 - P_L)}{4\mu L} r^2 [1 - (\frac{r}{R})^2] \qquad (7)$$

This expression indicates that the velocity distribution for laminar flow of incompressible fluids is parabolic. From this expression, we can obtain another equation such as the average velocity:

$$<v_z> = \frac{\int_0^{2\pi}\int_0^{R} v_z r dr d\theta}{\int_0^{2\pi}\int_0^{R} r dr d\theta} = \frac{(P_0 - P_L)R^2}{8\mu L} \qquad (8)$$

From the average velocity equation, we can obtain the volumetric flow rate which is the product of the cross sectional area of the cylinder (πR^2) by the average velocity as defined in equation (8). This is a rather famous result which was called the Hagen-Poiseuille law in honour of the two scientists who derived the formulation around 1840:

$$Q = \frac{\pi (P_0 - P_L) R^4}{8\mu L} \qquad (9)$$

Among assumptions that relate to this equation, first the tube should be long enough, so that end effects can be neglected. This relationship also applies only to laminar flow (i.e. Reynold number less than 2100) and Newtonian fluids. The fluid should behave like a continuum - this assumption is theoretically not valid for very dilute gases or very narrow capillary tubes, in which the molecular mean free path can be higher than the tube diameter and where we observe a slip flow or free molecular flow regimes. Finally, since the Hagen-Poiseuille equation is valid under steady-state, the flow should be time independent.

This mathematical development {from equation (1) to equation (9)} was developed long ago and was described elsewhere. In order to characterize the behaviour of a CSFC, we have made the assumption that in a pseudo steady-state system, the volumetric flow rate and the internal sampling vessel pressure should both be a function of time: the sampling time. Also, in this process, P_0 is equal to atmospheric pressure (P_{atm}) and internal pressure of the vessel is variable {P(t)}. This gives the following expression:

$$Q(t)=\frac{\pi(P_{atm}-P(t))R^4}{8\mu L} \tag{10}$$

The assumption is made that the air viscosity between the vacuum and ambient pressure remains constant. Remember that Hagen and Poiseuille also had to assume that the fluid density remains unchanged, which is certainly not the case considering the pressure differences over the CSFC operating range. Equation (10) is one of the original mathematical expressions used to develop the phenomenological model applied to the design of a CSFC. However, to obtain the set of equations, a second relationship has to be postulated.

In order to characterize the behaviour of a CSFC as to the relation between the flow rate and the internal pressure, we have started with this fundamental relation based on kinetic theory of gases called the ideal gas law relationship:

$$PV=n\mathbf{R}T \tag{11}$$

This equation is restated, considering the variation of two variables which are a function of sampling time (the internal sampling vessel pressure and the molar content):

$$P(t)=\frac{n(t)\mathbf{R}T}{V_s} \tag{12}$$

Now, as in the behaviour of a critical orifice when used on evacuated vessels, the volumetric flow rate remains constant during the time it required to fill more than half of the sampler's volume. Therefore in part of the process the sampled volume is expressed as:

$$V(t)=\int_0^t Q(t)dt \tag{13}$$

and if the flow rate is constant as we find experimentally:

$$V(t)=Q(t)t \qquad (14)$$

We finally relate the sampled volume with the molar content using the molar volume at standard temperature and pressure. We write:

$$n(t)=\frac{V(t)}{\overline{V}}=\frac{Q(t)t}{\overline{V}} \qquad (15)$$

Taking this expression and replacing in equation (12), we obtain:

$$P(t)=\frac{RTQ(t)t}{V_s\overline{V}} \qquad (16)$$

This last relationship is the second equation used to derive the phenomenological model developed to predict the geometry of a capillary column for the design of a novel flow controller: the capillary sampling flow controller.

The model was derived by resolving equation (10) and equation (16) in which one of the two unknown variables {P(t), Q(t)} can be removed to obtain a single equation. By the elimination of the internal pressure time function {P(t)}, we have obtained an expression of the volumetric flow rate {Q(t)} which is a function of the sampling time (t). We have expressed this equation with two constants (K_1, K_2) which have no physical meaning. This relationship is:

$$Q(t)=\frac{K_1}{1+K_2t} \tag{17}$$

where :

$$K_1=\frac{\pi P_{atm}R^4}{8\mu L} \tag{18}$$

$$K_2=\frac{\pi \mathbb{R}TR^4}{8\mu LV_s\overline{V}} \tag{19}$$

Again, using the same two equations we have obtained the pressure variable [P(t)] as a function of the sampling time by here, removing the flow rate variable. Again, two constants were defined (K_3, K_4) and this expression is:

$$P(t)=\frac{K_3P_{atm}t}{K_4-K_3t} \tag{20}$$

where:

$$K_3=\frac{\pi \mathbb{R}TR^4}{\overline{V}} \tag{21}$$

$$K_4=8\mu V_sL \tag{22}$$

Finally, to compute the sampled volume variations versus the sampling time, we have integrated the flow rate expression [equation (17),(18),(19)]:

$$V(t)=\int_0^t Q(t)dt=\int_0^t \frac{K_1}{1+K_2 t} \tag{23}$$

Resolving this equation, we have defined two other arbitrary constants (K_5, K_6) and obtained a solution for the sampled volume as a function of time integration {V(t)}:

$$V(t)=K_5 \ln(1+\frac{K_6 R^4}{L}t) \tag{24}$$

where:

$$K_5=\frac{P_{atm} V_s \overline{V}}{\mathbb{R}T} \tag{25}$$

$$K_6=\frac{\pi \mathbb{R}T}{8\mu V_s \overline{V}} \tag{26}$$

Finally, we have defined a value of V(t) equal to the final sampled volume (V_f) which should be between 0.5 and 0.7 of the sampler volume (V_s). Then, we obtained an expression of inlet restriction length of capillary (L) as a function of the sampling time (t). This relationship can be used to design a CSFC, considering a specified internal diameter of capillary column. This final relationship is:

$$L=\frac{K_6 R^4 t}{(e^{\frac{V_f}{K_5}}-1)} \tag{27}$$

Notations:

L	Length of inlet restrictive deactivated fused silica capillary column (m)
n	Number of moles (mole)
n(t)	Molar content time function (mole)
P_0	Inlet pressure inside capillary (Pa)
P_L	Outlet pressure inside capillary (Pa)
P_{atm}	Atmospheric pressure (Pa)
P(t)	Sampling pressure time function (Pa)
Q(t)	Volumetric sampling flow rate time function (m^3/s)
r	Radial distance in cylindrical coordinate (m)
R	Internal radius of restrictive deactivated fused silica capillary column (m)
$\mathbb{R}$	Gas constant (N · m/mole · K)
t	Integrated sampling time (sec)
T	Temperature (°K)
V	Molar volume (m^3/mole)
V(t)	Sampled volume time function (m^3)
V_f	Final sampled volume (m^3)
V_s	Canister sampler volume (m^3)
v_s	Velocity of fluid in longitudinal direction (m/s)
z	Longitudinal distance in cylindrical coordinate (m)

Symbols:

θ	Angle in cylindrical coordinate (radian)
τ_{rz}	Shear stress (N/m^2)

ρ Fluid density (kg/m^3)

π 3.14159...

μ Viscosity of air (poise)

This model was developed to estimate the geometry of the capillary in order to obtain a desired sampling time, whatever the sampler's volume. It does not characterize the velocity profile along the capillary.

From these considerations, the model predicts the sampling behavior for any size of evacuated sampling vessels such as Summa canisters, and estimate CSFC characteristics (internal diameter and length of capillary column) for a desired sampling period. Figs. 4a, 4b and 4c shows predicted design parameters of the capillary flow controller based on this model, when a 1 liter sampling vessel is used to collect 500 ml of sampled air (half-volume subpressurized samples). It can be seen that capillary internal diameter drastically affects the sampling time. Internal diameter greater than 0.25 mm would require very long length of capillary to restrict the flow and obtain sampling duration exceeding a few hours. However, the smallest internal diameter simulated (i.e 0.05 mm) offers wide passive integrated sampling times without using long lengths of capillary (i.e. approximately 4.5 meters of column for a sample duration of 30 days with a one liter vessel). These simulations can easily be performed with other sizes of sampling vessel and other internal diameters of capillary lines using the original model. Also the atmospheric pressure used in the model can be replaced by other inlet pressure when applied inside special locations (positive or negative pressure chambers) or for process monitoring.

An investigation was made of the impact of sampler size (internal volume of vessel) on the design of CSFC using a 0.05 mm ID capillary. Simulations were performed to evaluate the lengths of capillary to achieve different sampling times with different sampling vessel sizes. For samplers ranging from 100 ml to 40 liters, Fig. 5 illustrates the predicted length of capillary (from 0 to 200 cm) that a CSFC would need to integrate sampling time from 8 hours to one month. As the size of the sampler increases, the length of capillary rapidly decreases up to a point where variations in length can have an important effect on sampling time. In fact, these data show that short capillary tube (less than 5 cm) used to obtain specific sampling times is less accurate and this observation was also verified experimentally. This means that when bigger vessels (>5 liters) or short sampling time (<40 hours) are required, a capillary tube with larger internal diameter should be used in the design.

The theoretical effect of temperature affecting viscosity and molar volume was also simulated for a specific CSFC unit. The Sutherland's relationship was used to compute values of viscosity at different temperature. The predictive results showed the minor impact of ambient temperature on the overall sampling time and on the functioning of the invention. The shape and material of both vessel and capillary have no impact on flow control process. The major controlling factor is the total length of a specified internal diameter of capillary column or capillary tubing.

Many studies were performed to evaluate the performance of this invention. Investigation with different sizes of gas collection vessels using CSFC prototypes assembled with different lengths of fused silica capillary columns of 0.05 mm internal diameter were conducted to characterize the long-term sampling behavior. Generally, the mathematical model was shown to give good approximations for the appropriate geometry of capillaries. Results from experiments using predicted length (0.115 meter) of the capillary tube and internal diameter of 0.25 cm are presented in Fig. 6. for a temperature of 25°C and an inlet pressure of 1 atm. The sampled volume (data points) are based on pressure readings taken during time intervals. Two different readings are reported: one obtained from an electronic pressure transducer, others taken from a simple mechanical pressure gauge (Bourdon type). These data along with predicted pressure function were transformed into sampled volume using perfect gas law relations (Fig. 6, left axis). The pressure behavior which served to derive the predicted sampled volume was computed from equations (20),(21) and (22).

Flow rate predictions from model simulations are also reported on this graph (Fig. 6, right axis) and they were calculated from equations (17), (18) and (19). The CSFC was able to extend the duration of sampling 500 ml of ambient air for 24 hours. During this period, a linear relationship between sampled volume and time can be observed. The model prediction could very well estimate the time integration capability of this prototype although it does not reproduce entirely the experimental findings. In order to approximate the sampling flow rate during the first 24 hours, the data obtained was linearized from the prototypes and from the predictive model. These results are found in Fig. 7, for a 0.115m length, 0.05 mm diameter and 1 liter volume. Fig. 7 shows that the CSFC can easily deliver a constant sampling flow rate (between 0.23 ml/min to 0.35 ml/min) to collect an integrated passive sample of ambient air over its operating range. In fact, the model predicts a saturation process and hence, a less constant flow rate than what is observed experimentally. The regression coefficients (r^2) was higher in experiments (0.997) compared with those obtained from the theoretical relationship (0.978 for a slope of 0.27 ml/min). These experimental results demonstrate the validity of time integration properties gained with the CSFC. The small flow rate variation observed between prototypes can be explained by the differences in initial vacuum between samplers, or by calibration errors in pressure measuring devices. This has negligible effects on the linearity of sampled volume during the passive process.

Similar experiments were repeated to verify other integrated sampling times using many sizes of sampling vessel. These studies were accomplished to demonstrate the versatility of the CSFC and validate simulation results. Until now, the same effects have been observed: a constant flow rate can be achieved, until the internal pressure inside the vessel reaches a value between 0.5 to 0.65 atm. Using different lengths of deactivated fused silica capillary having a 0.05 mm internal diameter, the performance of this new mechanical flow controller was tested to estimate volumetric flow rates. Experiments were conducted using CSFC prototypes connected with vessels having sizes of 0.1; 0.5; 1 and 6 liters. A rectangular vessel machined from stainless steel having 150 ml volume (as schematically illustrated in Fig. 3) which can be applied for personal monitoring was also tested. From the data obtained, the experimental flow rate was calculated using linear regressions. These results are presented in Fig. 8 for a capillary tube of 0.05 mm diameter. The volumetric flow rates delivered by the CSFC given the capillary lengths are compared with the predicted relationship obtained from the model. The data points derived from individual experiments using various configurations of gas samplers follow closely the curve calculated from the model using theoretical considerations. In order to investigate in more detail the effect of the final sampled volume on the consistency of the volumetric flow rate offered by the CSFC, linear regression were made whether 40%, 50%, 60% or 70% of the sampler size was collected. These results are illustrated in Fig. 9. This experiment was made in a laboratory using a 500 ml Summa canister, a tube length of 1.25 m and diameter of 0.05 mm, a temperature of 25°C and inlet pressure of 1 atm. and data were taken over more than three weeks. Fig. 9 shows that when more than 60% to 65% of the vessel is filled with the gas sample, the pressure gradient is not sufficient to deliver a precise passive constant sampling flow rate. Otherwise, when such low flow rates are achieved, the operating range of this mechanical controller can provide very broad integrated sampling times, in this case ranging from 7 to almost 14 days. Table 1 summarize the results calculated from this analysis. Regression coefficients which are related to the precision of the sampling rate were over 99% during a large interval of time. Volumetric flow rate was maintained at 0.018±0.001 ml/min over a long integrated sampling time. This particular configuration of passive sampler which required a CSFC designed with 1.25 meters of capillary having an internal diameter of 0.05 mm was developed to be applied inside the Russian orbital station Mir.

Table -1-

final sampled volume		integrated sampling duration	volumetric sampling flow rate	correlation coefficient (r^2)
(ml)	(%)	(day)	(ml/min)	%
200	40	7	0.019	99.6
250	50	10	0.018	99.6
300	60	12	0.017	99.3
350	70	15	0.016	98.9

The behavior or other internal diameters of capillary inlet restriction were also investigated. The predicted length of capillary (ID 0.10 mm) to obtain a 24 hour integrated sampling time using a 6 liter evacuated vessel was found to be within 10% error. The validity of using two different ID of capillary linked together with a vacuum connector was tested. The purpose was to verify if a sample could be collected meters away from the vessel, where access is restricted and/or hazardous. A 5 meter long capillary with a wider internal diameter (ID 0.25 mm) connected to the appropriate length of restrictive capillary (ID 0.05 mm) was used. The wider capillary did not influence the overall time integration controlled by the smaller diameter capillary. This important result demonstrates that the CSFC can be used to collect samples some distance away from the samplers.

Experimental results supported by extensive model simulations proved that the CSFC can effectively be used for time integrated passive collection of gas and ambient air with evacuated sampling vessels. The demonstration was principally applied to long-term sampling which is still impossible using present methodologies. The CSFC can also be used for short sampling periods. The relationships between the geometry of capillary (total length and internal diameter) with relevant factors including sampling time and sampler size were established. This most valuable set of equations provides the basis to estimate CSFC geometry according to selected sampling time and sampler size. Simple experimentation can confirm the estimate or provide the information required to adjust precisely the length of capillary needed to meet the passive time integrated sampling period desired.

The capacity of the CSFC to average sampling time is one of its major attributes. Extended sampling periods which can be obtained from the CSFC can contribute to a better and faster evaluation of mean exposure. For example, five daily samples are required at present to assess worker exposure to workplace contaminants over a period of one week. With an appropriate CSFC, a unique sample taken separately for eight hours during each working day would estimate mean exposure adequately. The sampler would only have to be opened and closed at the beginning and end of a work shift. It can also be used to sample sporadic contaminant release episode to determine the nature of airborne chemicals.

Special procedures are required to analyze components of a gas matrix collected as subpressurized samples inside sampling vessels. For volatile organic chemicals (VOC) such as aromatic (benzene, toluene, xylenes, etc), halogenated (vinyl chloride, chloroform, dichloromethane, etc) and other classes of toxic chemicals, a gas chromatograph coupled with a benchtop mass spectrometer (GC/MS) may play an important role in the laboratory. These analytical instruments provide a means to quantify subppb(v) levels of target contaminants using predominant ions of full scan mass spectra, combined with the retention times of signals acquired from the chromatograms. In most GC/MS techniques developed for the analysis of VOC in ambient air, an injection unit is used to preconcentrate the VOC prior to the analysis. For this purpose, cryogenic or sorbent trapping can be used and normally, special water management procedures such as sorbent dry purging need to be implemented to maximize the sensitivity of the mass spectrometer detector.

Fig. 10 illustrates the analytical system that was used to characterize the levels of VOC in the validation and field studies where gas samples were collected with the controller.

With further reference to Fig. 10, an analytical assembly 100 includes a purge and trap autosampler 103, a flow measurement read-out box 104, a diaphragm vacuum pump 106, a mass flow controller 108, a purge and trap describing unit 110, a direct split interface 112, a gas chromatograph 114, an autosampler syringe injector 116, a mass spectrometer detector 118 and a computer control station 120.

Thus a purge and trap injection device was modified. One purge vessel was bypassed and replaced by a three-way valve using appropriate tubing and connectors to allow the injection of gas samples from vessels. The mass flow controller 108 was connected between the vent port of this unit and the vacuum pump 106 that is used to pull out the sample into the sorbent trap. Analytes are trapped at constant flow rate during a known time interval, dry purged, thermally desorbed and transferred into the gas chromatograph 114/mass spectrometer 118. In this system, a direct split interface 112 is used to connect the purge and trap injector with the gas chromatograph 114. The vessel can be connected directly to the system, and gas samples are handled and analyzed for VOC. When the sample does not need analytical enrichment, a more simple injection device and analytical detectors can be used. For the analysis of gases such as carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), oxygen (O_2) and methane (CH_4), sample aliquots can be taken from a gas tight syringe and injected directly to an on-column port of the gas chromatograph column 114. Simpler detectors based on electrical conductivity (ECD) or flame ionization (FID) are more appropriate than a mass spectrometer.

With further reference to Fig. 11, there is shown a device 130 for sample management prior to laboratory analysis in which vessel 132 has a syringe adapter 134 and a gas tight syringe 136; and a device 138 having vessel 140 with a pressure transducer 142 and a calibrated reading box 144.

Fig. 11 shows the type of devices that are required before the analysis of the gas samples collected using the CSFC. First, the controller is disconnected from the vessel and replaced by a syringe adapter. Gas sample can be withdrawn inside a gas tight syringe.

Internal pressure may be monitored using a pressure transducer interfaced with a calibrated reading box as shown in Fig. 11. This procedure is required when the vessels need to be pressurized. With the analytical system presented in Fig.10, samples are best delivered to the injector if no vacuum exist. Before they are analyzed, the samples can be mixed with purified air so that aliquots can be withdrawn for analysis. This operation dilutes the samples by a factor between 2 to 4, but with the high resolution obtained from new analytical systems, this laboratory dilution does not have a significant effect on the results obtained.

Compared with many of the actual sampling methodologies, the use of CSFC with evacuated sampling vessel does not require calibrations and the sampling procedures are completely independent of any power source. The CSFC can be reconditioned with purified, humidified and pressurized (10-20 psi) nitrogen, helium or air maintained at elevated temperature (100-250°C) and applied in reverse flow, hence it can be use more than once. The sampling vessels can also be cleaned using a reconditioning system where a source of humidified cleaned gas or a vacuum can be delivered. Fig. 12 presents a schematic view of the type of device that is required to prepare the sampling vessel for field applications and/or laboratory studies.

With further reference to Fig. 12, device 150 includes Summa canisters 152, a vacuum pulp 154, a pressure gauge 156 (-30in Hg to 30 psi), an outlet filter 158, an inlet filter 160, a humidifying chamber 162 and manual valves 164.

This system is operated by switching the manual valves 164 to fill the canisters 152 with pure humidified gas and then to apply a vacuum given by the pump 154. These cycling steps are repeated three times or more and then the canisters 152 are kept under complete vacuum and ready to be reused.

When similar laboratory procedures can be implemented, the CSFC can provide a simple and precise method to collect inorganic gases, volatile organic gases and vapors. As compared with actual sampling methodologies using sorbent tubes, no solvents are required to analyze the passive samples collected using the CSFC.

For different air components such as particulate or reactive gases, other procedures can eventually be used. Here, the vessel would be used only to generate the motion of gas. Before entering the vessel, target contaminants would be trapped on appropriate media, (ex.: filters) installed in leak free cartridges between the CSFC and the source of vacuum. The CSFC would provide the appropriate flow rate through the intermediate collecting devices.

With the CSFC, the monitoring operation is simplified to the extent of opening and closing the valve on the evacuated vessels. It can easily be automated. Compared to existing methodologies, it does not require qualified professionals to perform the sampling tasks.

Validation studies were made to demonstrate the reliability of this new atmospheric sampler. An experiment was performed where a CSFC designed to sample during 60 hour using a 500 ml evacuated Summa canister was connected using a Teflon tube directly to a 6 liter container filled at 5 psi with a standard gas mixture of 40 VOC each at 100 ppb(v). This gas mixture was transferred through the CSFC and at the end of the passive sampling period, the contents of both cylinders were analyzed in the GC/MS. Results were compared and Fig. 13 shows the relationship that was found between the levels of each VOC whether they were delivered to the sampler or collected over the long integrated sampling time. Each data point correspond to a single chemical. Globally, this experiment was conducted to prove that the CSFC does not introduce any contaminations in the gas chemistries collected for laboratory analysis. Loss of chemicals or appearance of artifacts could limit its application. According to the results presented in Fig. 13, there is no evidence that the sampling train generates interferences, considering the overall errors of the procedures (dilution, analysis). All parts of the CSFC are made of materials (e.g. deactivated fused silica and stainless steel) known to minimize the presence of active sites. Fig. 14 presents the chromatograms from the GC/MS analysis of the standard gas mixture that was collected during this experiment. The signals of every chemical of this gas matrix was correctly identified. No other chemicals (artifacts) were found. This static validation study was able to demonstrate that the capillary sampling flow controller can effectively collect samples which reproduce the nature of the atmosphere at the sampling locations.

The use of appropriate geometry of capillaries to control the flow rate at such low levels raised a question concerning possible separation effects inside the tube. As an analogy, the separation of a chromatographic column can be estimated using the Van Deemter equation. This relationship expresses the height equivalent to a theoretical plate which is an indication of the separation efficiency as a function of three factors that may influence the retention of molecules inside a column. This equation is written as:

$$HETP = A + \frac{B}{v_z} + Cv_z \qquad (28)$$

where HETP is the height equivalent to a theoretical plate, A is the factor which represents the eddy diffusion, B is the longitudinal molecular diffusion and C is the mass transfer coefficient in the stationary phase. In the CSFC, a plain capillary without internal packing or stationary phase is used so the factors A and C are not considered. The only factor which can influence the separation is the axial molecular diffusion and based on Einstein's law of diffusion, equation (28) can be written as:

$$HETP = \frac{2D_z}{v_z} \tag{29}$$

where D_z is the diffusion coefficient for a binary mixture which is measured in cm^2/s, and V_z is the average longitudinal velocity of molecules in cm/s. The average velocity was calculated theoretically for different lengths of 0.05 mm internal diameter capillary using the cross-sectional area and the simulation results of volumetric flow rate. As an example, the tabulated diffusion coefficient for a mixture of air and dichloroethylene (0.1 cm^2/s) was used, and values of HETP were computed as a function of capillary length used in the design of CSFC. These results are illustrated in Fig. 15. A linear relationship between the height equivalent to theoretical plate and the length of capillary is predicted based on assumptions and considering the profile of average velocities of gas samples

These data can also be expressed to show the relationship between the average velocity and the HETP. This was done to compare the results with basic theory of separation. Fig. 16 shows simulation results that were performed to study the validity of the capillary sampling flow controller. Chromatographic columns are often characterized by their number of theoretical plates. This number can be estimated using the length of column divided by the HETP. With this simple equation, calculations were performed and the number of theoretical plates was found to be independent of the length of capillary. Using a capillary of 0.05 mm in internal diameter, any lengths will introduce approximately 16,750 theoretical plates of separation for a mixture of air and dichloroethylene. Normally, GC columns need more than 200,000 plates to be efficient. From this theoretical analysis, it was shown that the level of separation which could eventually interfere in the sampling of gas chemistries is relatively low.

In order to prove that this effect is small enough to have a minor impact on the reliability of CSFC, an experiment was conducted in the laboratory using the GC/MS. The separation column inside the GC was replaced by 1 metre of deactivated fused silica column with 0,05 mm internal diameter. This capillary was directly connected between the GC injection port and the MS ion trap maintained under vacuum. The GC flow rate was reduced at atmospheric pressure and the system was kept isothermal to reproduce the conditions encountered on the field when a CSFC is used. A binary mixture of air and xylene was injected as a pulse to simulate the entry of a gas sample passing through the controller and collected inside the sampling vessel. Fig. 17 presents the chromatogram that was obtained from this experiment where 1 µl of this mixture was injected in the system with a gas tight syringe one minute after the detector and the acquisition were started. Rapidly, the mixture arrived at the detector over a time interval of less than 5 seconds. Mass spectra of air (m/e 28) was found to be more predominant in the beginning of the signal when compared with the mass spectra of xylene (m/e 91) which was higher at the end of this peak. As predicted from theoretical considerations using Van Deemter and Einstein relationships, a small separation was observed inside the capillary due to the molecular diffusion. However, these phenomena occurred over periods of seconds. This separation effect cannot have any influence on the validity of samples taken using the CSFC considering that sampling durations are extended to minutes, hours, days or months.

From every theoretical and experimental validation study performed up to date, the reliability and the applicability of the capillary sampling flow controller were demonstrated. The CSFC can fulfill many needs in air quality monitoring.

Considering the possibilities offered by the novel flow controller, different configurations of CSFC have been used in the field. 21 long term stationary samples were collected outdoor around a sanitary landfill during one week periods using 1 litre and 6 litre Summa canisters. These samples were diluted with ultra pure air and analyzed through gas chromatography/mass spectrometry (GC/MS) to quantify low levels of 50 volatile organic chemicals. Methane content was also measured using gas chromatography/flame ionization detection (GC/FID). Field testings were also conducted to assess the indoor air quality inside a domestic wastewater and pulp mill treatment plant and in residences. 6 litres Summa canisters were used to sample during periods of one, two or three weeks. In all of these cases, the analysis was able to provide appropriate results which represent the mean average concentrations of airborne pollutants integrated over a long duration. Fig. 18 shows the chromatogram obtained from the analysis of one of these sample using the GC/MS.

Finally, the CSFC is now being used aboard the

Russian orbital station Mir as a first trial made by the US and Russian space agencies to evaluate this invention. Ten prototypes designed to achieve a 7 days sampling time using 500 ml canister were assembled and initially tested (see Fig. 9). Four of these units were launched in Soyuz TM-23 the 21st of February 1996. They are being used inside Mir to collect air samples before and after the docking with the Priroda module. Samples will be analyzed in the laboratory when they return from space.

The capillary sampling flow controller represents an improvement in passive monitoring applied to air quality, to source characterization or to process control. Considering the simplicity and the low cost of the CSFC, combined with its ability to control the sampling period, this invention should find various other applications. It can be applied in the monitoring of many types of gas contaminants or gas components in various type of environments.

WE CLAIM

1. A sampling assembly for the time integrated passive collection of a gas or ambient air comprising a sample vessel having a negative atmosphere, said vessel having a gas inlet and being operatively connected to a sampling flow controller comprising an elongated capillary tube having an inlet port and an outlet port with a gas flow passage therebetween, said outlet port communicating with the vessel, said capillary tube having a length and an internal diameter selected such as to provide flow control of gas or ambient air at said gas inlet of the vessel.

2. An assembly according to claim 1, wherein the length and internal diameter are selected in accordance with the relationship

$$L=\frac{K_6R^4t}{(e^{\frac{V_f}{K_5}}-1)}$$

wherein

L is the length of the capillary in meters,

R is the internal radius of the capillary in meters,

V_f is the final sampled volume in cubic meters,

t is the time in seconds, and

K_5 and K_6 are constants for the system in which

$$K_5=\frac{P_{atm}V_s\overline{V}}{\mathbb{R}T}$$

and

$$K_6 = \frac{\pi \mathbb{R} T}{8 \mu V_s \overline{V}}$$

wherein

P_{atm} is atmospheric pressure (Pa)

V is the molar volume (m^3/mole)

$\mathbb{R}$ is the gas constant (N.m/mol.k)

T is the temperature (°K), and

V_s is the volume of the vessel in cubic meters.

3. An assembly according to claim 2, wherein said sample vessel has a volume of 50 ml to 50,000 ml, said length ranges from 5 cm to 5000 cm and said internal diameter ranges from 0.05 mm to 0.53 mm.

4. An assembly according to claim 3, wherein said inlet port is operatively connected to a filter adapted to prevent entry of particulate matter into said flow passage, and a pressure measuring device is operatively connected between said outlet port and said gas inlet.

5. An assembly according to claim 2, wherein said capillary tube is a deactivated fused silica column.

6. An assembly according to claim 2, wherein said capillary tube is enclosed within a protective housing.

7. An assembly according to claim 6, wherein said housing contains packing material for absorbing vibrations and preventing breakage of the tube during transportation or handling.

8. An assembly according to claim 2, further including mounting means for mounting said vessel on a [illegible] support adapted to be worn by a person, said vessel [illegible] being of a size and weight suitable for being carried by the person on the support; and means for mounting the inlet port adjacent the breathing zone of the person.

9. A process of time integrated sampling for the analysis of a gas comprising the steps of:

introducing a gas sample at a substantially constant flow rate into an evacuated vessel along an elongated capillary tube having an inlet port and an outlet port with a flow passage therebetween, including selecting said capillary tube to be of a specified length and internal diameter to provide flow control at said outlet port and a predetermined sampling duration.

10. A process according to claim 9, wherein said length and internal diameter are selected employing mathematical equations derived from a phenomenological model.

11. A process according to claim 10, wherein the length and internal diameter are selected in accordance with the relationship

$$L=\frac{K_G R^4 t}{\left(e^{\frac{V_s}{K_s}}-1\right)}$$

wherein

L is the length of the capillary in meters,

R is the internal radius of the capillary in meters,
V_f is the final sampled volume in cubic meters,
t is the time in seconds, and
K_5 and K_6 are constants for the system in which

$$K_5 = \frac{P_{atm} V_s \overline{V}}{\mathbb{R} T}$$

and

$$K_6 = \frac{\pi \mathbb{R} T}{8 \mu V_s \overline{V}}$$

wherein
P_{atm} is atmospheric pressure (Pa)
$\overline{V}$ is the molar volume (m^3/mole)
$\mathbb{R}$ is the gas constant (N.m/mol.k)
T is the temperature (°K), and
V_s is the volume of the vessel (m^3).

12. A process according to claim 11, wherein said evacuated vessel has a volume of 50 ml to 50,000 ml, said length ranges from 5 cm to 5000 cm and said internal diameter ranges from 0.05 mm to 0.53 mm.

13. A process according to claim 11, wherein said inlet port is operatively connected to a filter, and including a step of filtering particulate matter from the gas sample entering said inlet port to prevent entry of said particulate matter into said flow passage, and further including a step of monitoring pressure of the gas developed in said vessel, from said gas sample.

14. A process according to claim 11, wherein said capillary tube is a deactivated fused silica column.

15. A process according to claim 9, wherein said gas is ambient air.

16. A sampling flow controller for time integrated flow of gas or ambient air during collection comprising, in combination:

an elongated capillary tube having an inlet port and an outlet port with a gas flow passage therebetween,

means for communicating said outlet port with a sample vessel adapted to be held under a negative pressure, and

a filter operatively connected to said inlet port for prevention of entry of particulate matter into said flow passage,

said capillary tube having a length and an internal diameter selected such as to provide flow control of gas or ambient air at said outlet port.

17. A controller according to claim 16, wherein the length and internal diameter are selected in accordance with the relationship

$$L = \frac{K_6 R^4 t}{\left(e^{\frac{t_F}{K_5}} - 1\right)}$$

wherein

L is the length of the capillary in meters,

R is the internal radius of the capillary in meters,

V_f is the final sampled volume in cubic meters,
t is the time in seconds, and
K_5 and K_6 are constants for the system in which

$$K_5 = \frac{P_{atm} V_s \overline{V}}{\mathbb{R} T}$$

and

$$K_6 = \frac{\pi \mathbb{R} T}{8 \mu V_s \overline{V}}$$

wherein
P_{atm} is atmospheric pressure (Pa)
V is the molar volume (m^3/mole)
$\mathbb{R}$ is the gas constant (N.m/mol.k)
T is the temperature (°K), and
V_s is the volume of the vessel (m^3).

18. A controller according to claim 17, wherein said length ranges from 5 cm to 5000 cm and said internal diameter ranges from 0.53 mm.

19. A controller according to claim 17, wherein said capillary tube is enclosed within a protective housing containing packing material for absorbing vibrations and preventing breakage of the tube during transportation or handling, and including an elongate sampling line connecting said inlet port and said filter.

20. A controller according to claim 17, further including a pressure measuring device operatively connected to said outlet port.

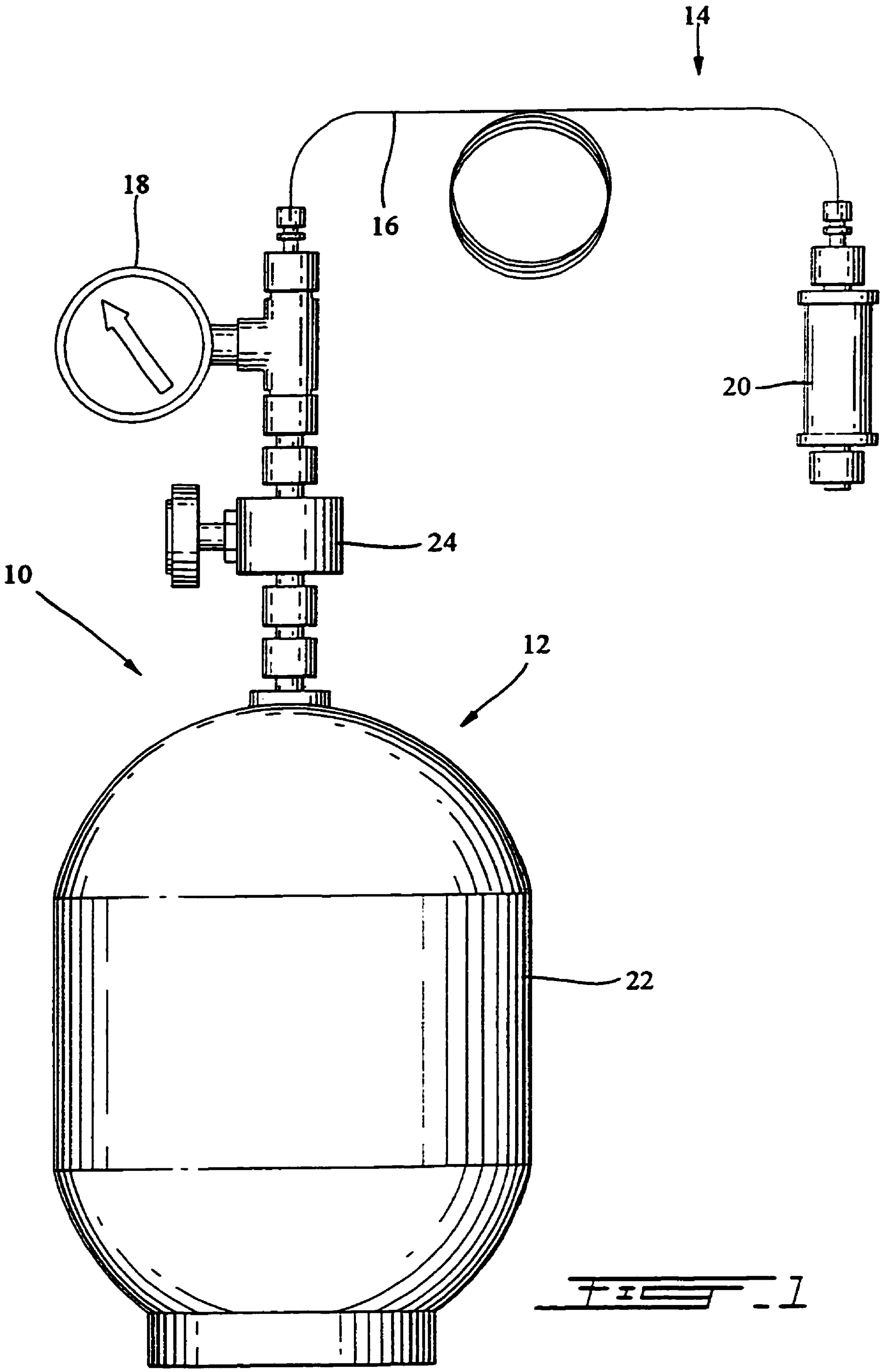


FIG. 1

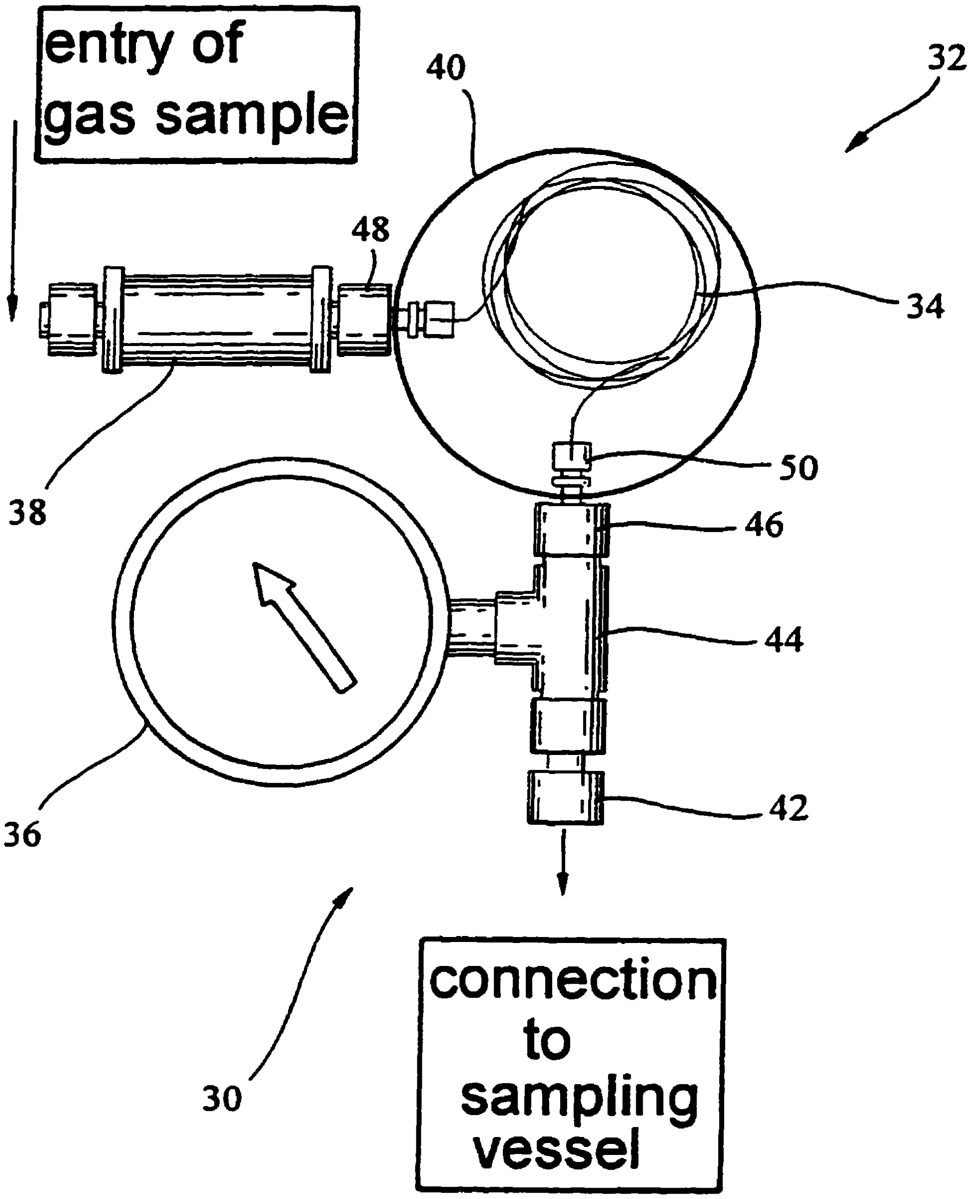

entry of gas sample
40
32
48
34
38
50
46
44
36
42
30
connection to sampling vessel

FIG. 2

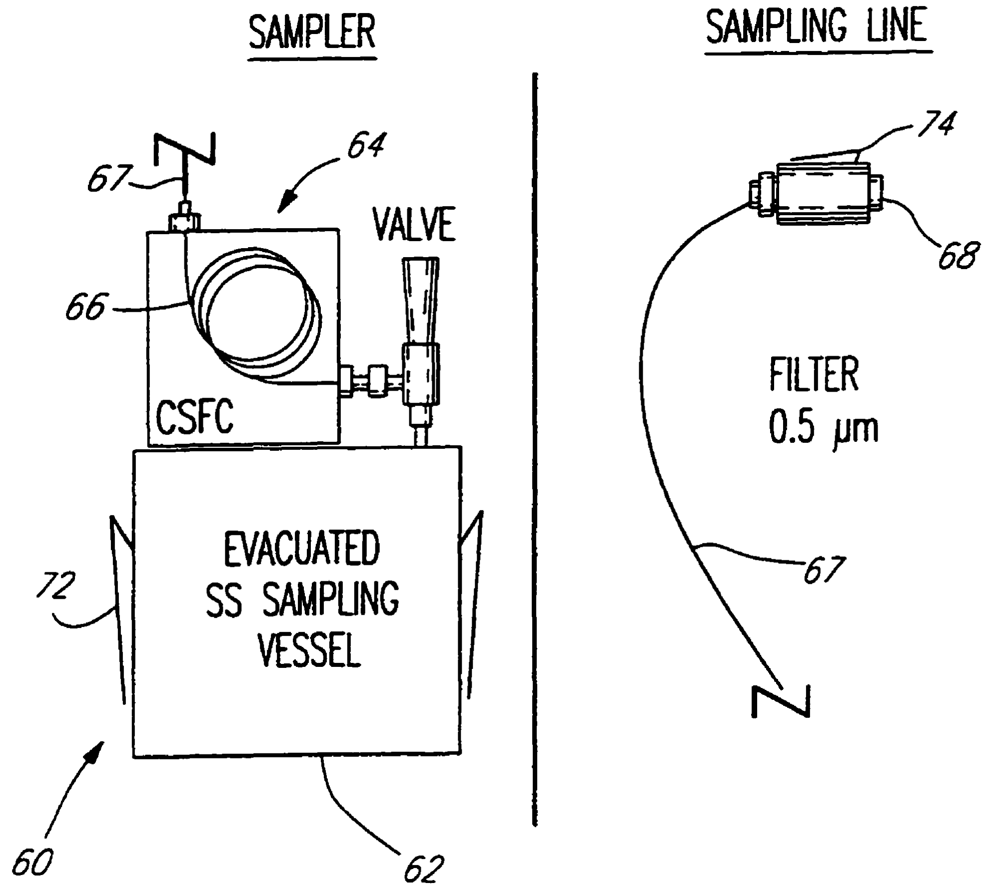

SAMPLER
SAMPLING LINE
64
67
VALVE
74
66
68
CSFC
FILTER
0.5 µm
EVACUATED
SS SAMPLING
VESSEL
72
67
60
62

FIG. 3

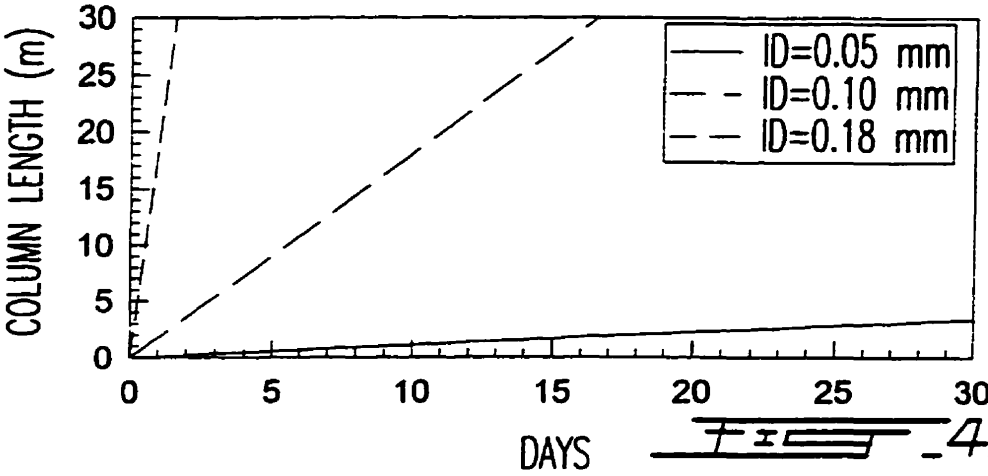


Fig. 4a

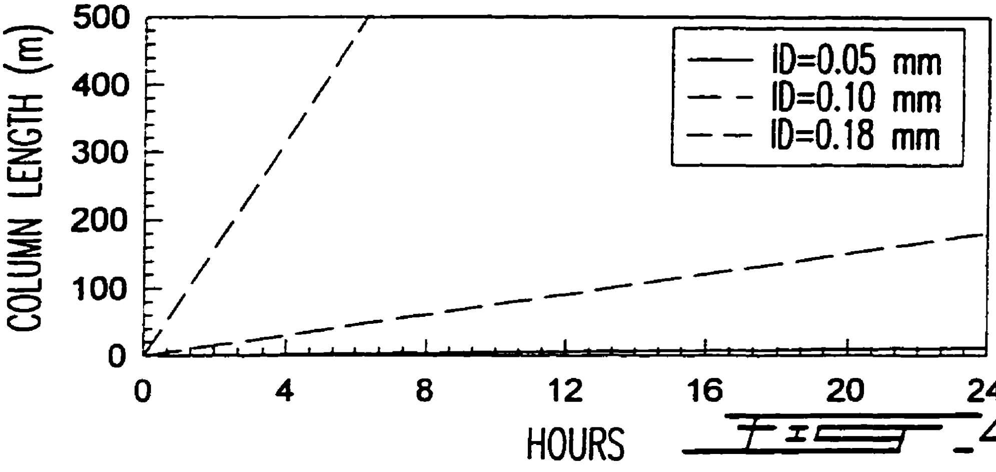


Fig. 4b

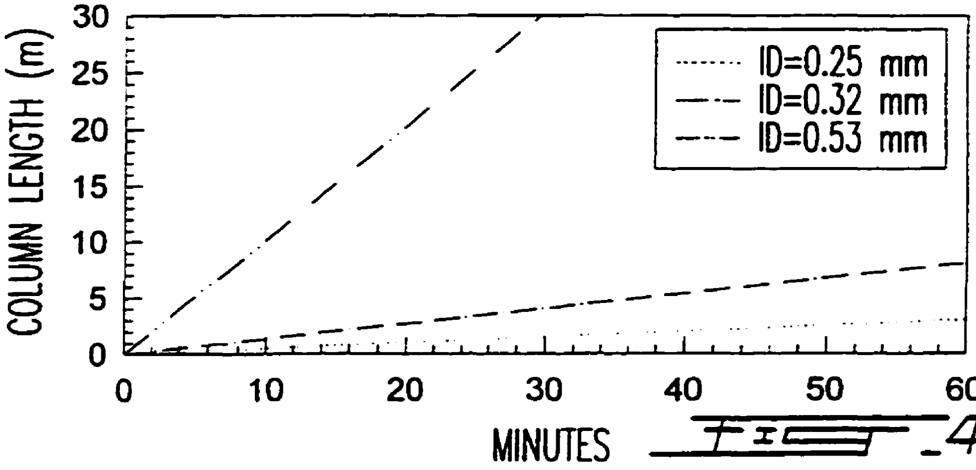


Fig. 4c

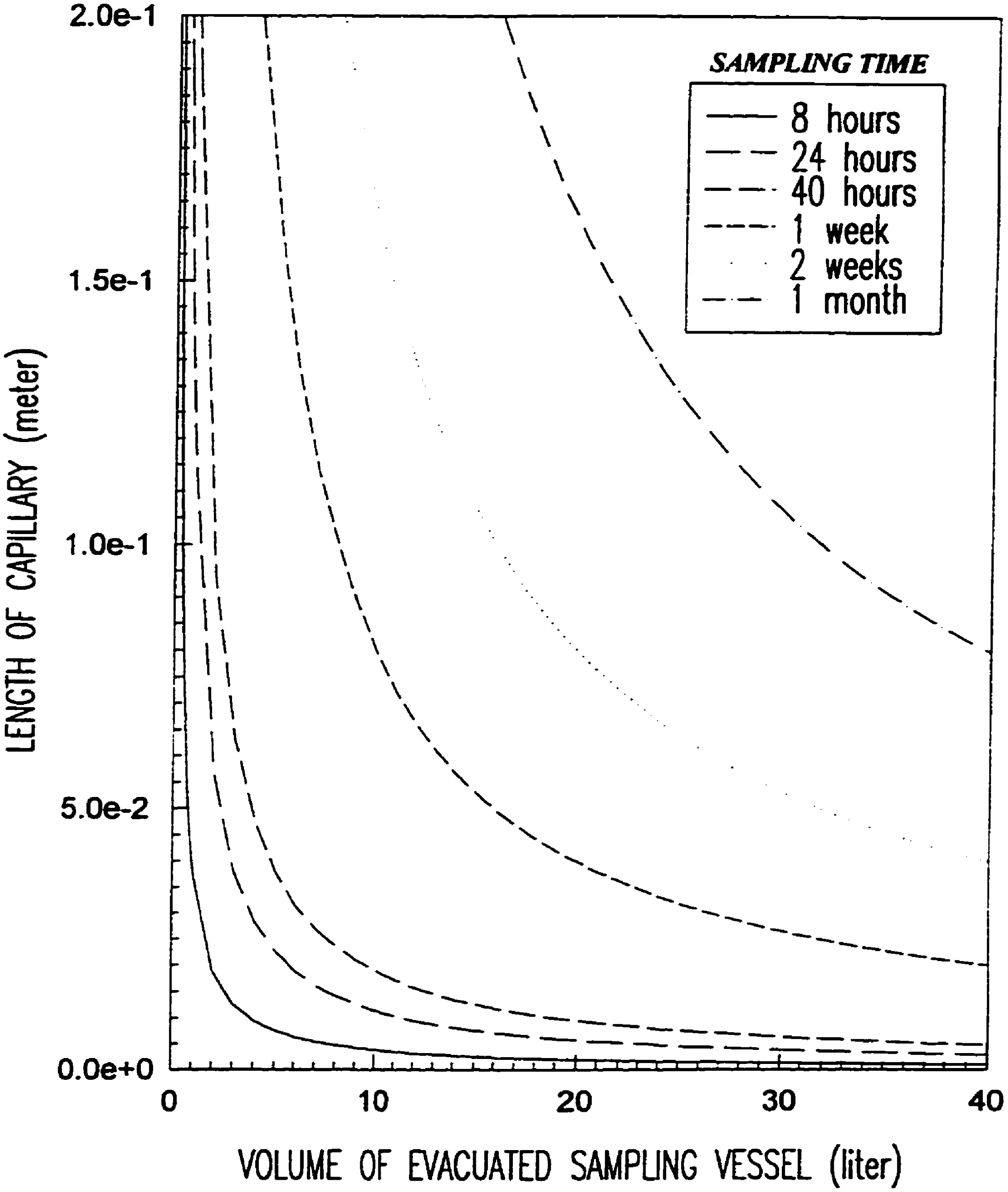

2.0e-1
1.5e-1
1.0e-1
5.0e-2
0.0e+0
LENGTH OF CAPILLARY (meter)
0
10
20
30
40
VOLUME OF EVACUATED SAMPLING VESSEL (liter)
SAMPLING TIME
8 hours
24 hours
40 hours
1 week
2 weeks
1 month

FIG. 5

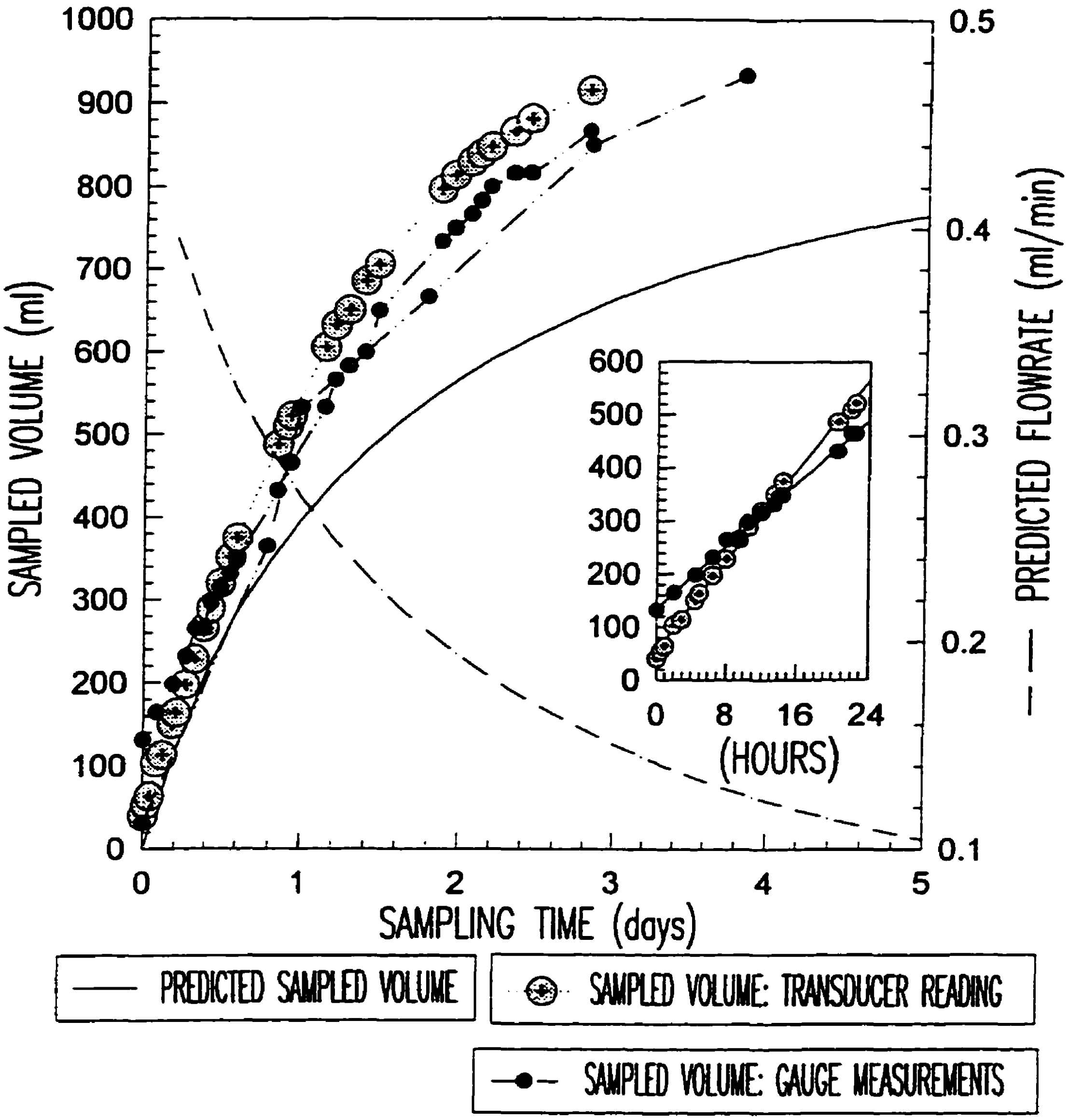

1000
900
800
700
600
500
400
300
200
100
0
SAMPLED VOLUME (ml)
0.5
0.4
0.3
0.2
0.1
PREDICTED FLOWRATE (ml/min)
0
1
2
3
4
5
SAMPLING TIME (days)
600
500
400
300
200
100
0
0
8
16
24
(HOURS)
PREDICTED SAMPLED VOLUME
SAMPLED VOLUME: TRANSDUCER READING
SAMPLED VOLUME: GAUGE MEASUREMENTS

FIG_6

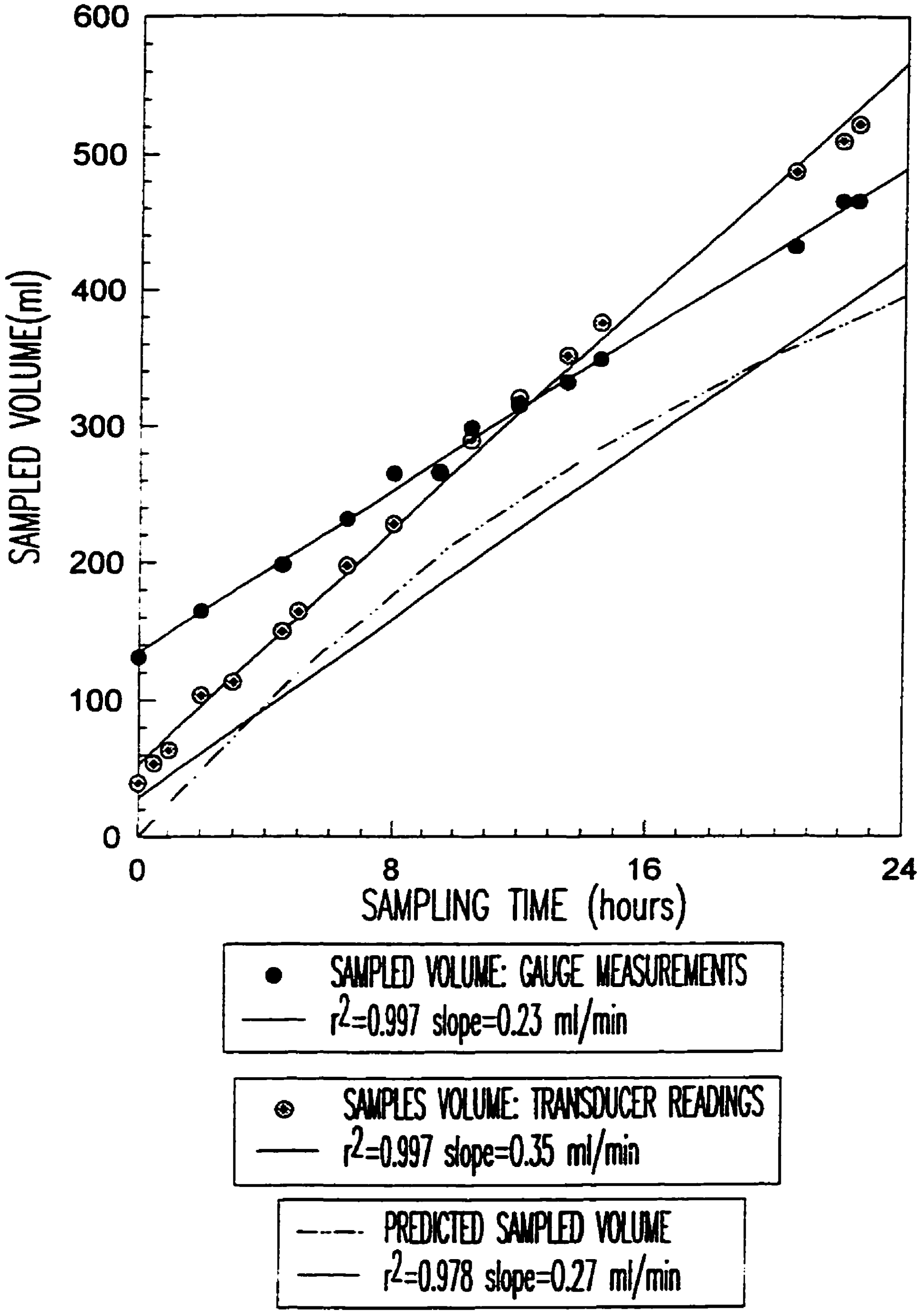

600
500
400
300
200
100
0
SAMPLED VOLUME(ml)
0
8
16
24
SAMPLING TIME (hours)
SAMPLED VOLUME: GAUGE MEASUREMENTS
r2=0.997 slope=0.23 ml/min
SAMPLES VOLUME: TRANSDUCER READINGS
r2=0.997 slope=0.35 ml/min
PREDICTED SAMPLED VOLUME
r2=0.978 slope=0.27 ml/min

FIG. 7

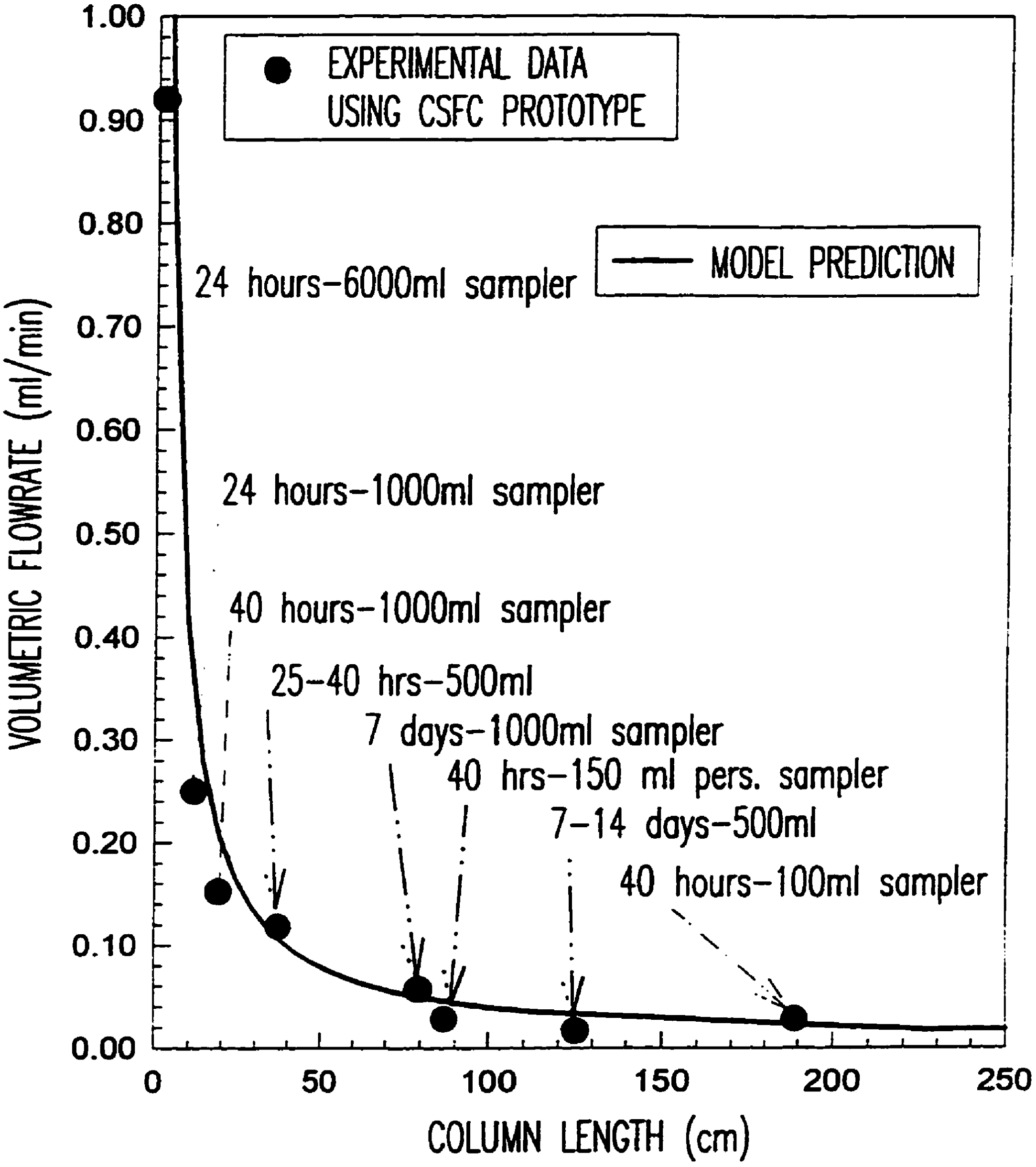

1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
VOLUMETRIC FLOWRATE (ml/min)
0
50
100
150
200
250
COLUMN LENGTH (cm)
● EXPERIMENTAL DATA USING CSFC PROTOTYPE
MODEL PREDICTION
24 hours-6000ml sampler
24 hours-1000ml sampler
40 hours-1000ml sampler
25-40 hrs-500ml
7 days-1000ml sampler
40 hrs-150 ml pers. sampler
7-14 days-500ml
40 hours-100ml sampler

FIG_8

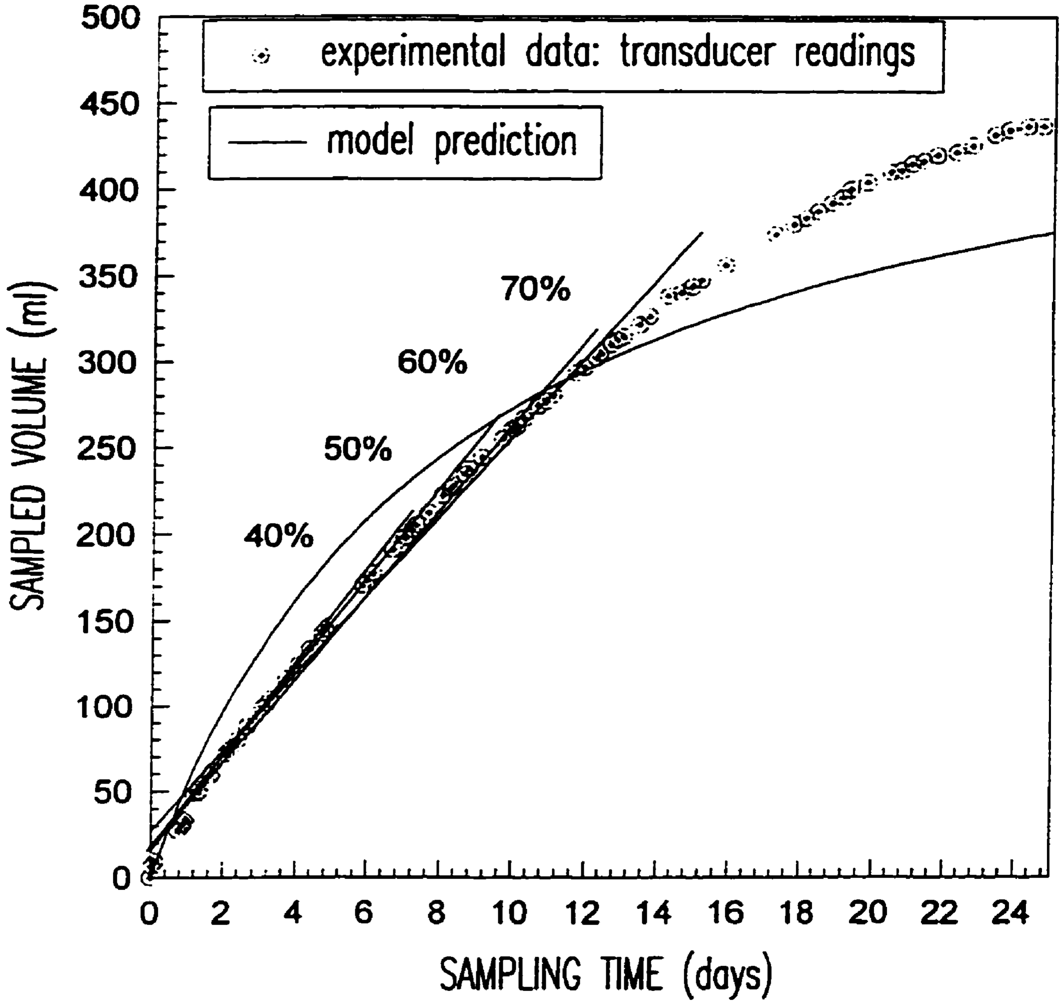

experimental data: transducer readings
model prediction
40%
50%
60%
70%
SAMPLED VOLUME (ml)
0
50
100
150
200
250
300
350
400
450
500
0
2
4
6
8
10
12
14
16
18
20
22
24
SAMPLING TIME (days)

FIG. 9

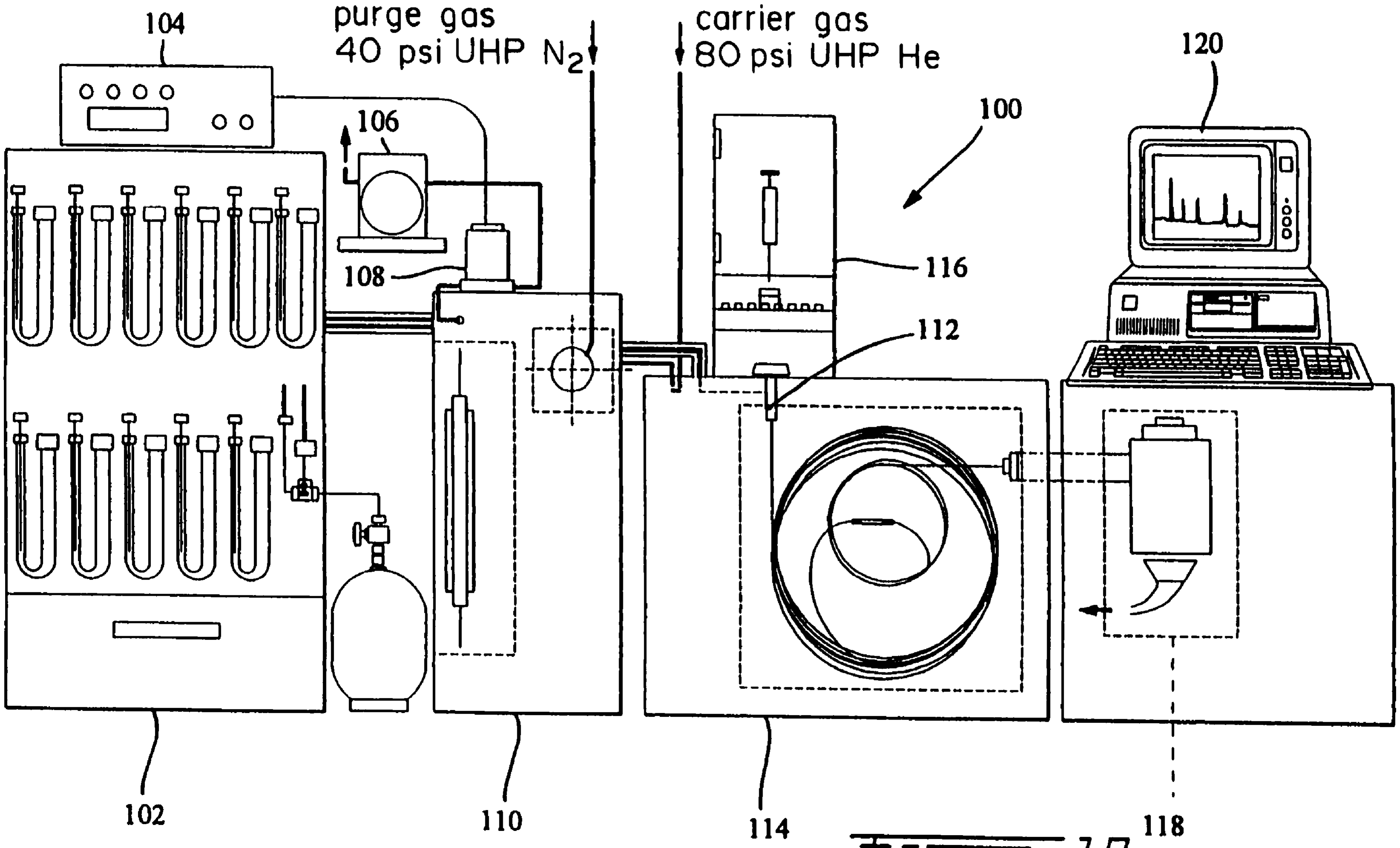

104
purge gas
40 psi UHP N_2
carrier gas
80 psi UHP He
120
106
100
116
108
112
102
110
114
118

FIG-10

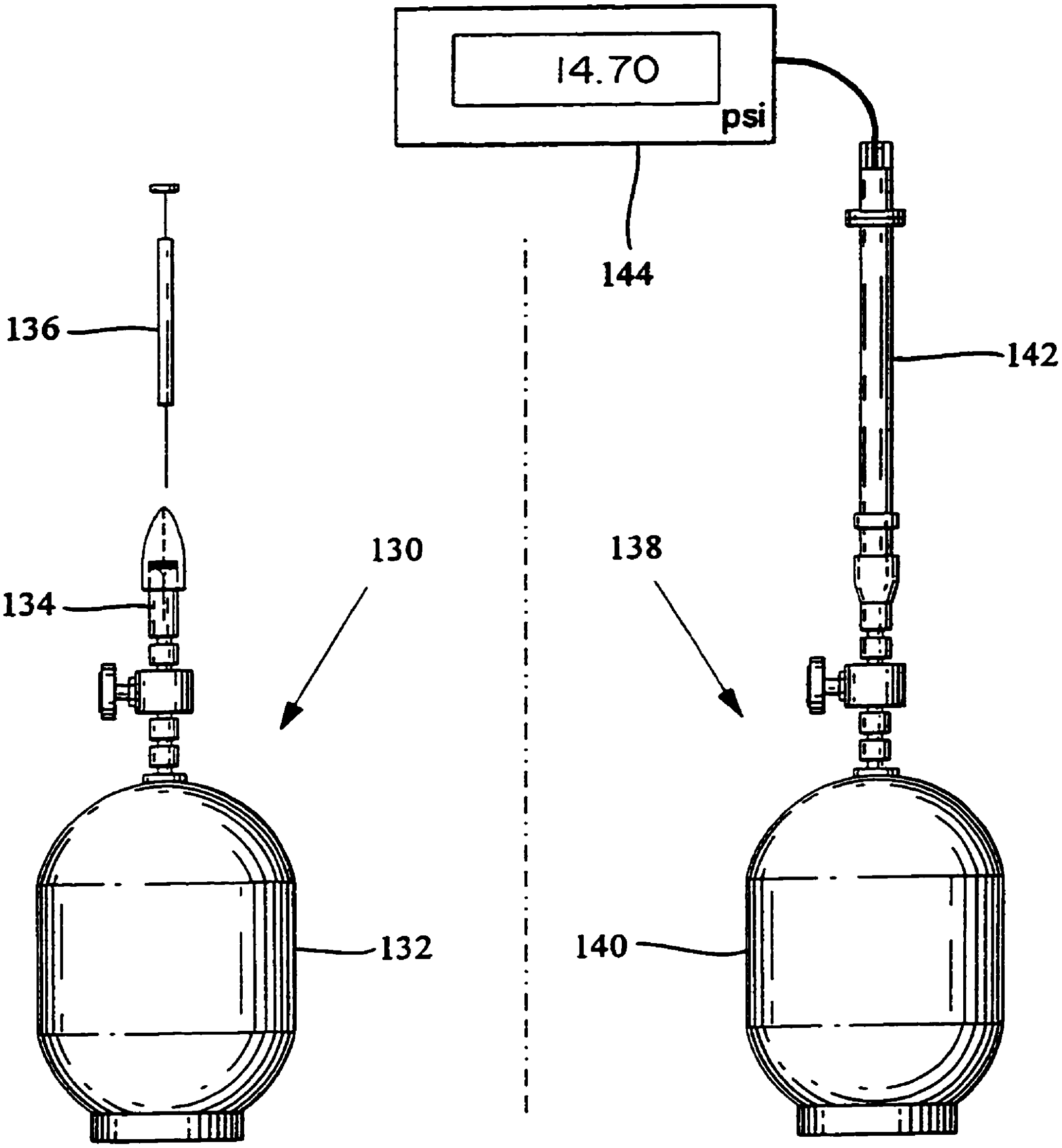


FIG. 11

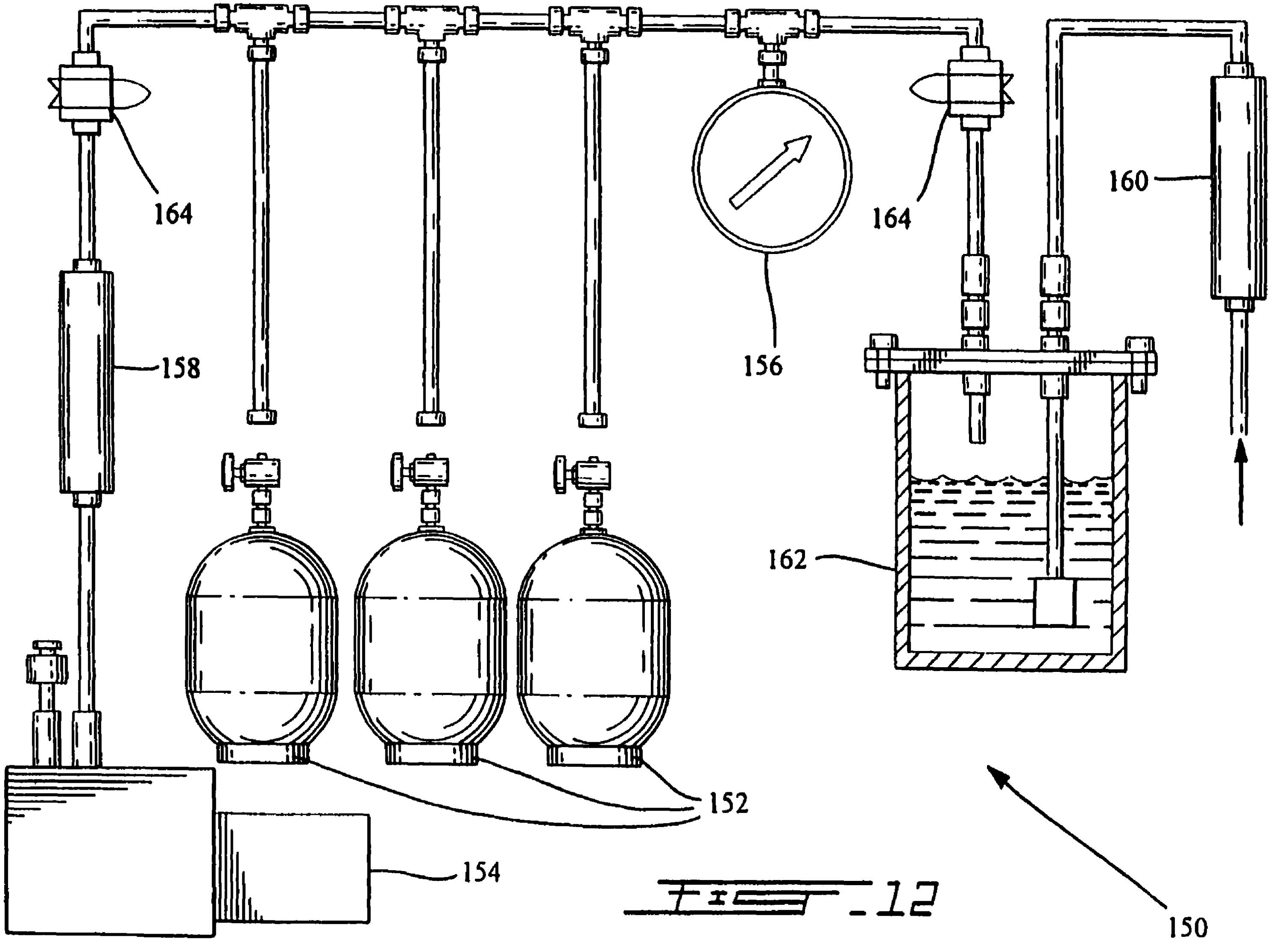


FIG. 12

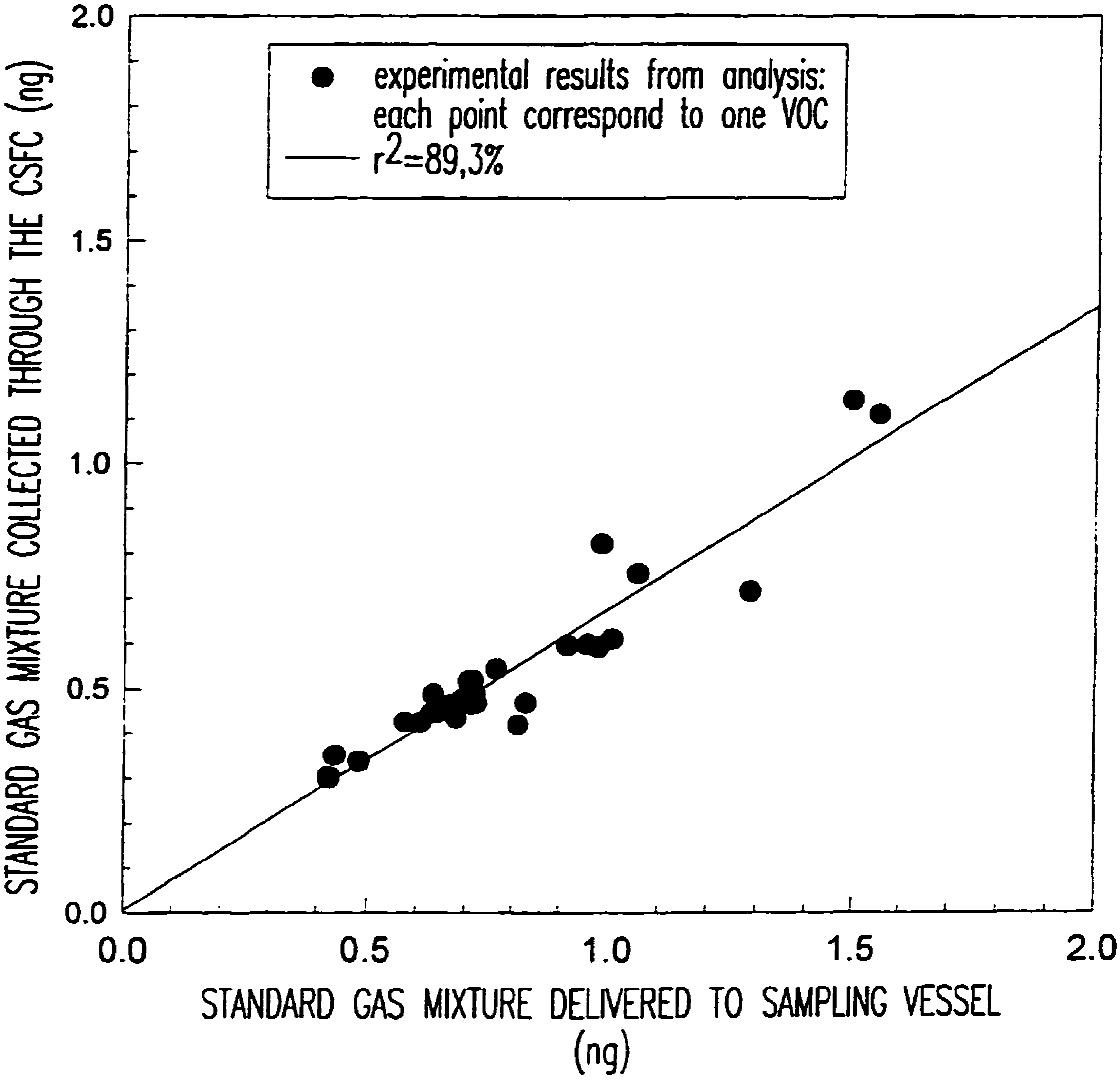
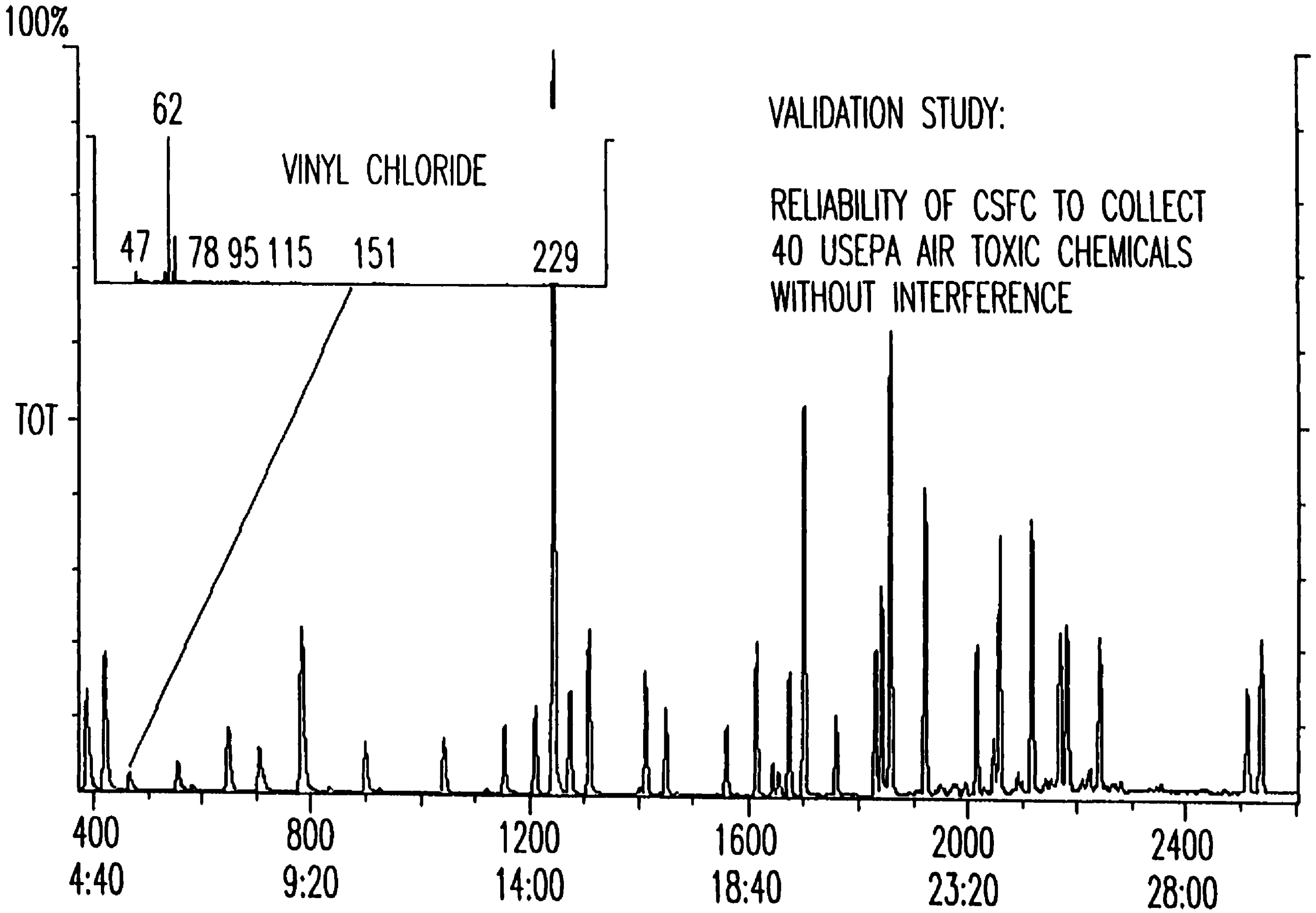
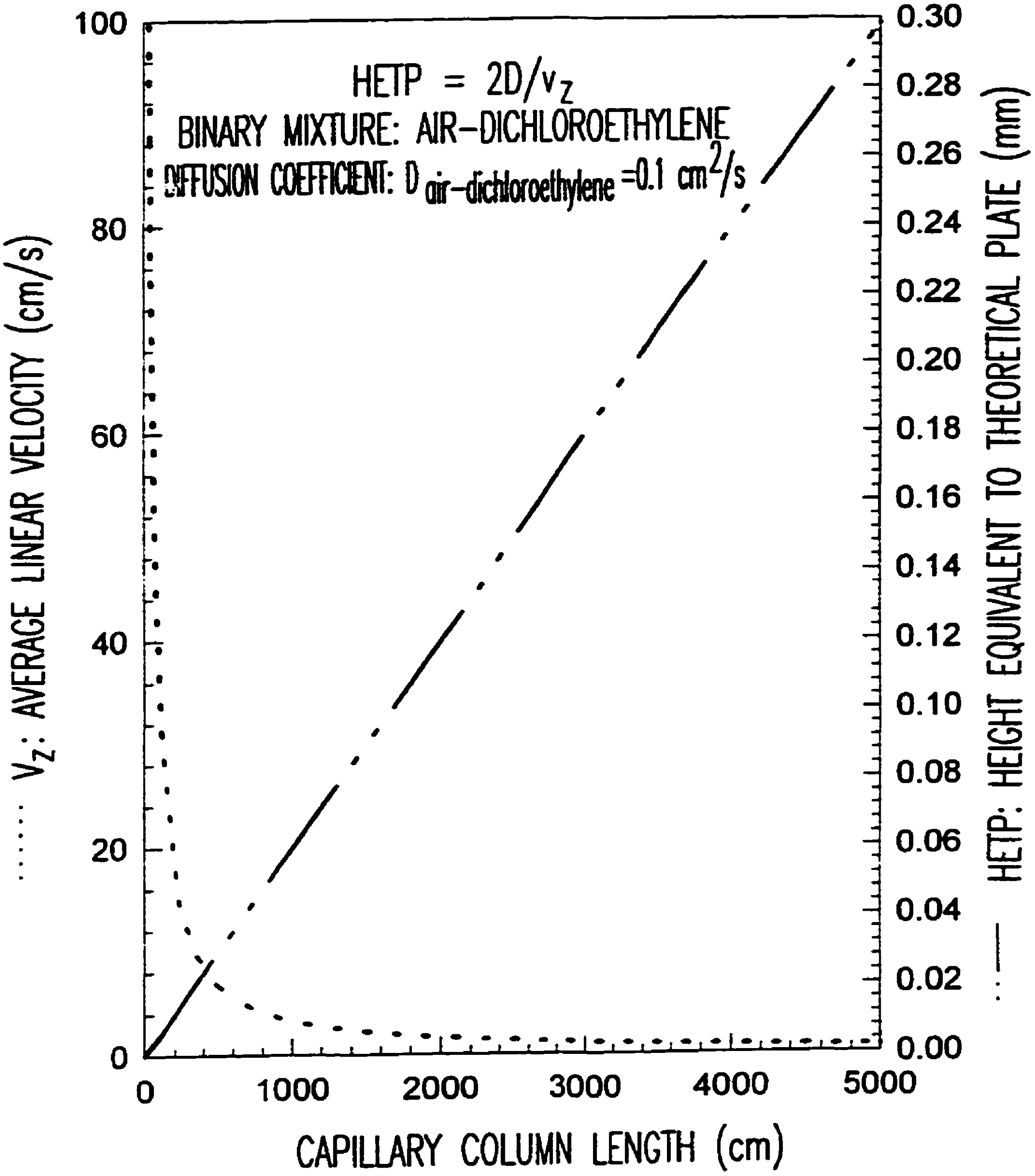

2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
● experimental results from analysis: each point correspond to one VOC
r2=89,3%
STANDARD GAS MIXTURE COLLECTED THROUGH THE CSFC (ng)
STANDARD GAS MIXTURE DELIVERED TO SAMPLING VESSEL (ng)

FIG. 13



100%
TOT
62
VINYL CHLORIDE
47
78 95 115
151
229
VALIDATION STUDY:
RELIABILITY OF CSFC TO COLLECT
40 USEPA AIR TOXIC CHEMICALS
WITHOUT INTERFERENCE
400
4:40
800
9:20
1200
14:00
1600
18:40
2000
23:20
2400
28:00

FIG. 14



HETP = 2D/v_Z
BINARY MIXTURE: AIR-DICHLOROETHYLENE
DIFFUSION COEFFICIENT: $D_{air-dichloroethylene}$ = 0.1 cm^2/s
v_Z: AVERAGE LINEAR VELOCITY (cm/s)
HETP: HEIGHT EQUIVALENT TO THEORETICAL PLATE (mm)
CAPILLARY COLUMN LENGTH (cm)
0
20
40
60
80
100
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22
0.24
0.26
0.28
0.30
0
1000
2000
3000
4000
5000

FIG. 15

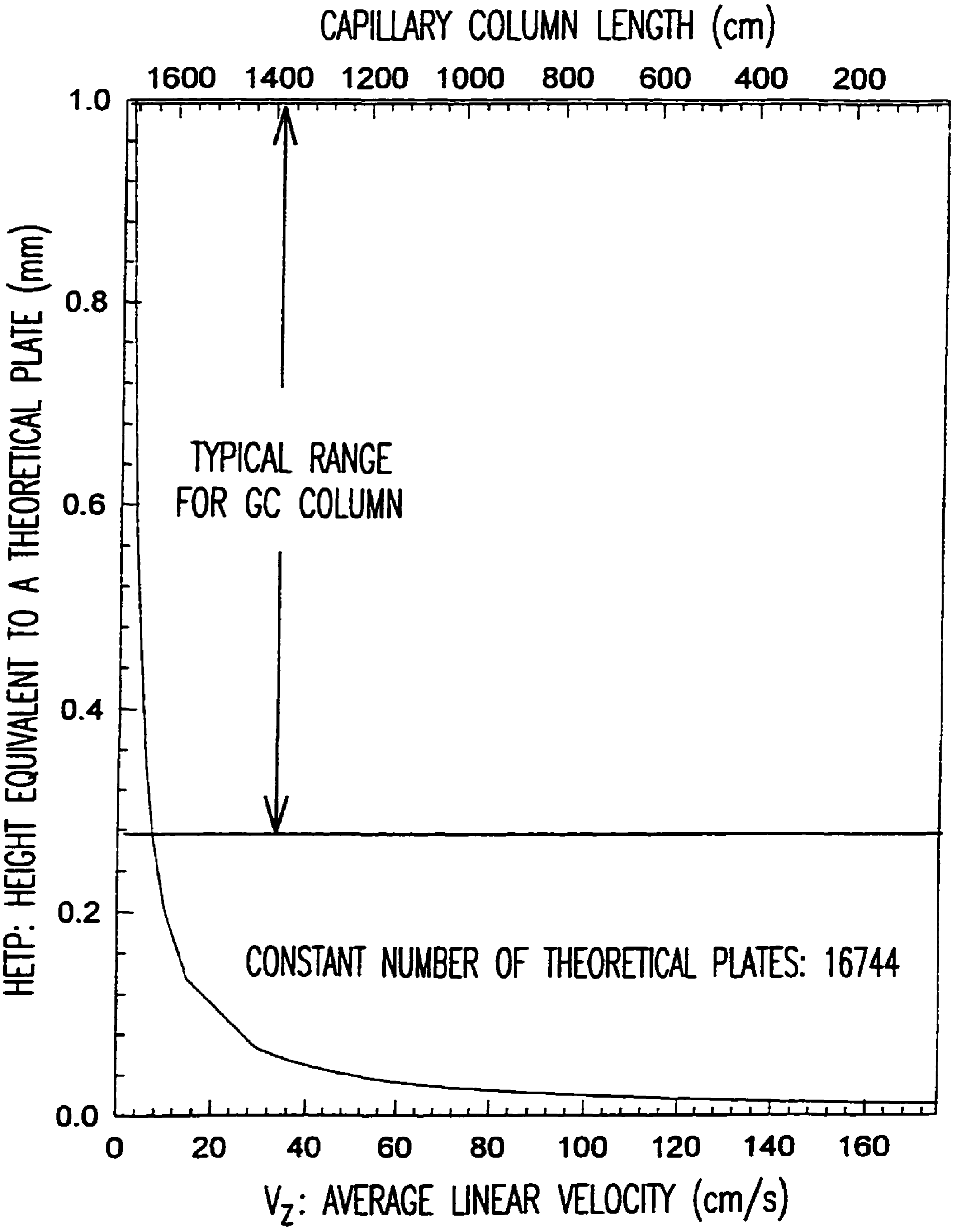

CAPILLARY COLUMN LENGTH (cm)
1600
1400
1200
1000
800
600
400
200
1.0
0.8
0.6
0.4
0.2
0.0
HETP: HEIGHT EQUIVALENT TO A THEORETICAL PLATE (mm)
TYPICAL RANGE FOR GC COLUMN
CONSTANT NUMBER OF THEORETICAL PLATES: 16744
0
20
40
60
80
100
120
140
160
V_Z: AVERAGE LINEAR VELOCITY (cm/s)

FIG - 16

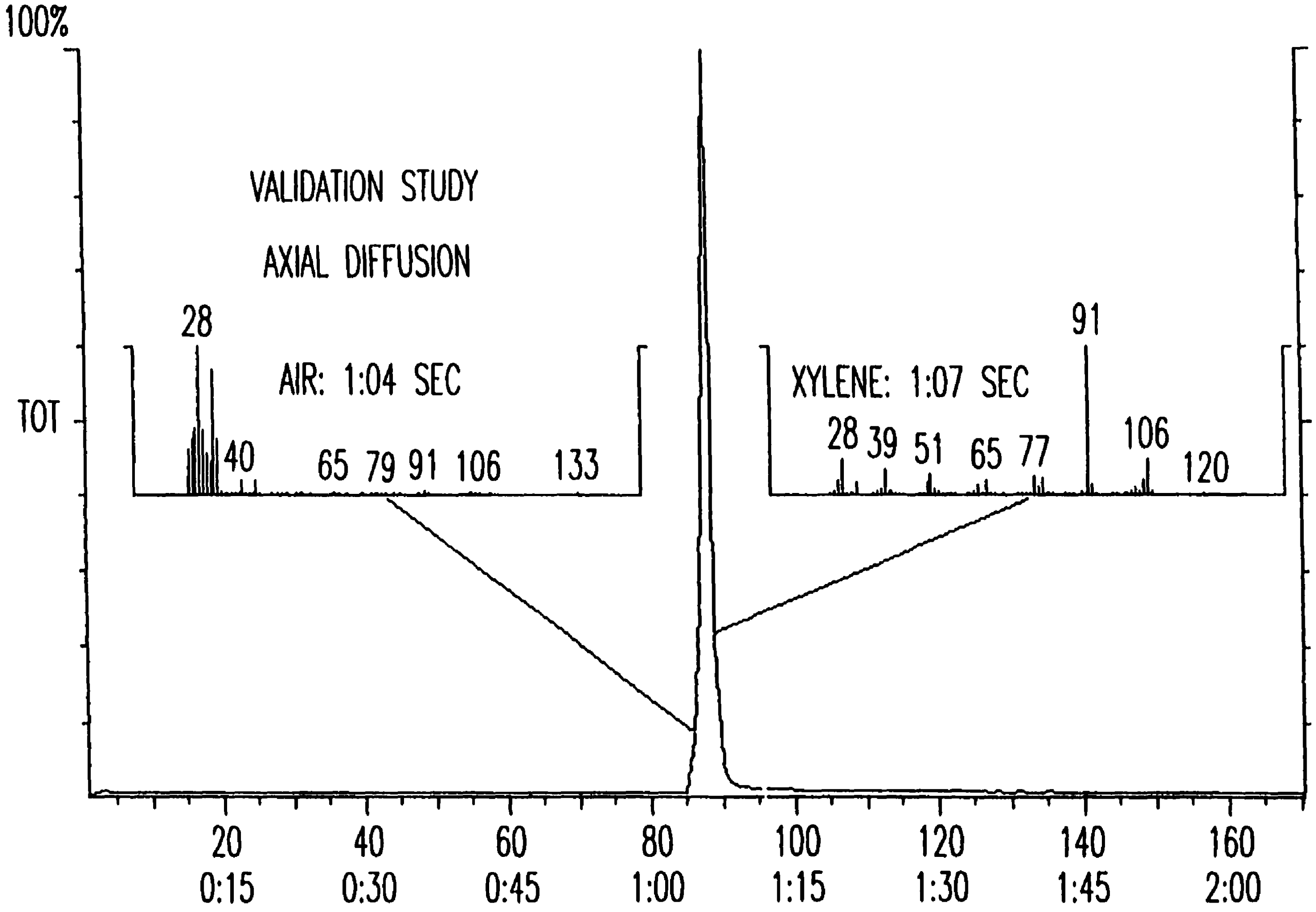

100%
TOT
VALIDATION STUDY
AXIAL DIFFUSION
28
AIR: 1:04 SEC
40
65
79
91
106
133
91
XYLENE: 1:07 SEC
28
39
51
65
77
106
120
20
0:15
40
0:30
60
0:45
80
1:00
100
1:15
120
1:30
140
1:45
160
2:00

FIG. 17

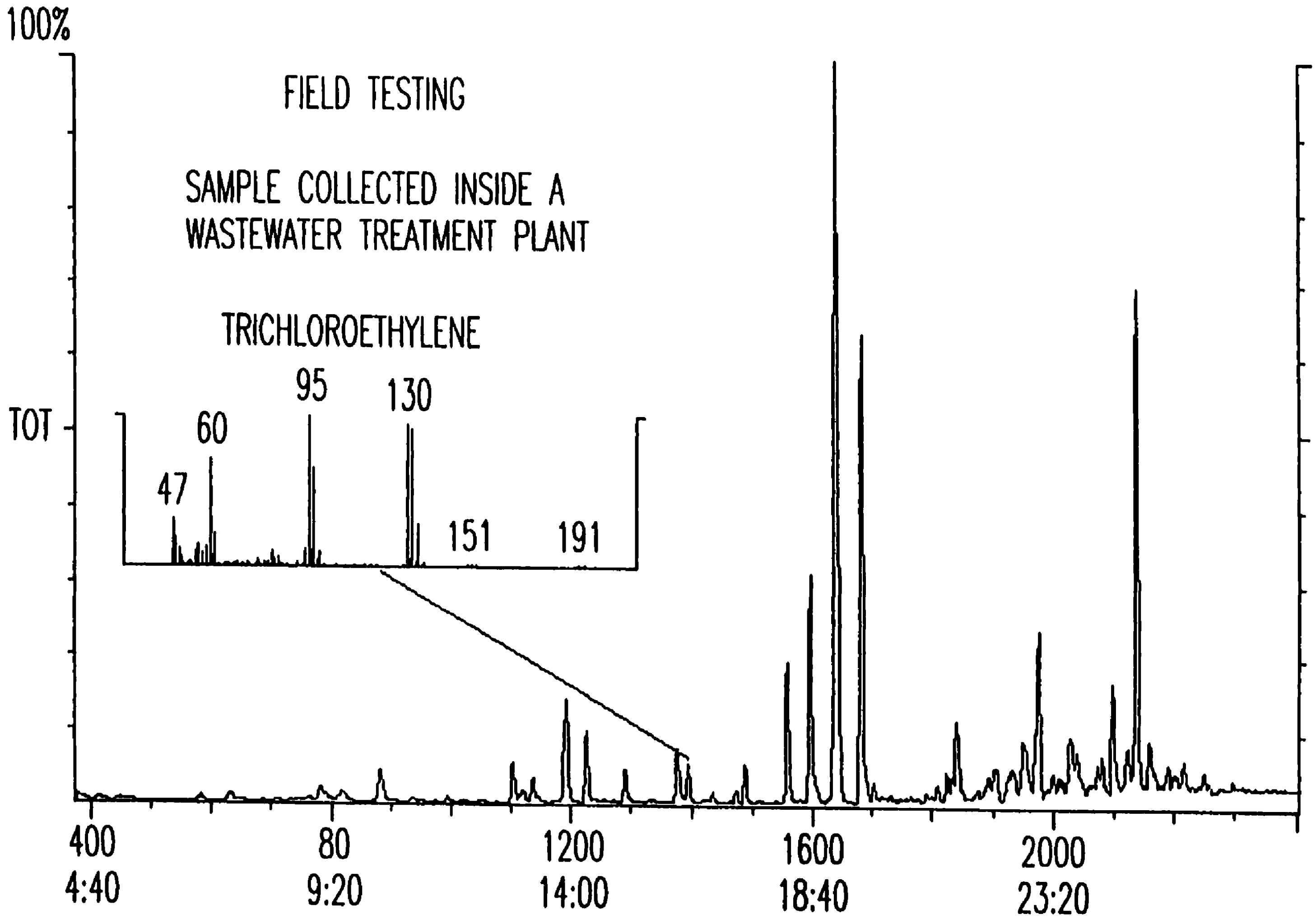
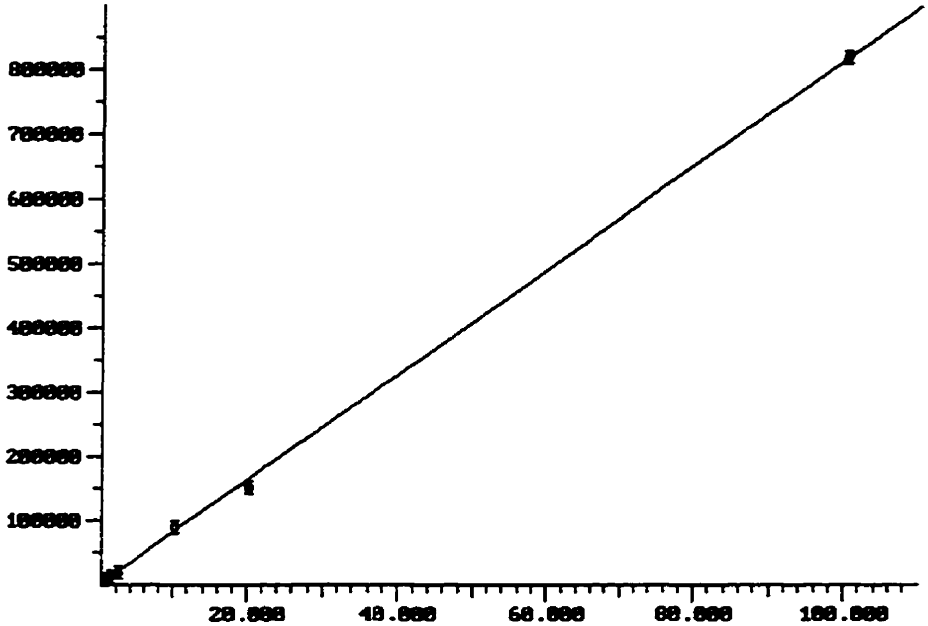

100%
FIELD TESTING
SAMPLE COLLECTED INSIDE A WASTEWATER TREATMENT PLANT
TRICHLOROETHYLENE
95
130
60
47
151
191
TOT
400
4:40
80
9:20
1200
14:00
1600
18:40
2000
23:20

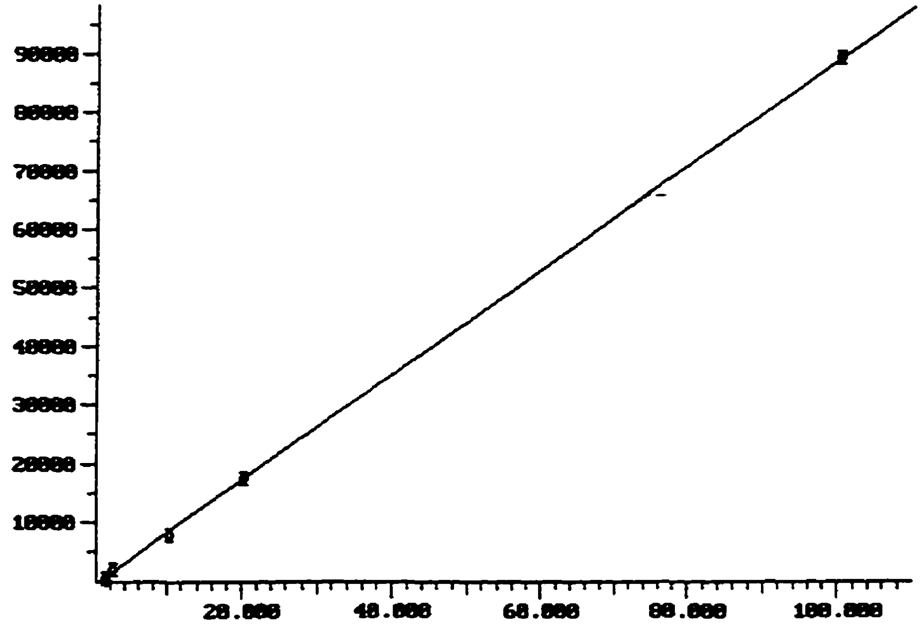
FIG. 18

APPENDIX-2: Calibration curves for VOCs

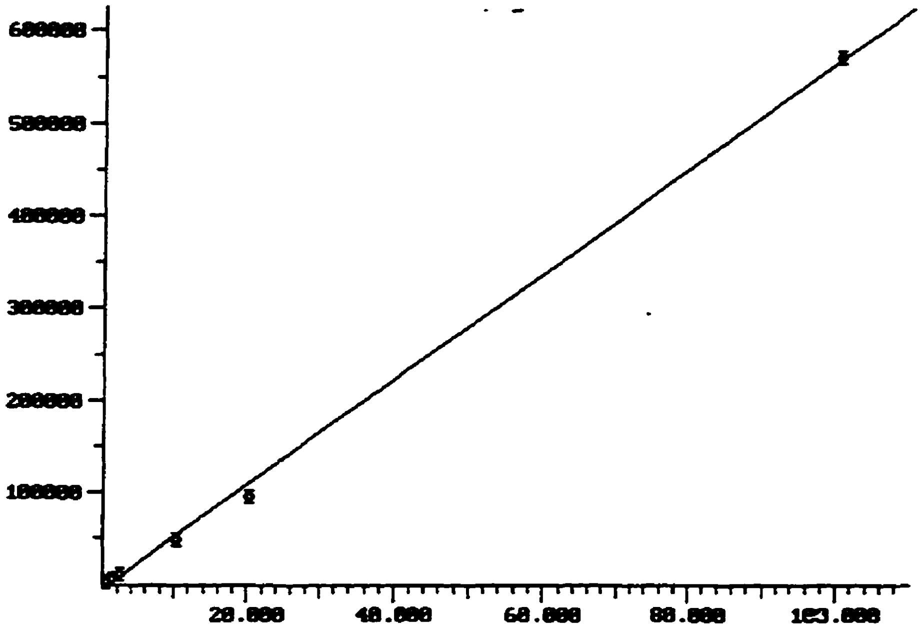
```
Calibration Plot (Ext Stds)   Filename: UMIXLOWP    Correlation  Coeff: 1.000
Dichlorodifluoromethane       Compound: 1 of 54     Standard Deviation: 6.500
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



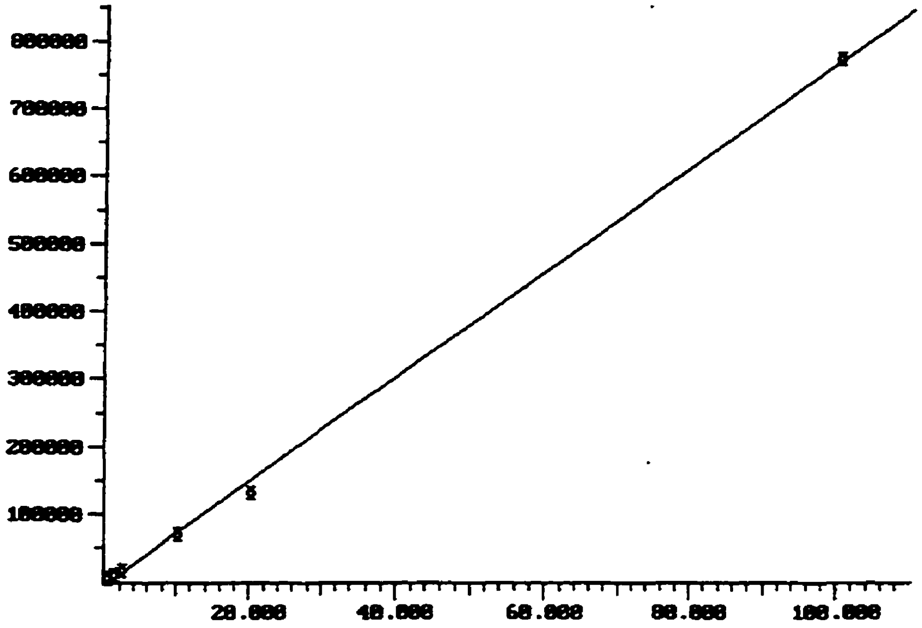
```
Calibration Plot (Ext Stds)   Filename: UMIXLOWP    Correlation  Coeff: 1.000
Chloromethane                 Compound: 2 of 54     Standard Deviation: 0.325
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



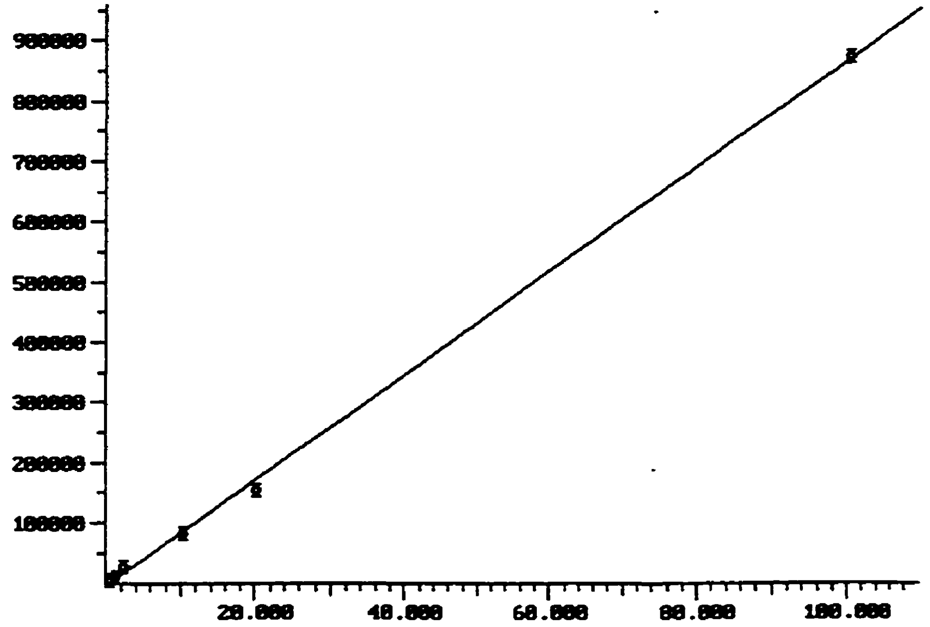
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Vinyl chloride Compound: 3 of 54 Standard Deviation: 6.987
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



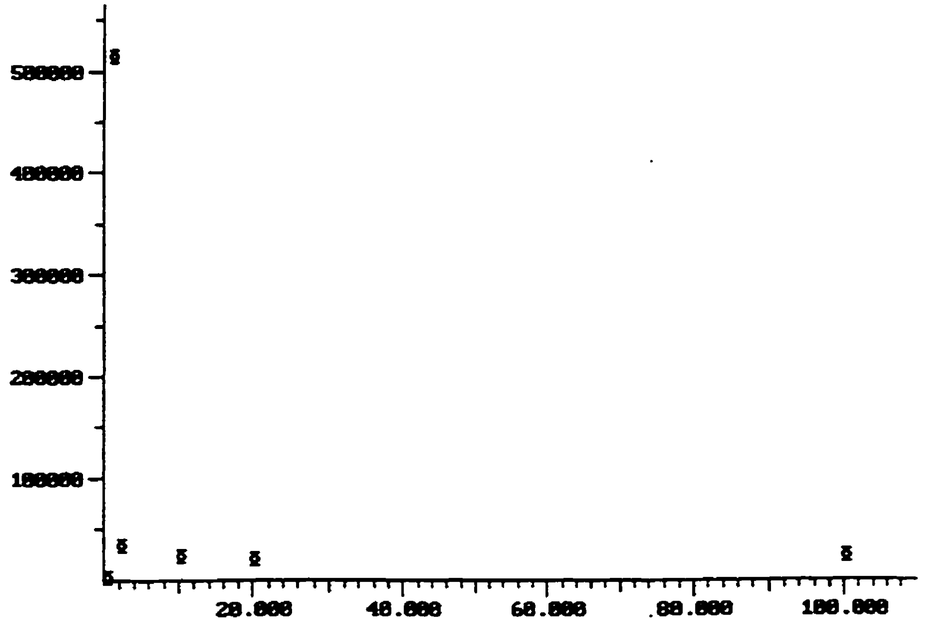
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 1.000
Trichlorofluoromethane Compound: 4 of 54 Standard Deviation: 0.779
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



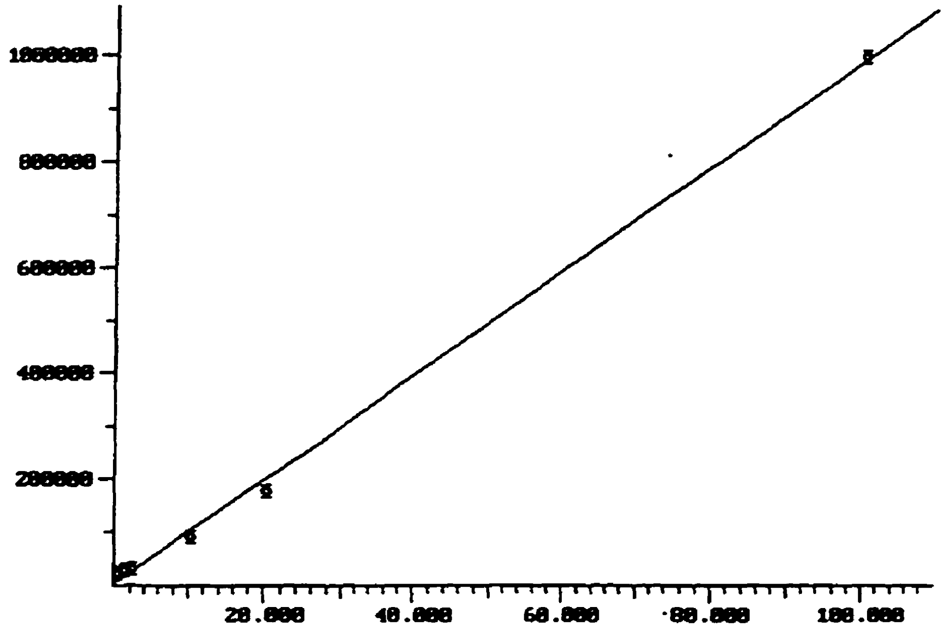
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 1.000
1,1-Dichloroethene Compound: 5 of 54 Standard Deviation: 9.549
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



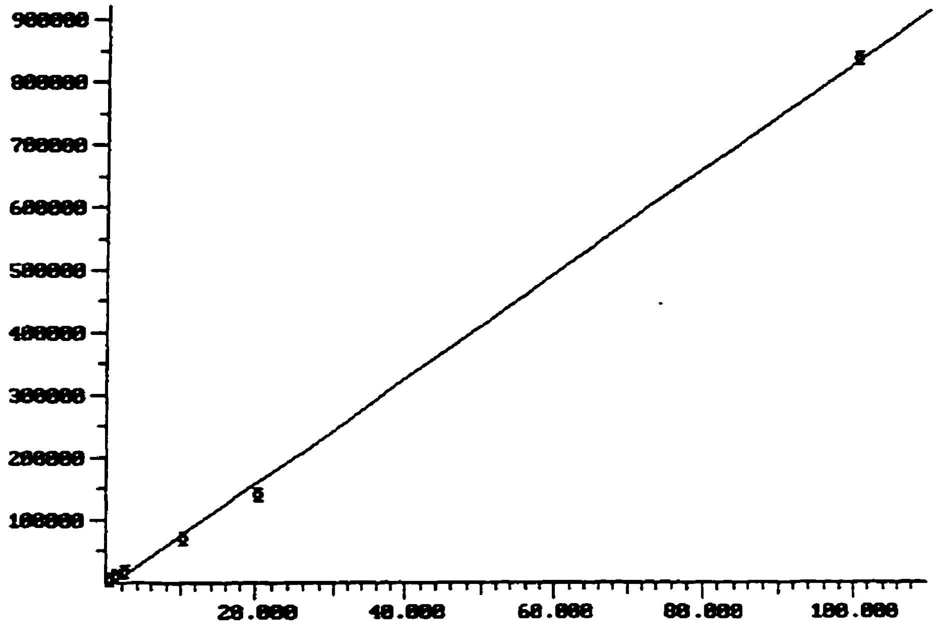
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.259
Carbon Disulfide Compound: 6 of 54 Calibration Points: 6
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



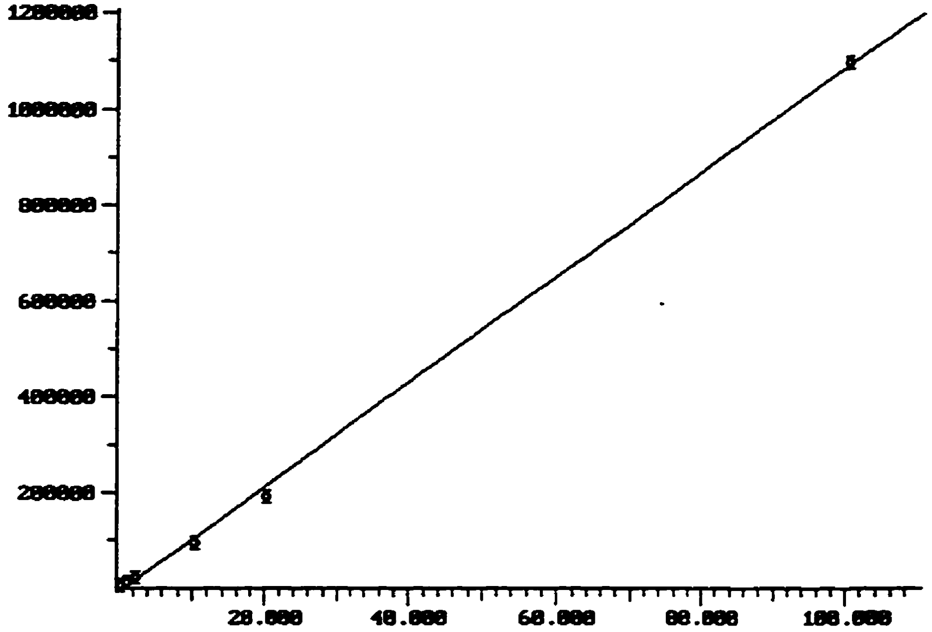
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Dichloromethane Compound: 7 of 54 Standard Deviation: 14.859
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



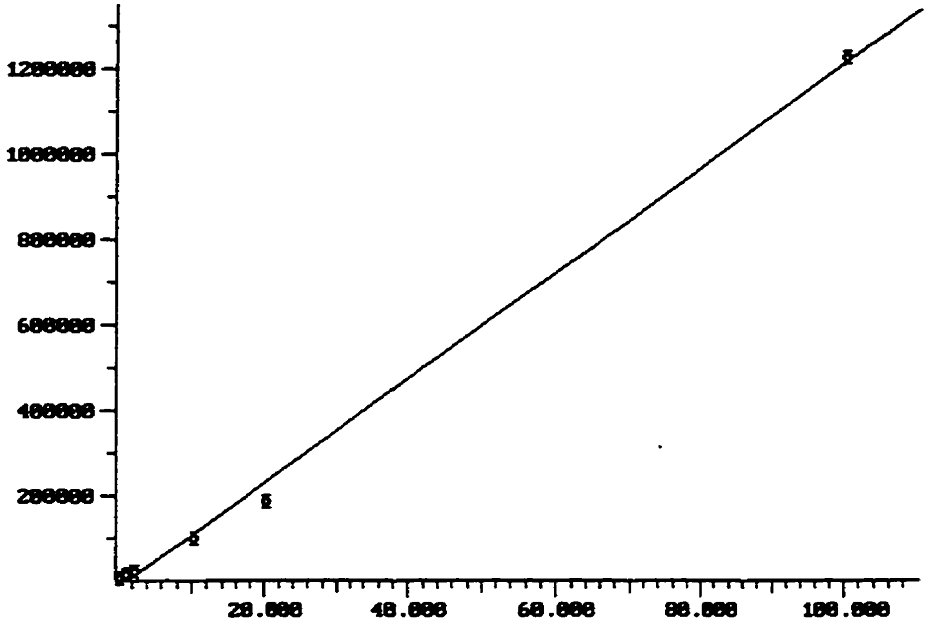
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
trans-1,2-Dichloroethene Compound: 8 of 54 Standard Deviation: 10.481
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



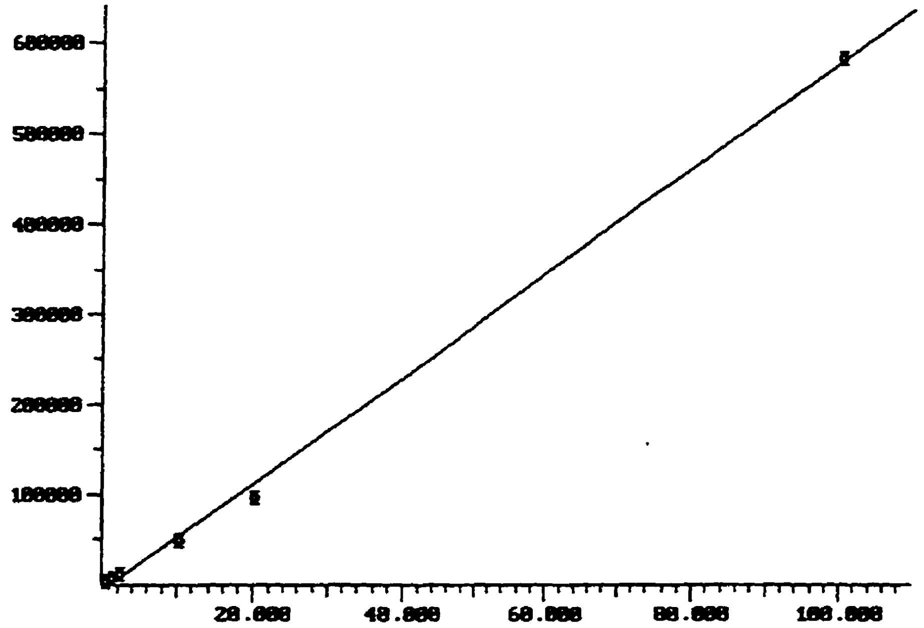
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 1.000
1,1-Dichloroethane            Compound: 9 of 54     Standard Deviation: 11.344
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



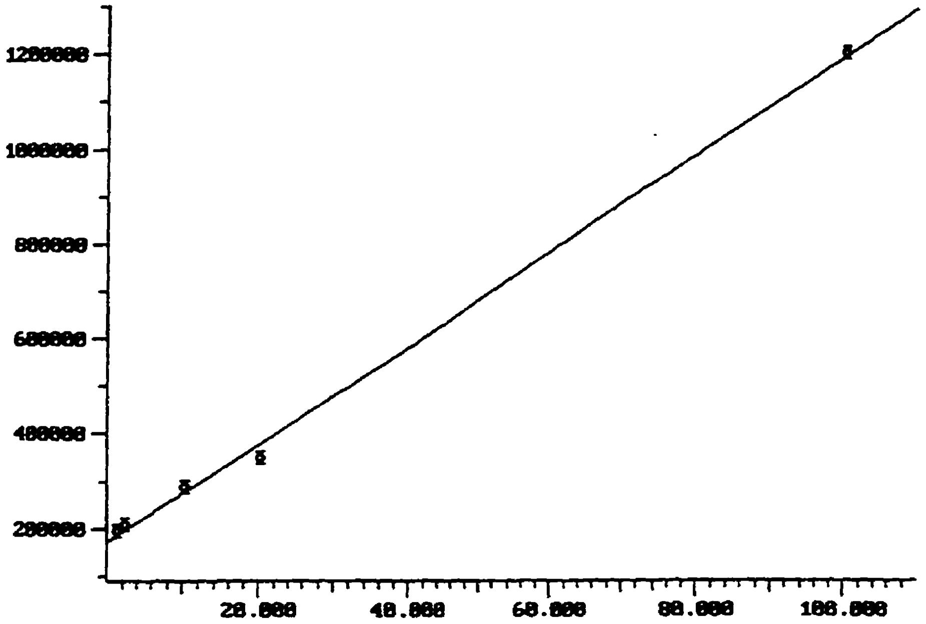
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
2,2-Dichloropropane           Compound: 10 of 54    Standard Deviation: 22.533
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



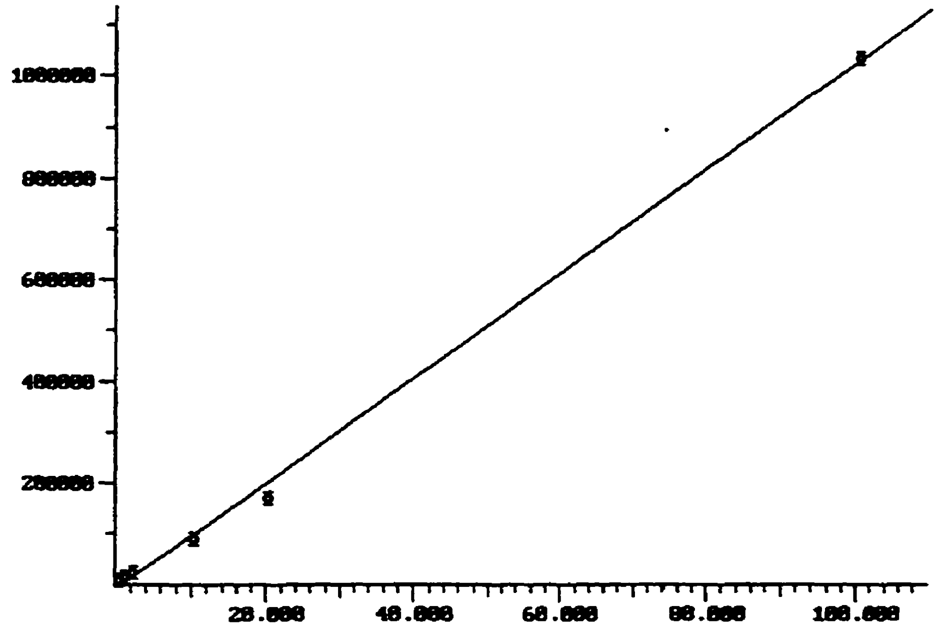
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Bromochloromethane Compound: 11 of 54 Standard Deviation: 7.933
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



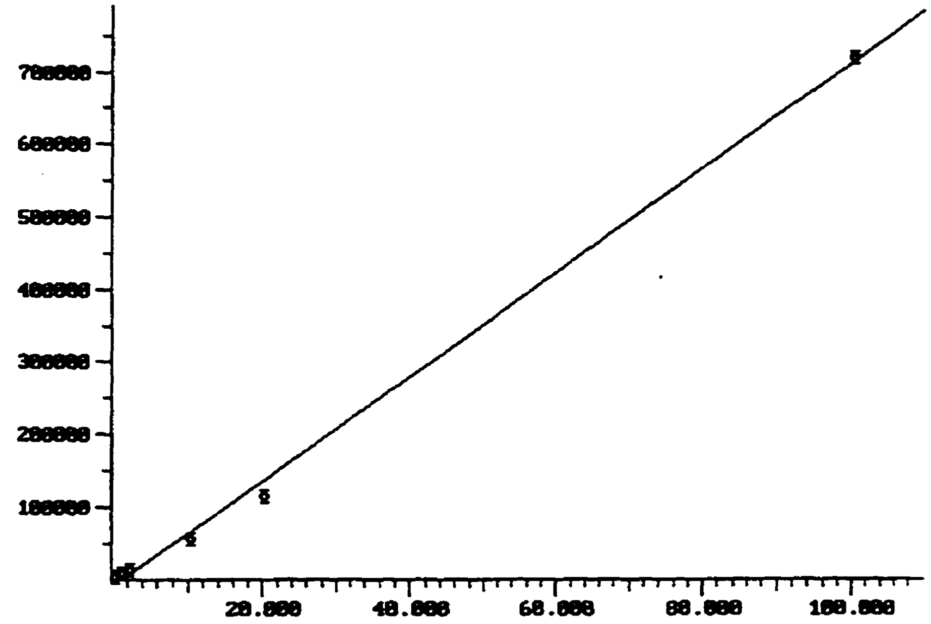
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Chloroform Compound: 12 of 54 Standard Deviation: 16.713
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



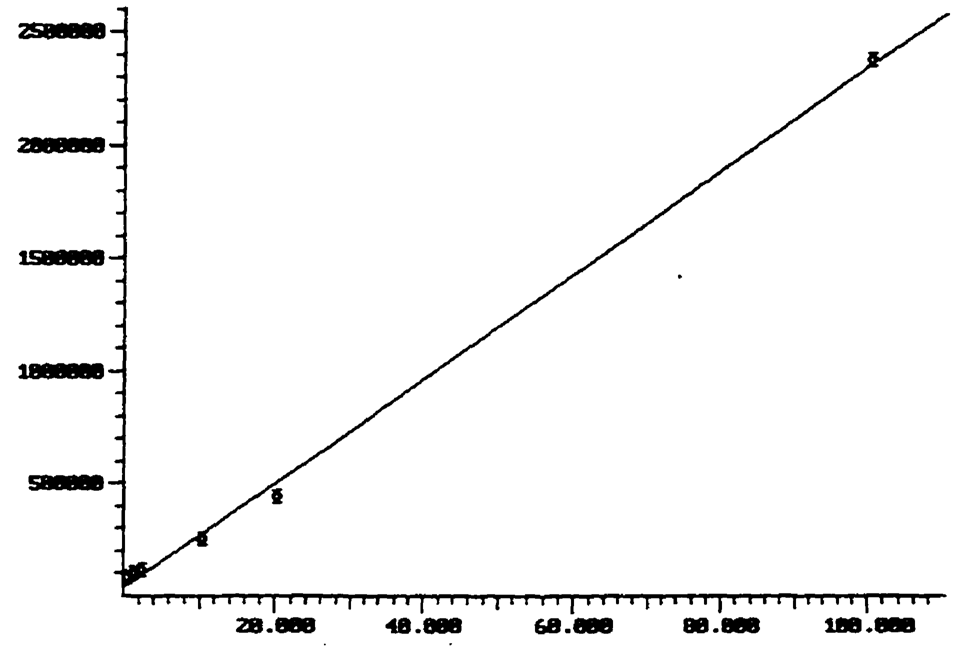
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
1,1,1-Trichloroethane Compound: 13 of 54 Standard Deviation: 15.008
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin:Lin)



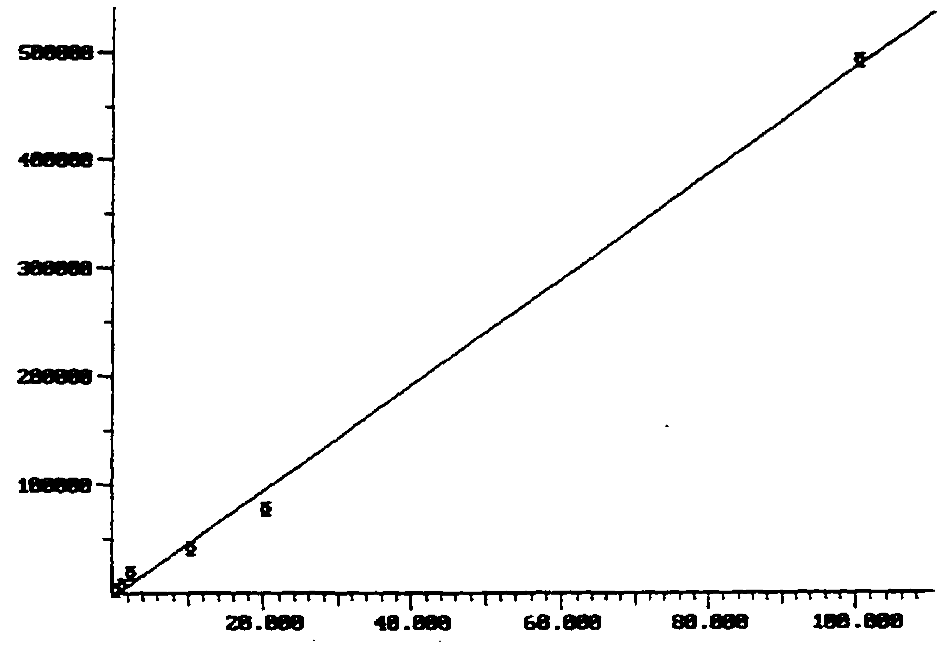
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Carbon tetrachloride Compound: 14 of 54 Standard Deviation: 11.528
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin:Lin)



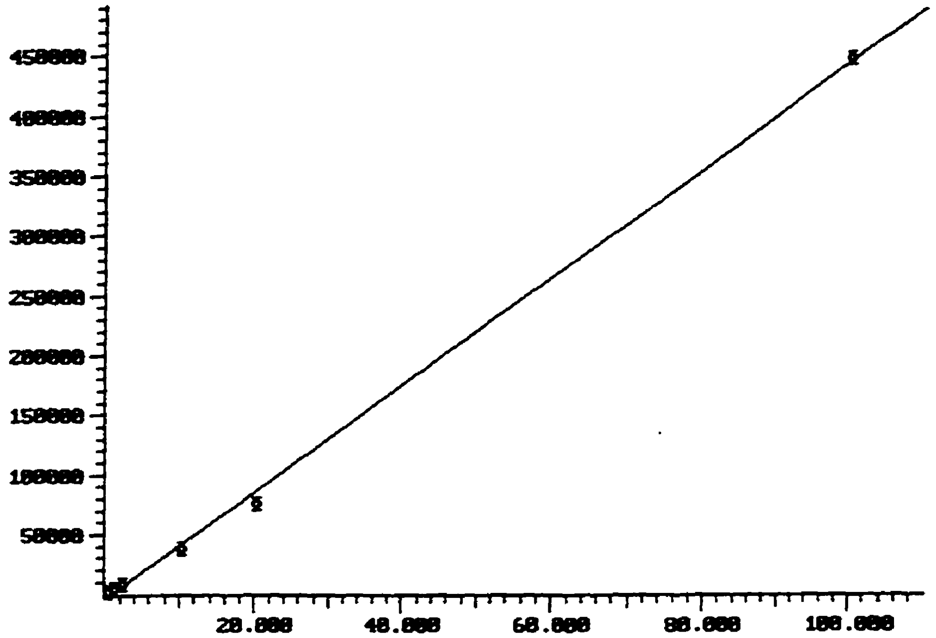
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Benzene Compound: 15 of 54 Standard Deviation: 37.268
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



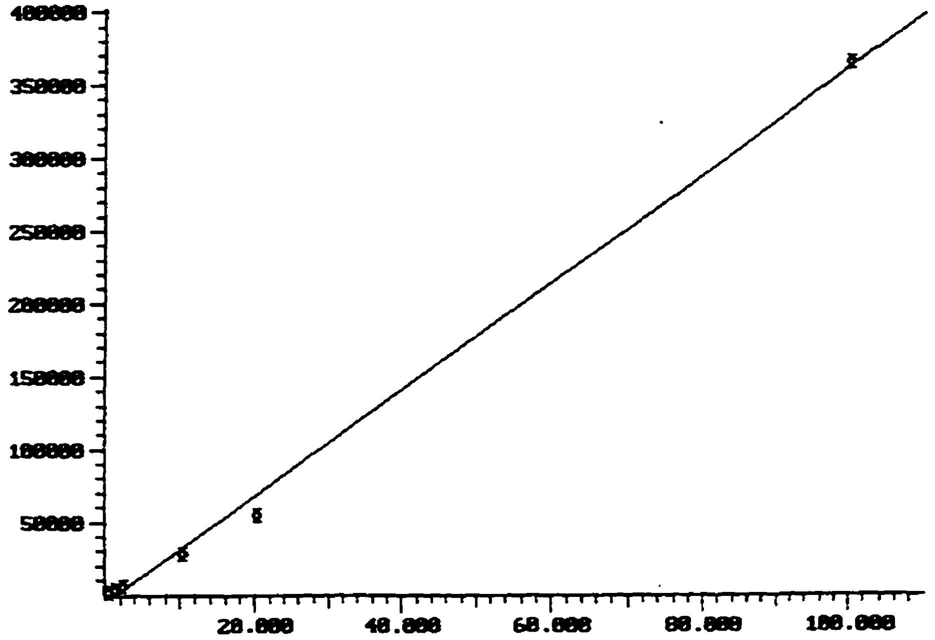
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.998
Trichloroethene Compound: 16 of 54 Standard Deviation: 9.702
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



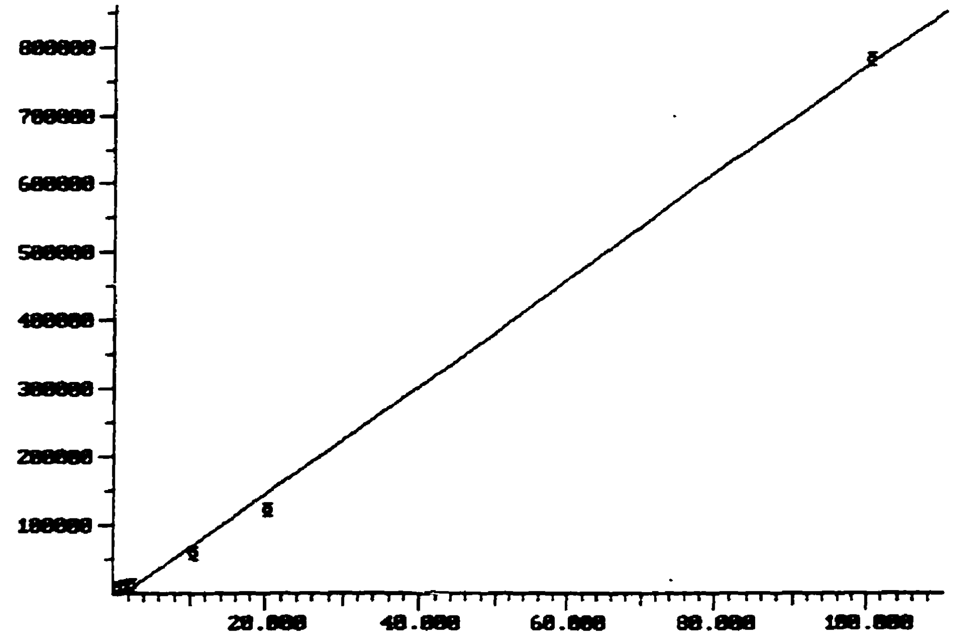
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 1.000
1,2-Dichloropropane           Compound: 17 of 54    Standard Deviation: 5.115
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



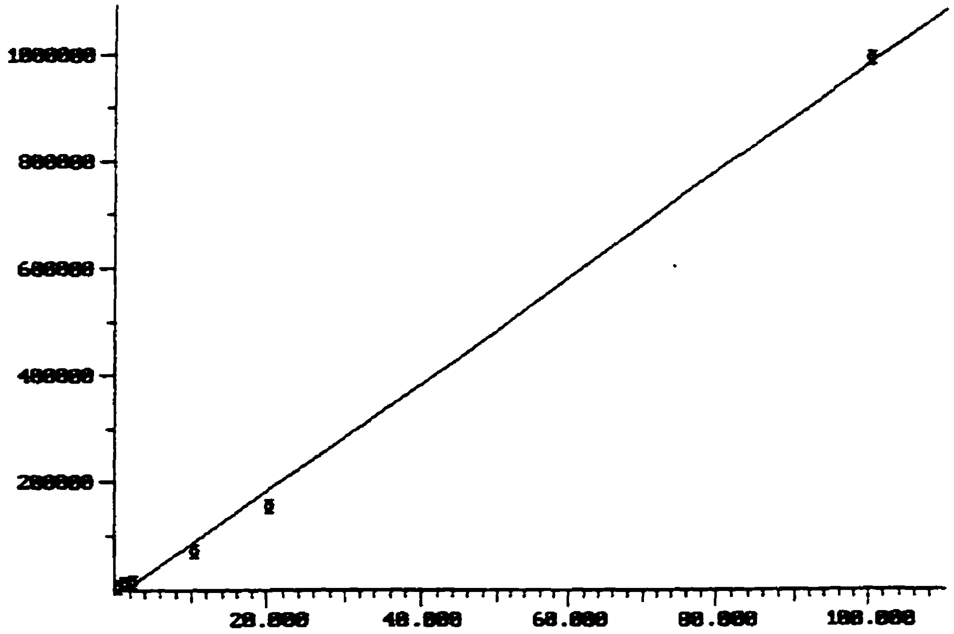
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
Dibromomethane                Compound: 18 of 54    Standard Deviation: 6.900
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



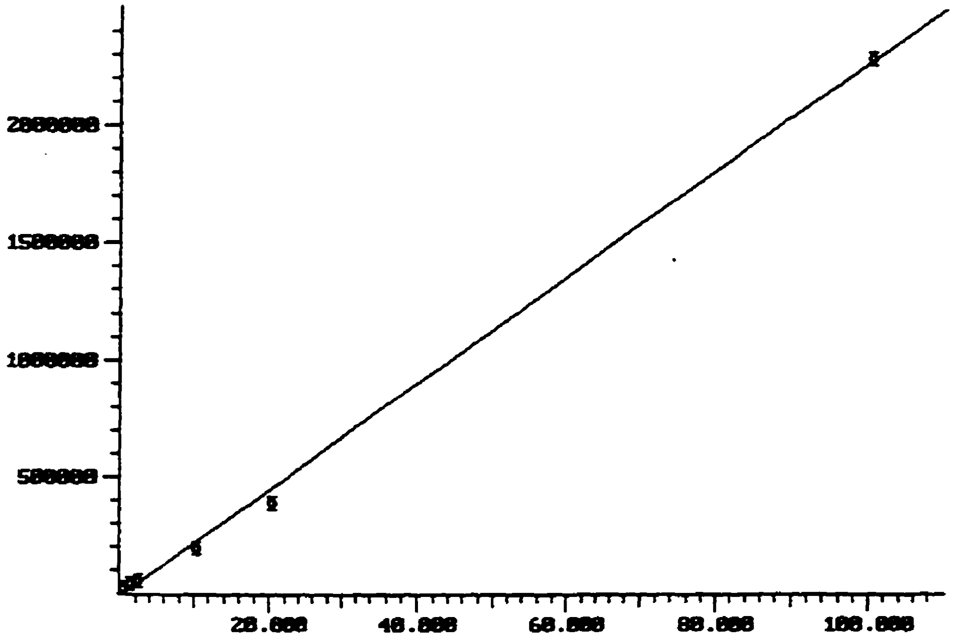
```
Calibration Plot (Ext Stds)    Filename: VMIXLOWP    Correlation  Coeff: 0.999
Bromodichloromethane           Compound: 19 of 54    Standard Deviation: 13.708
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



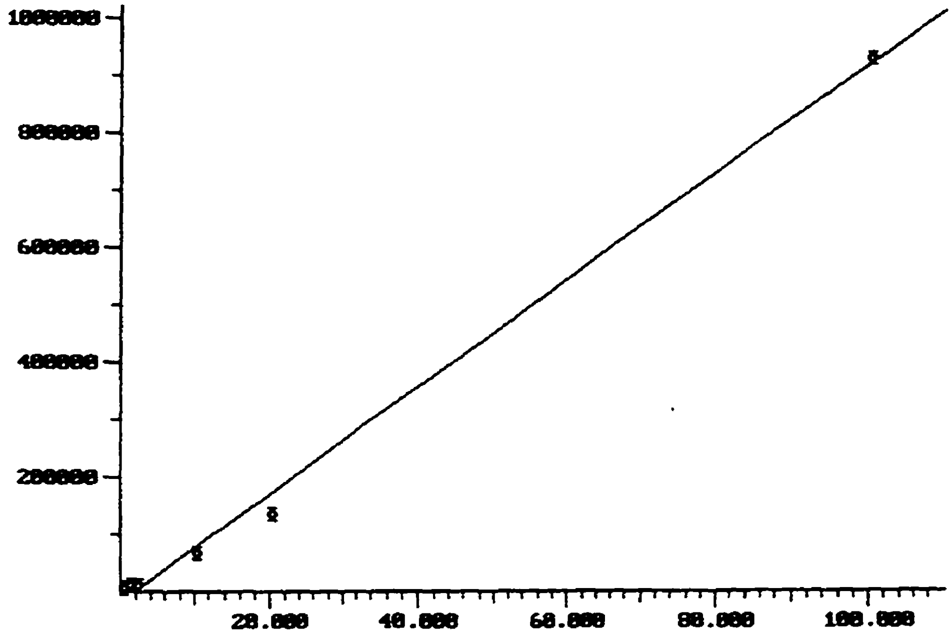
```
Calibration Plot (Ext Stds)    Filename: VMIXLOWP    Correlation  Coeff: 0.999
trans-1,3-Dichloropropene      Compound: 20 of 54    Standard Deviation: 16.726
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



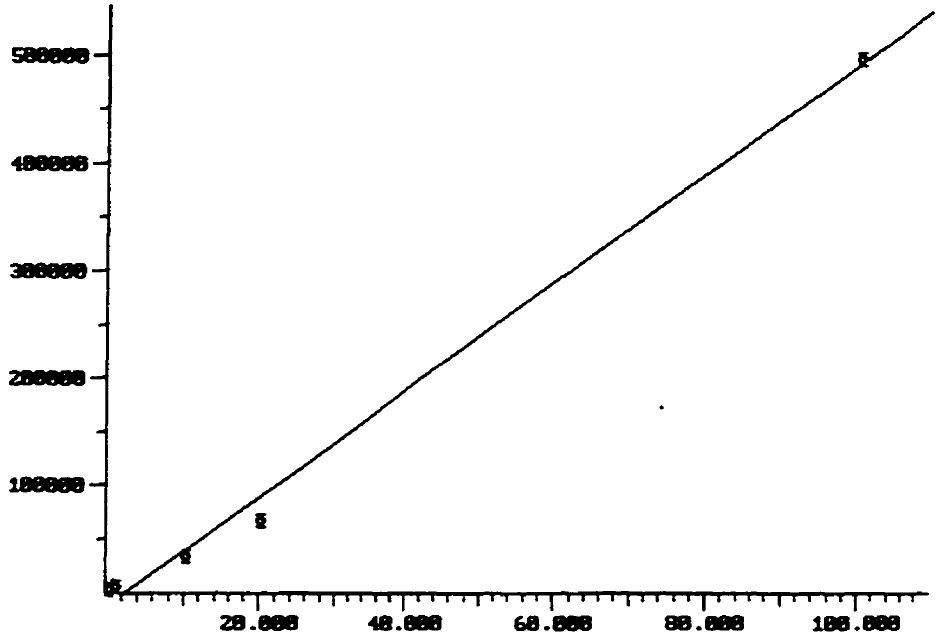
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
Toluene                       Compound: 21 of 54    Standard Deviation: 31.394
(Peak Area of Sample) vs (Amount of Sample Injected)               (Lin|Lin)
```



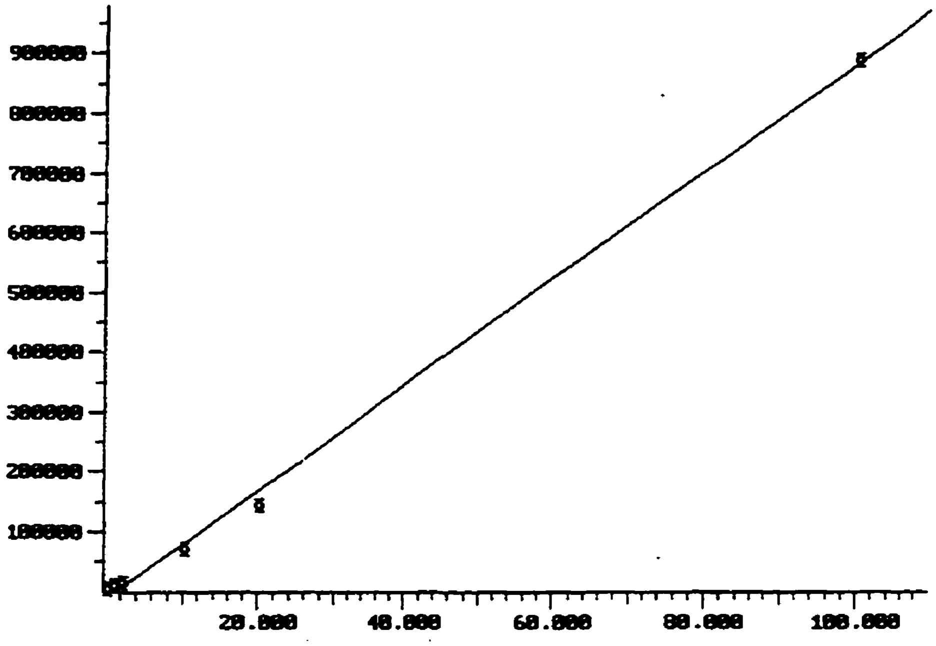
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.998
cis-1,3-Dichloropropene       Compound: 22 of 54    Standard Deviation: 10.964
(Peak Area of Sample) vs (Amount of Sample Injected)               (Lin|Lin)
```



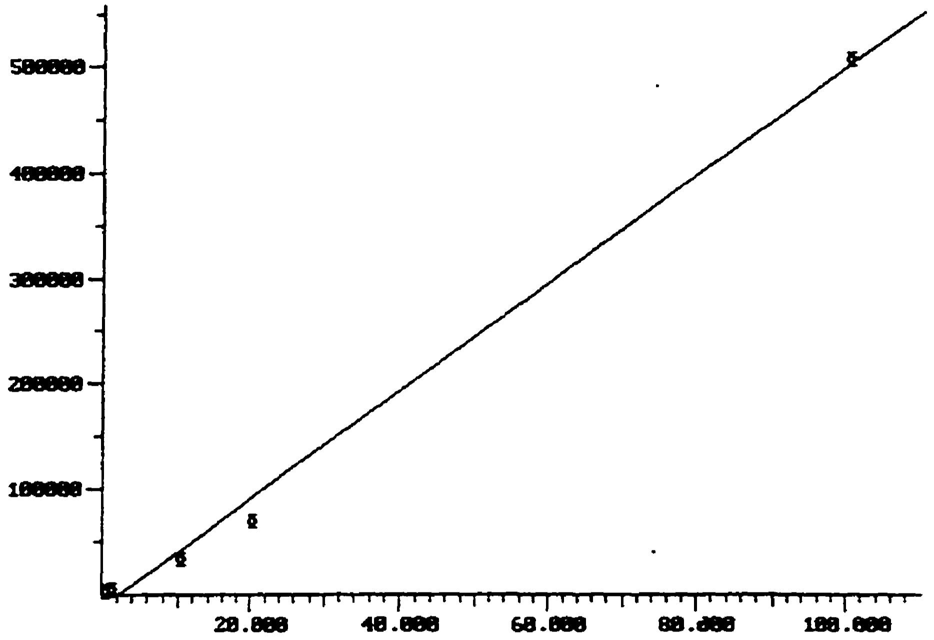
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.998
1,1,2-Trichloroethane Compound: 23 of 54 Standard Deviation: 12.559
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



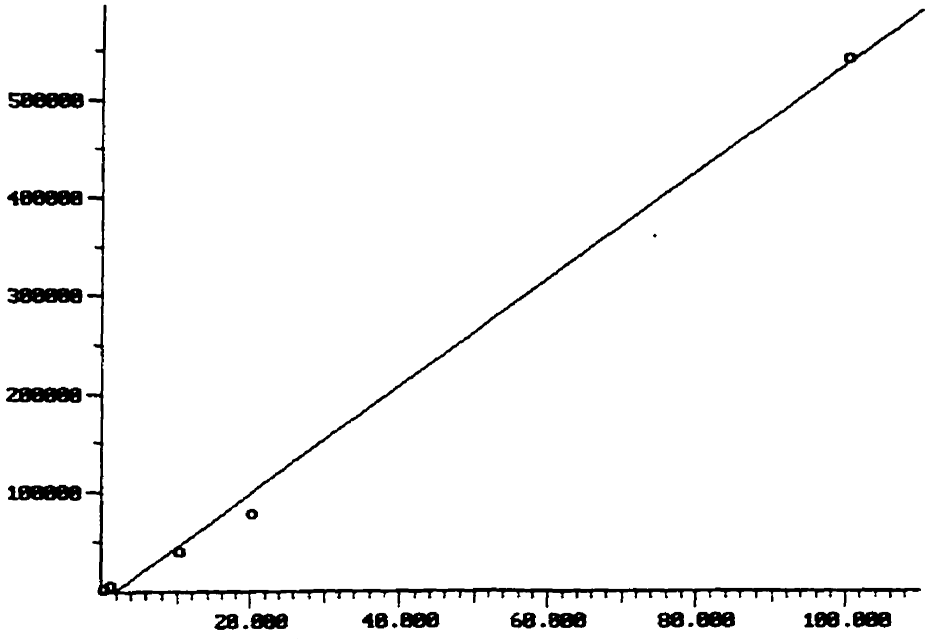
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
1,3-Dichloropropane Compound: 24 of 54 Standard Deviation: 12.985
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



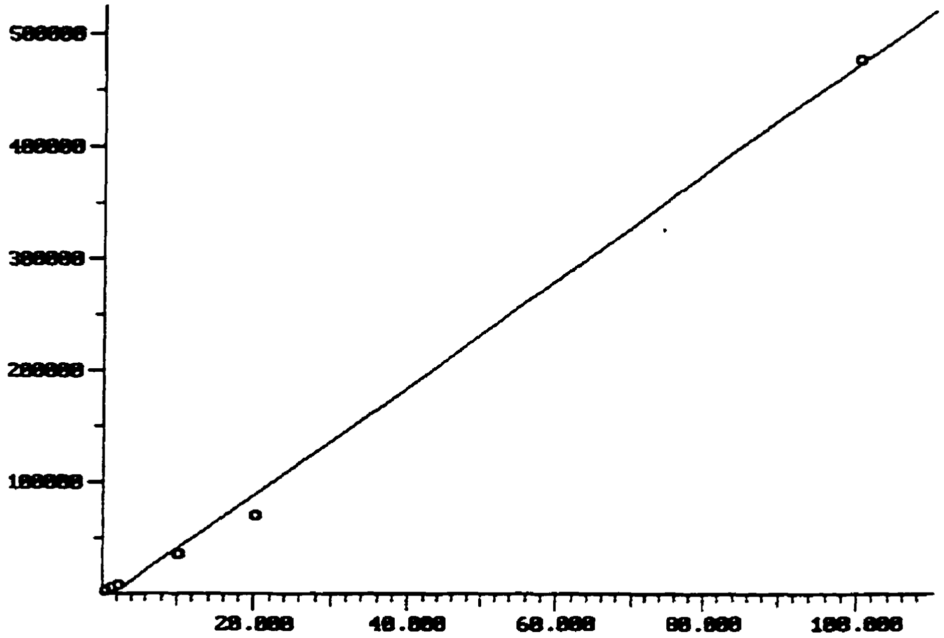
Calibration Plot (Ext Stds)   Filename: VMIXLOWP   Correlation Coeff: 0.998
Dibromochloromethane   Compound: 25 of 54   Standard Deviation: 12.967
(Peak Area of Sample) vs (Amount of Sample Injected)   (Lin|Lin)



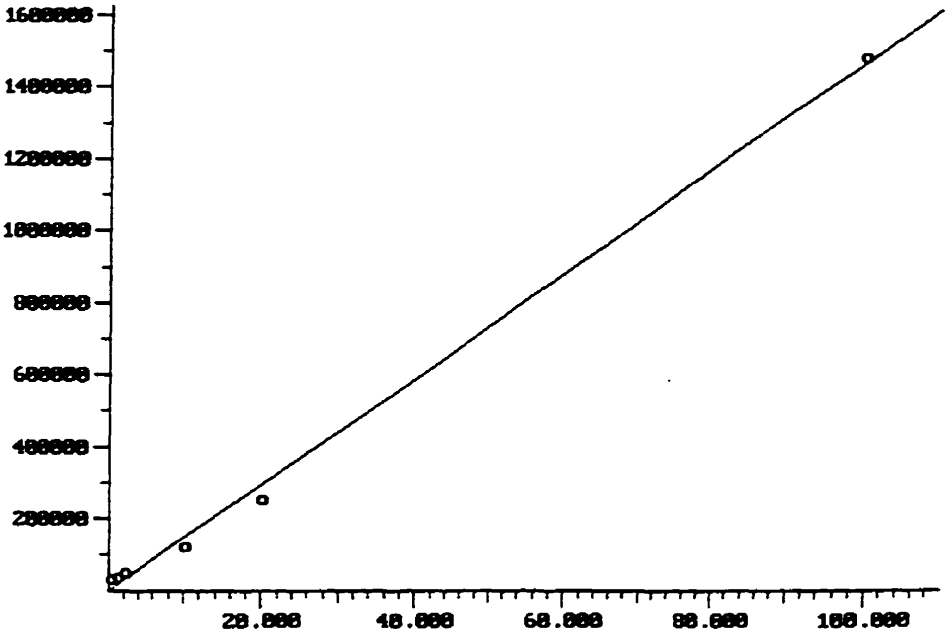
Calibration Plot (Ext Stds)   Filename: VMIXLOWP   Correlation Coeff: 0.998
1,2-Dibromoethane   Compound: 26 of 54   Standard Deviation: 12.189
(Peak Area of Sample) vs (Amount of Sample Injected)   (Lin|Lin)



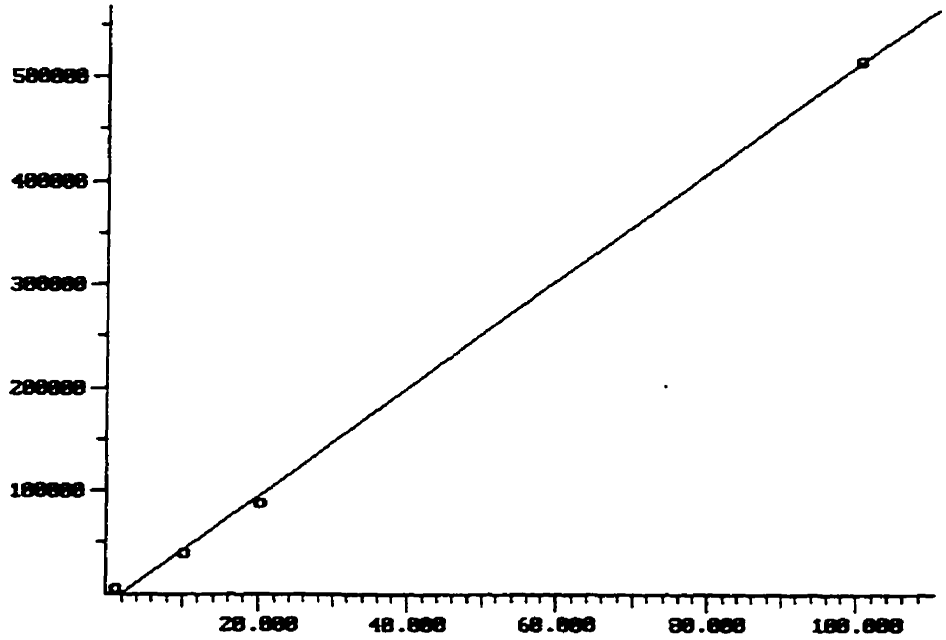
```
Calibration Plot (Ext Stds)   Filename: UMIXLOWP   Correlation  Coeff: 0.998
Tetrachloroethene             Compound: 27 of 54   Standard Deviation: 9.762
(Peak Area of Sample) vs (Amount of Sample Injected)              (Lin|Lin)
```



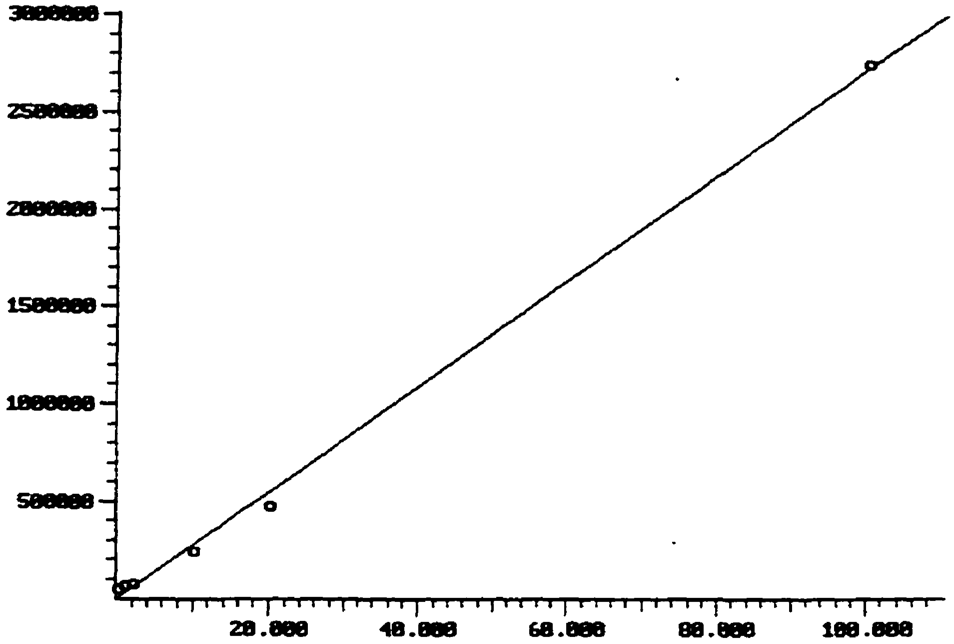
```
Calibration Plot (Ext Stds)   Filename: UMIXLOWP   Correlation  Coeff: 0.999
Chlorobenzene                 Compound: 28 of 54   Standard Deviation: 26.766
(Peak Area of Sample) vs (Amount of Sample Injected)              (Lin|Lin)
```



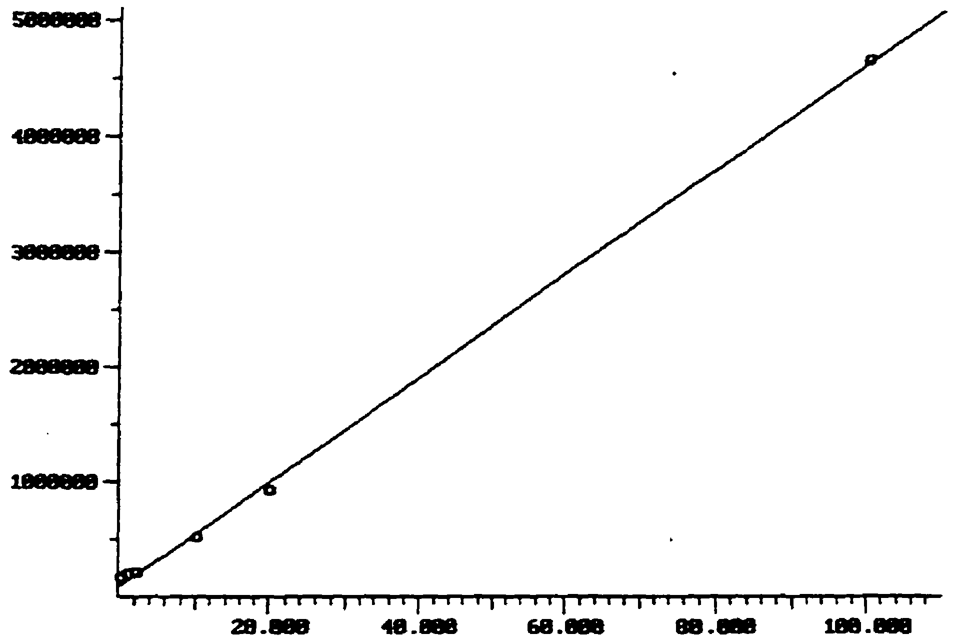
Calibration Plot (Ext Stds) **Filename: VMIXLOWP** **Correlation Coeff: 1.000**
1,1,1,2-Tetrachloroethane **Compound: 29 of 54** **Standard Deviation: 6.507**
(Peak Area of Sample) vs (Amount of Sample Injected) **(Lin:Lin)**



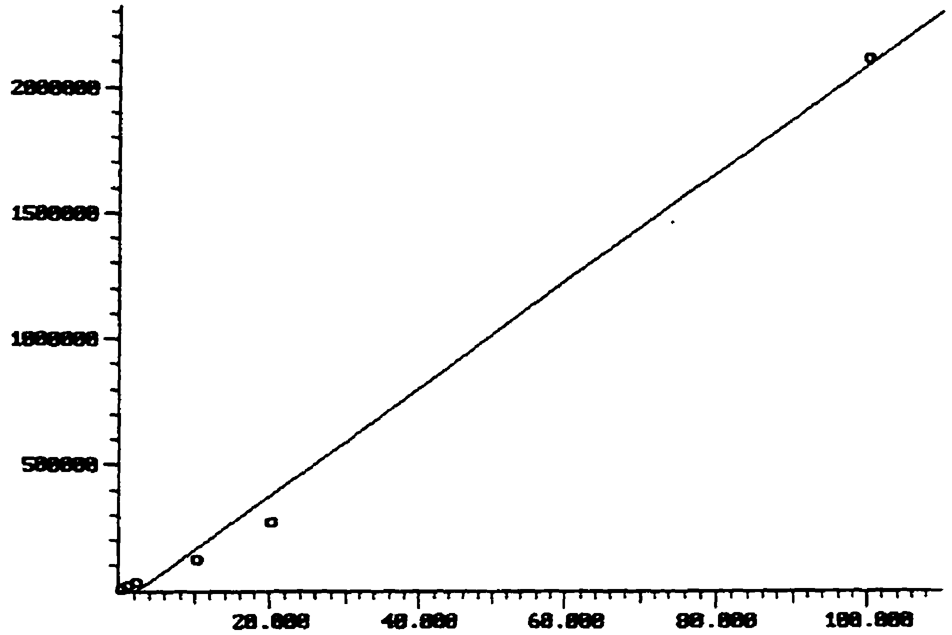
Calibration Plot (Ext Stds) **Filename: VMIXLOWP** **Correlation Coeff: 0.999**
Ethylbenzene **Compound: 30 of 54** **Standard Deviation: 40.746**
(Peak Area of Sample) vs (Amount of Sample Injected) **(Lin:Lin)**



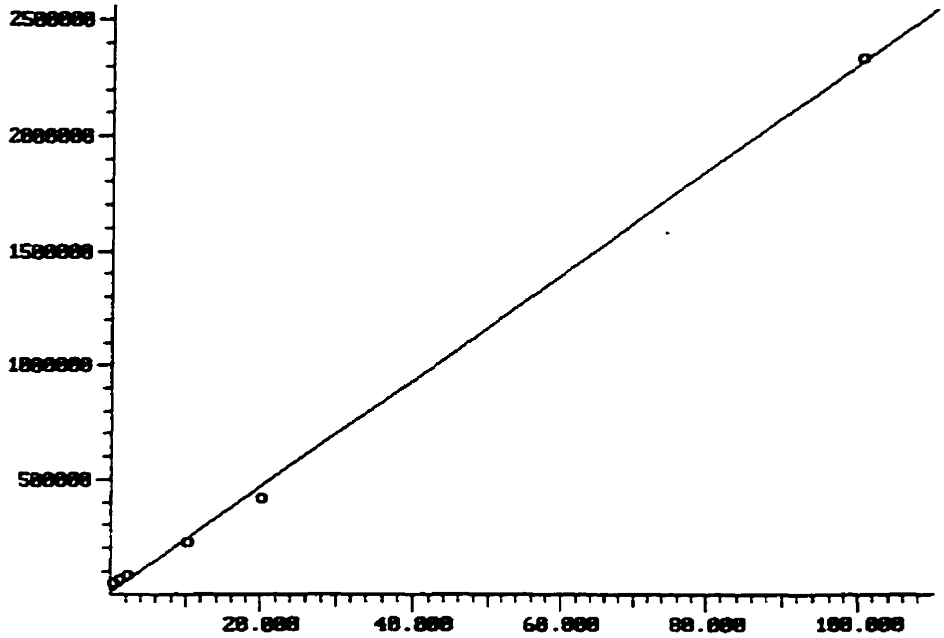
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 1.000
m,p-Xylene Compound: 31 of 54 Standard Deviation: 40.060
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



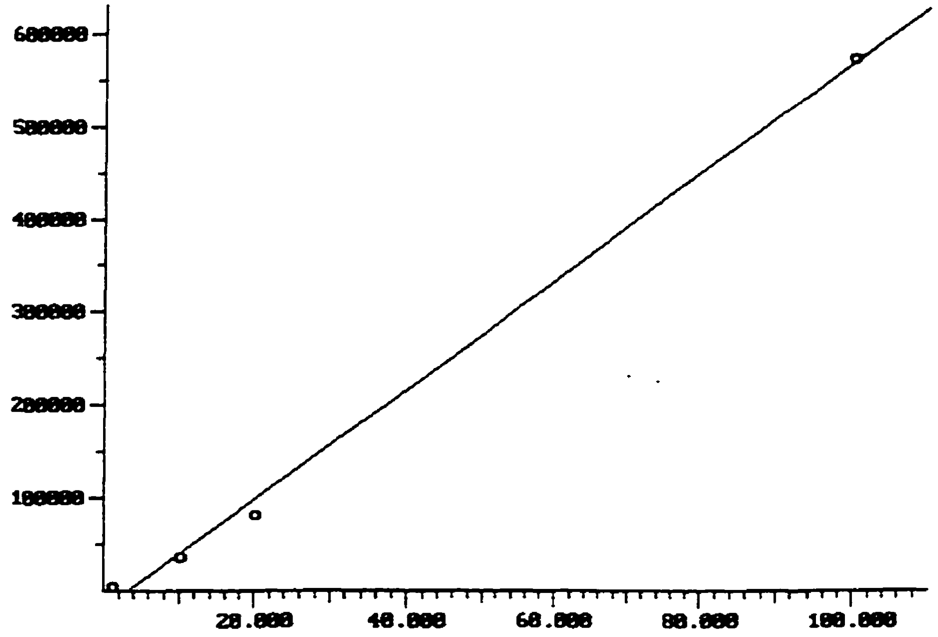
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.997
Styrene Compound: 32 of 54 Standard Deviation: 57.624
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



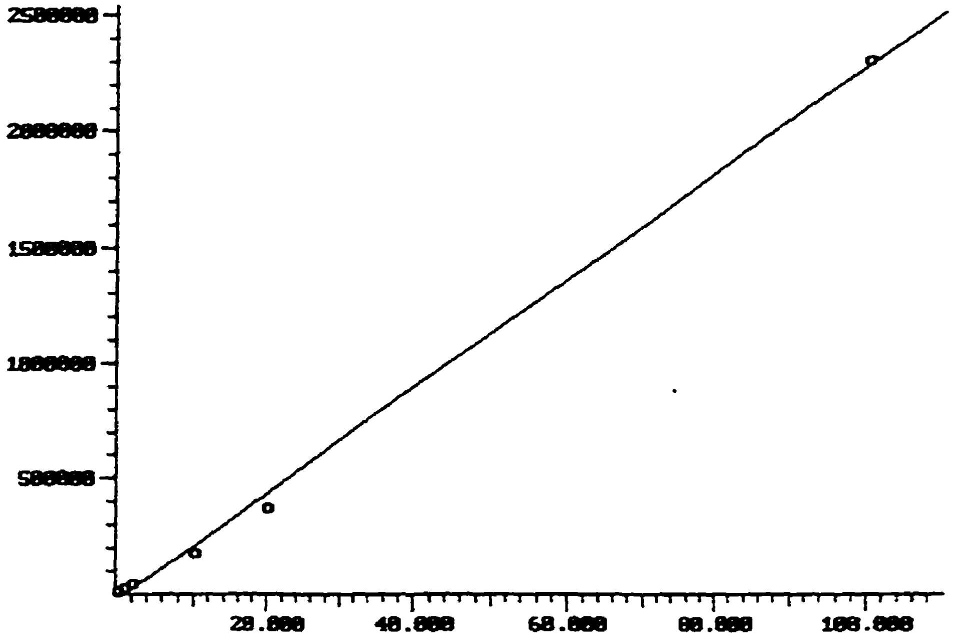
```
Calibration Plot (Ext Stds)    Filename: VMIXLOWP    Correlation  Coeff: 0.999
o-Xylene                       Compound: 33 of 54    Standard Deviation: 33.203
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin!Lin)
```



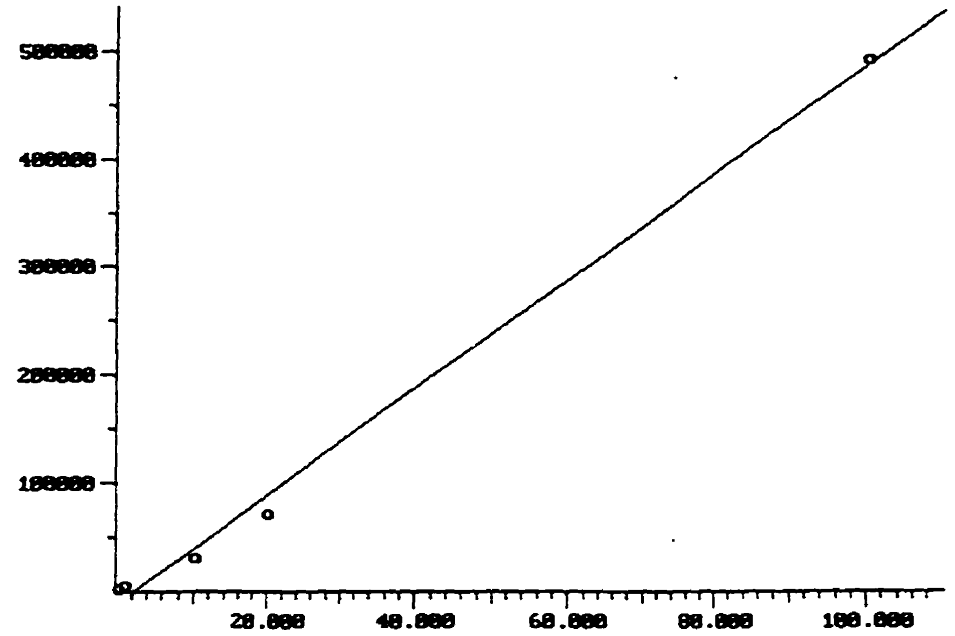
```
Calibration Plot (Ext Stds)    Filename: VMIXLOWP    Correlation  Coeff: 0.998
Bromoform                      Compound: 34 of 54    Standard Deviation: 13.304
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin!Lin)
```



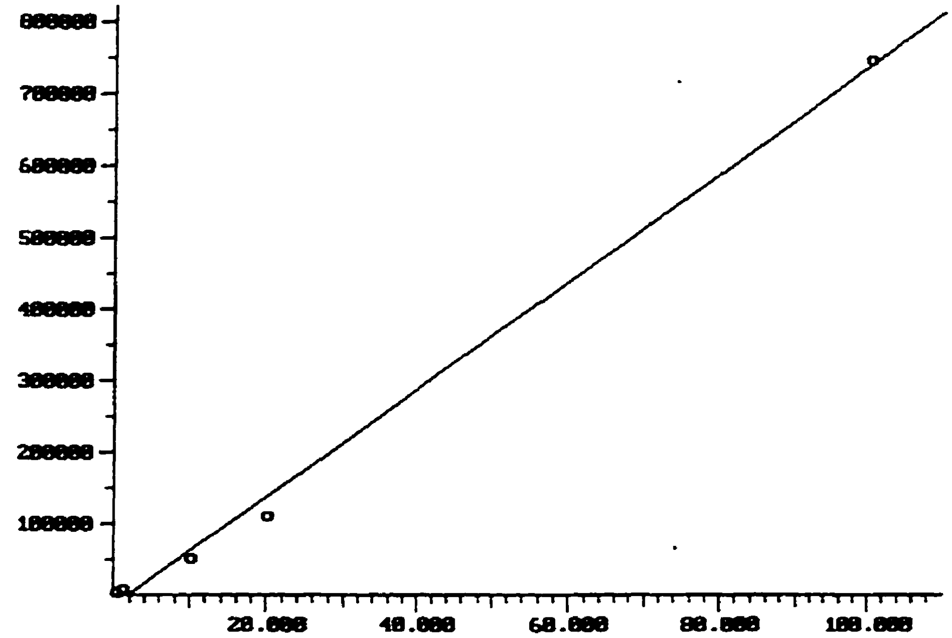
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
Isopropylbenzene Compound: 35 of 54 Standard Deviation: 35.151
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin!Lin)



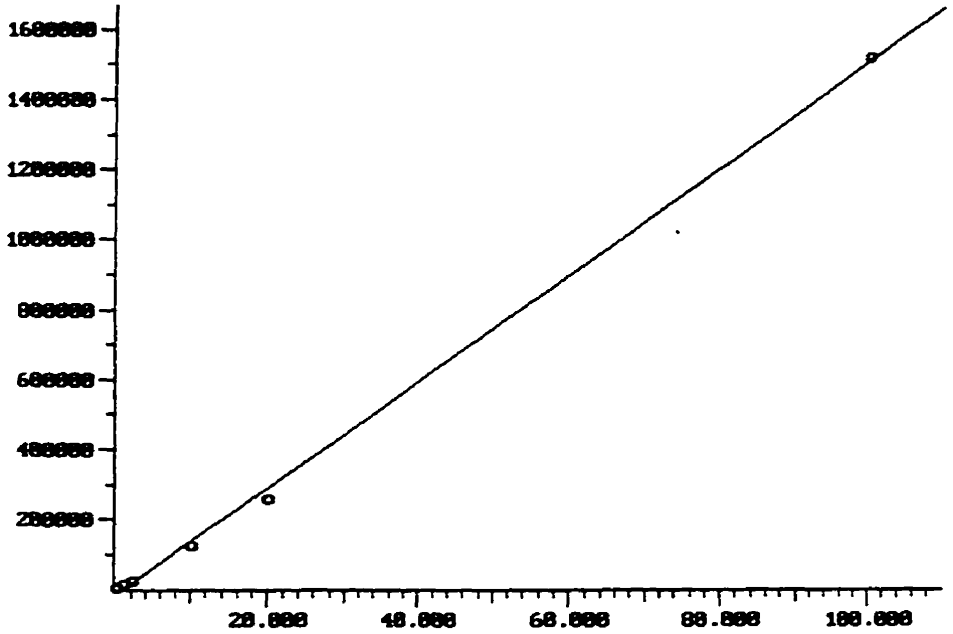
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.998
1,1,2,2-Tetrachloroethane Compound: 36 of 54 Standard Deviation: 11.739
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin!Lin)



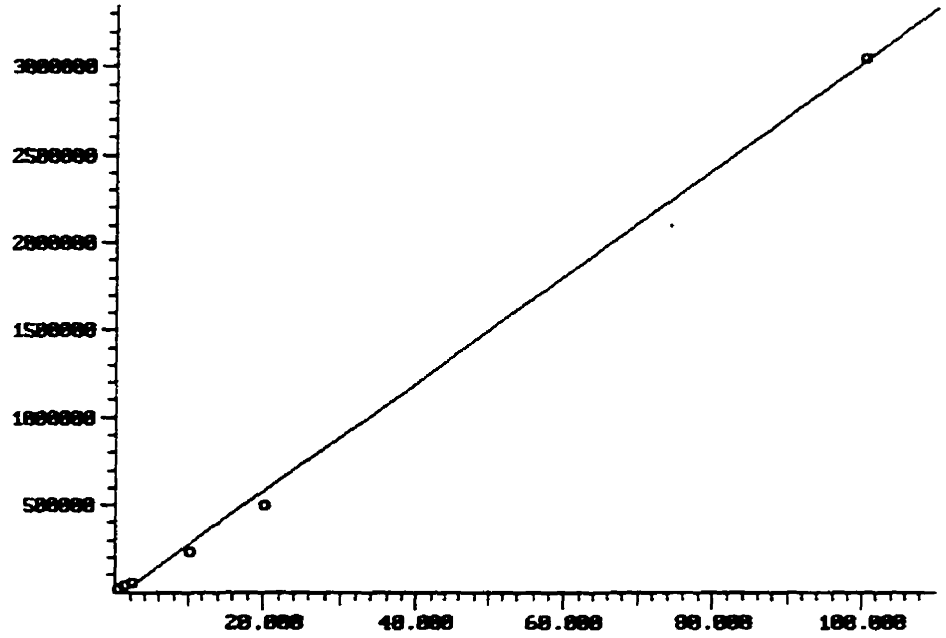
Calibration Plot (Ext Stds) **Filename: VMIXLOWP** **Correlation Coeff: 0.998**
1,2,3-Trichloropropane **Compound: 37 of 54** **Standard Deviation: 15.985**
(Peak Area of Sample) vs (Amount of Sample Injected) **(Lin|Lin)**



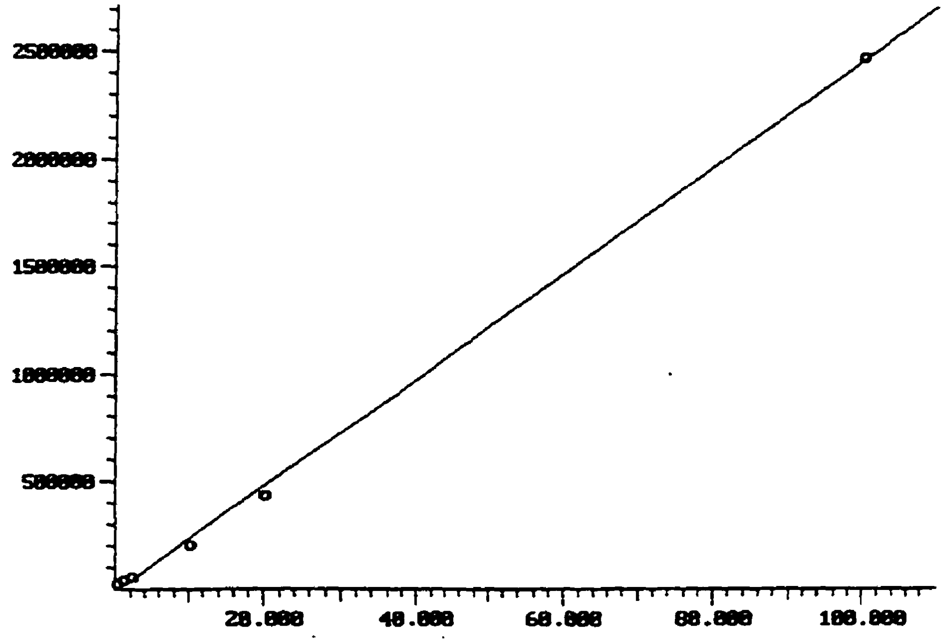
Calibration Plot (Ext Stds) **Filename: VMIXLOWP** **Correlation Coeff: 0.999**
Bromobenzene **Compound: 38 of 54** **Standard Deviation: 17.462**
(Peak Area of Sample) vs (Amount of Sample Injected) **(Lin|Lin)**



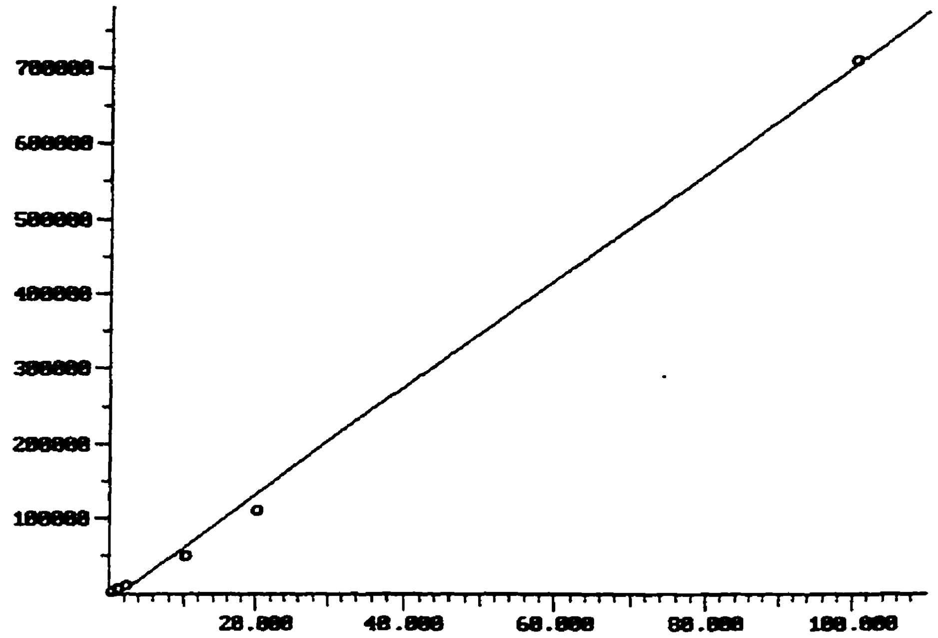
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP   Correlation  Coeff: 0.999
4-chlorobenzene               Compound: 39 of 54   Standard Deviation: 43.389
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



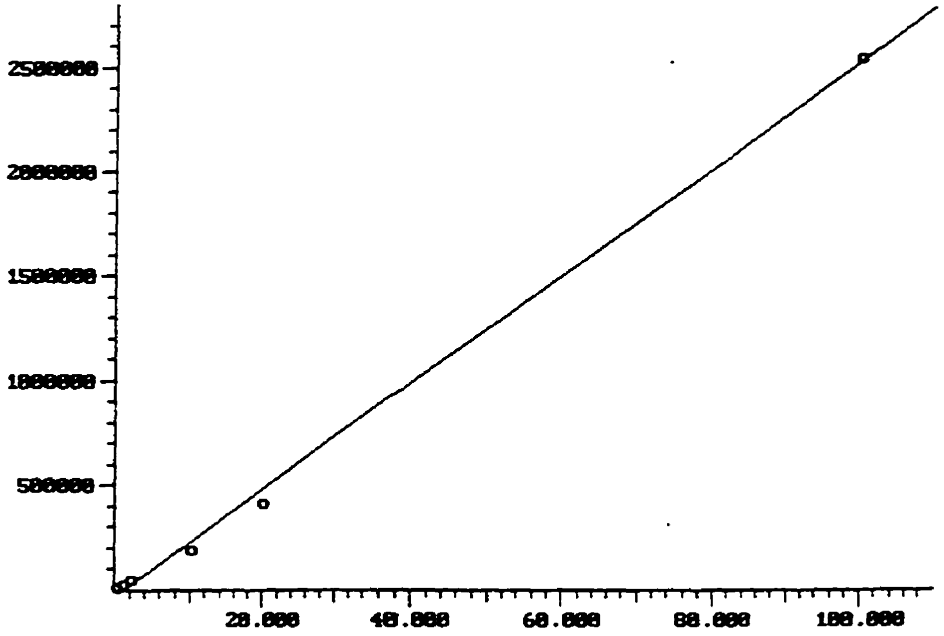
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP   Correlation  Coeff: 0.999
1,3,5-Trimethylbenzene        Compound: 40 of 54   Standard Deviation: 20.859
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin!Lin)
```



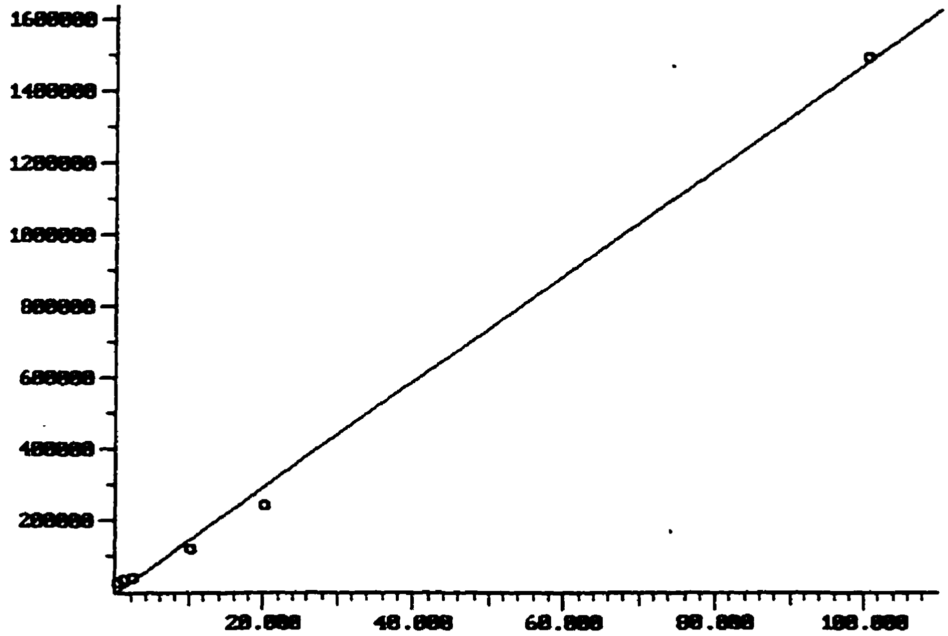
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
2-chlorotoluene Compound: 41 of 54 Standard Deviation: 12.317
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin!Lin)



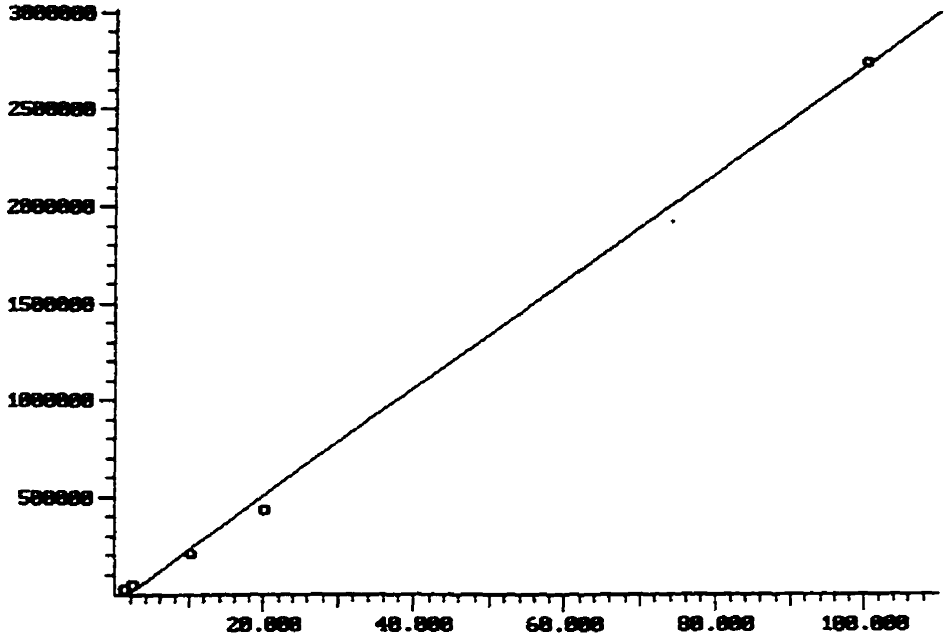
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
ter-Butylbenzene Compound: 42 of 54 Standard Deviation: 38.365
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin!Lin)



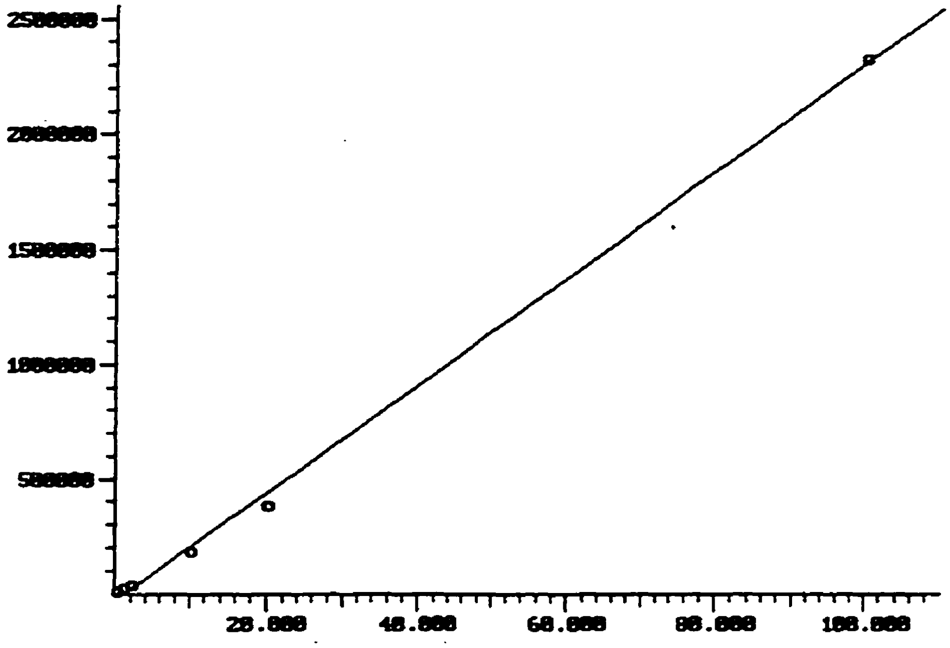
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
n-Propylbenzene               Compound: 43 of 54    Standard Deviation: 27.337
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin|Lin)
```



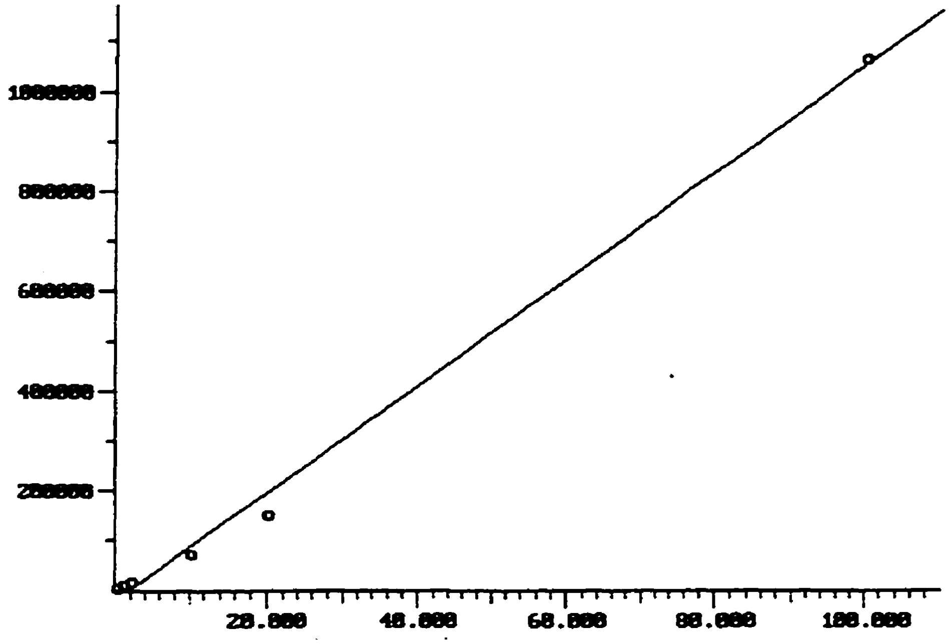
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
1,2,4-Trimethylbenzene        Compound: 44 of 54    Standard Deviation: 44.007
(Peak Area of Sample) vs (Amount of Sample Injected)                 (Lin|Lin)
```



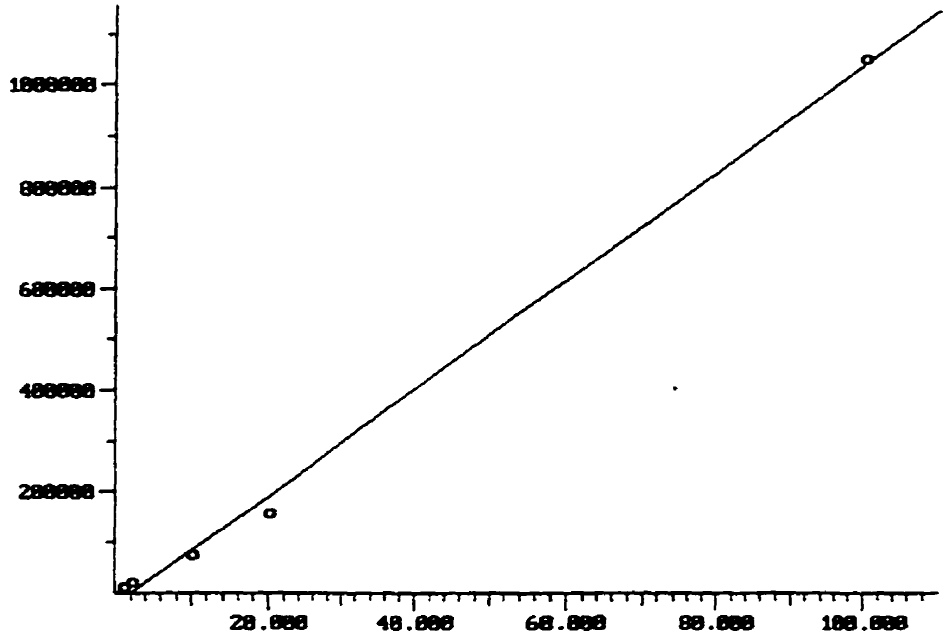
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.999
4-Isopropyltoluene Compound: 45 of 54 Standard Deviation: 33.738
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



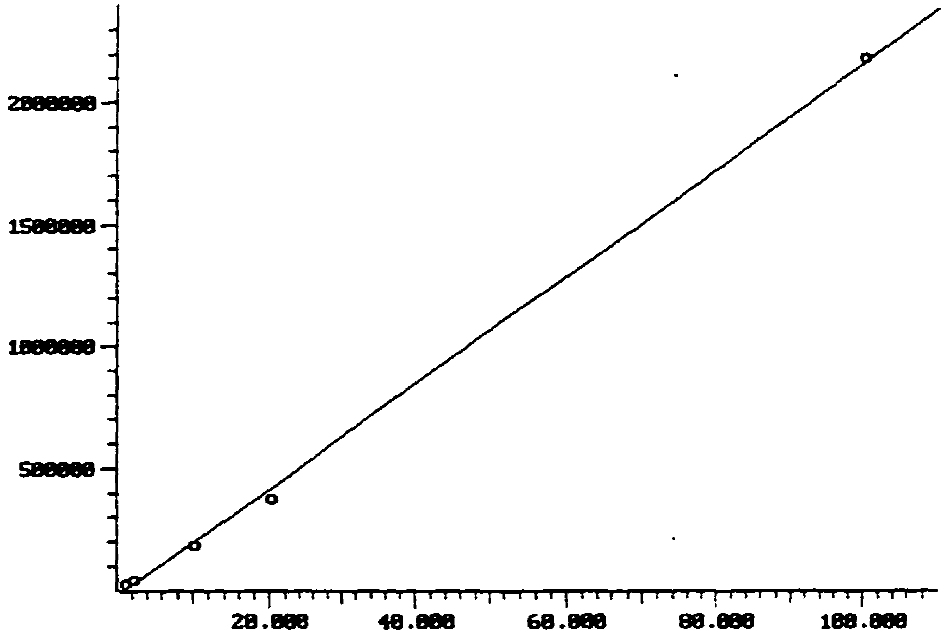
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 0.998
1,3-Dichlorobenzene Compound: 46 of 54 Standard Deviation: 23.589
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



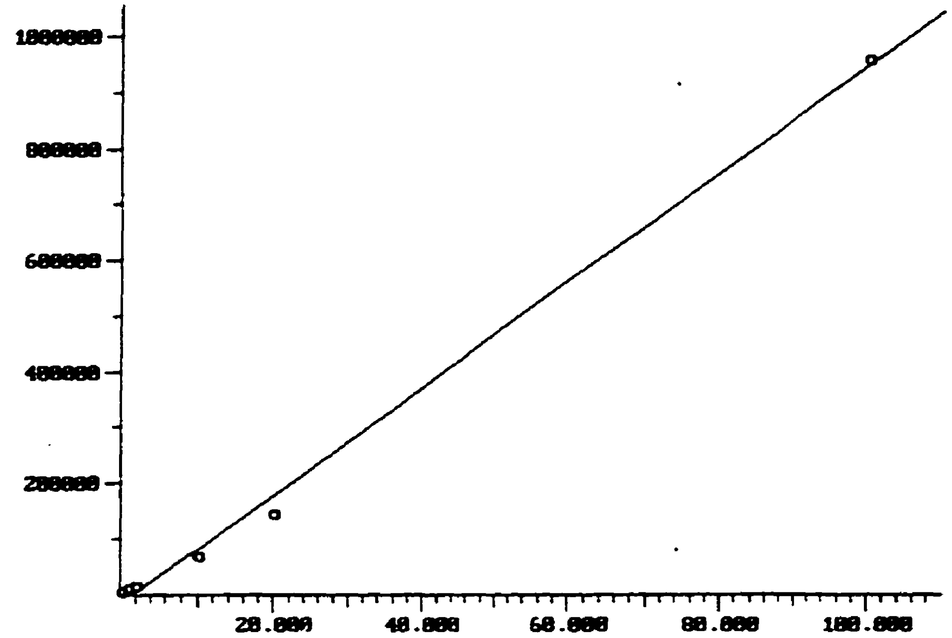
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.999
1,4-Dichlorobenzene           Compound: 47 of 54    Standard Deviation: 20.979
(Peak Area of Sample) vs (Amount of Sample Injected)               (Lin:Lin)
```



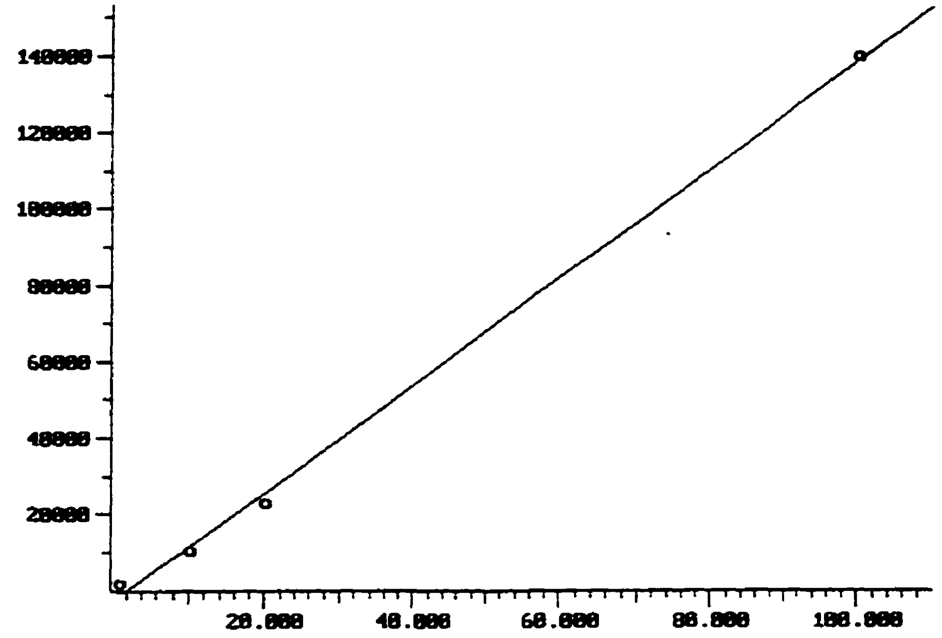
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 1.000
n-Butylbenzene                Compound: 48 of 54    Standard Deviation: 23.745
(Peak Area of Sample) vs (Amount of Sample Injected)               (Lin:Lin)
```



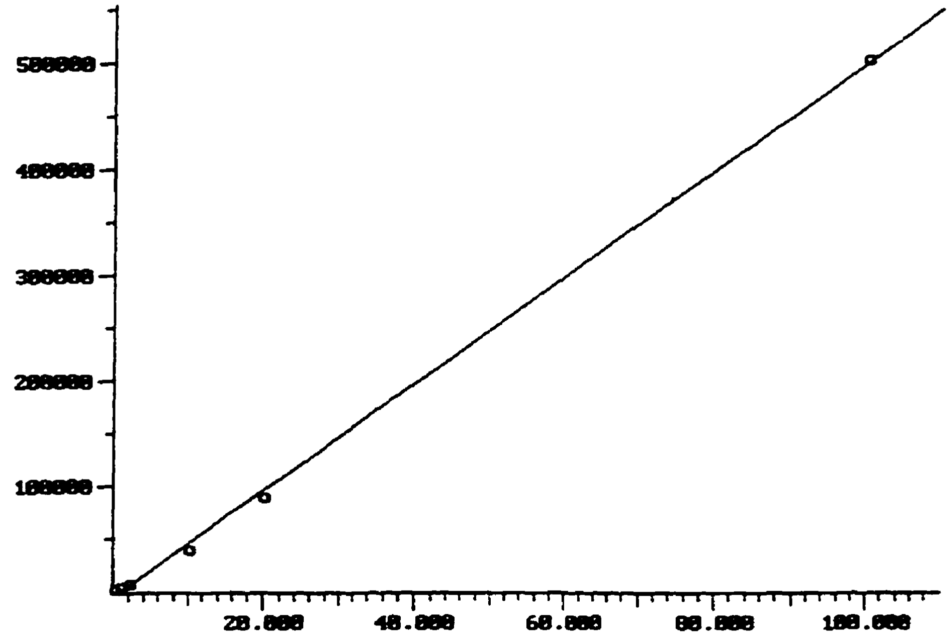
Calibration Plot (Ext Stds) Filename: UMIXLOWP Correlation Coeff: 0.999
1,2-Dichlorobenzene Compound: 49 of 54 Standard Deviation: 10.547
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



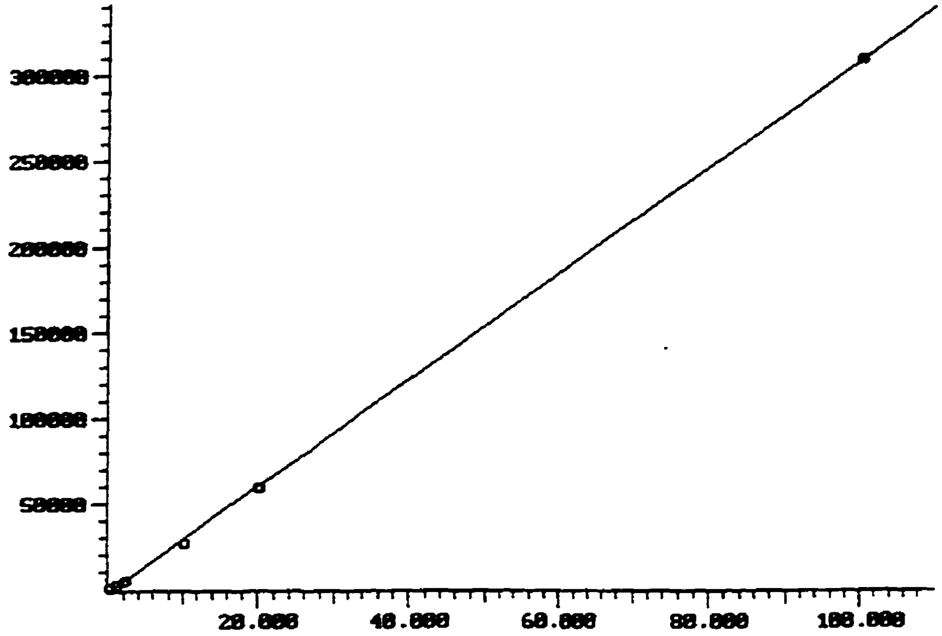
Calibration Plot (Ext Stds) Filename: UMIXLOWP Correlation Coeff: 0.999
1,2-Dibromo-3-chloropropane Compound: 50 of 54 Standard Deviation: 2.140
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



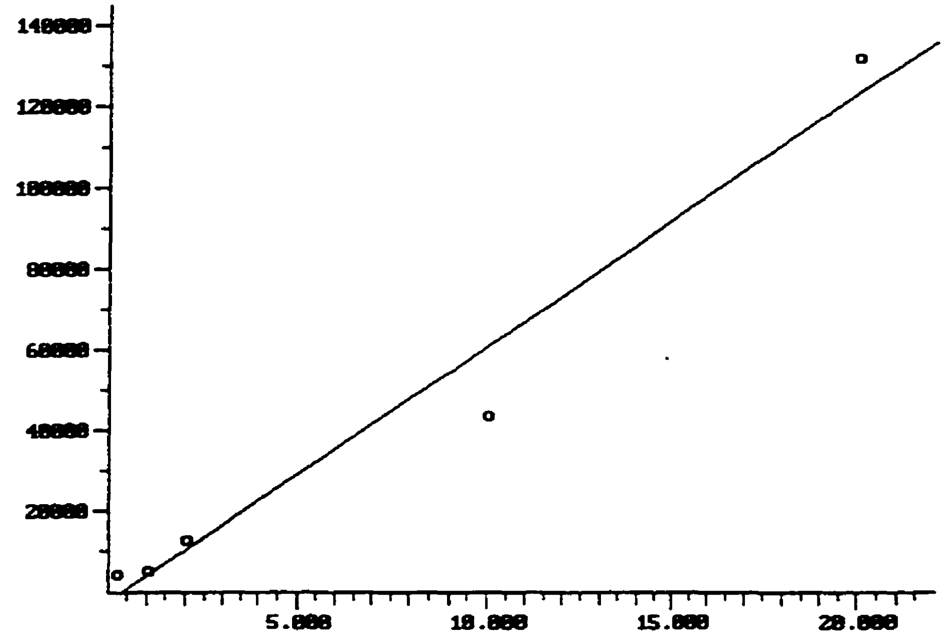
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 1.000
1,2,4-Trichlorobenzene Compound: 51 of 54 Standard Deviation: 4.969
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



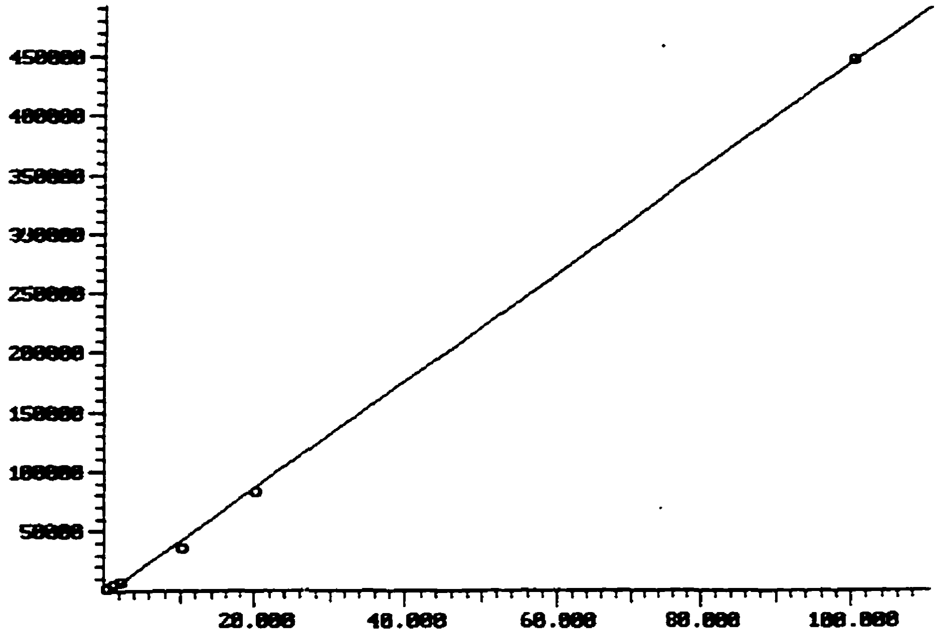
Calibration Plot (Ext Stds) Filename: VMIXLOWP Correlation Coeff: 1.000
Hexachlorobutadiene Compound: 52 of 54 Standard Deviation: 1.722
(Peak Area of Sample) vs (Amount of Sample Injected) (Lin|Lin)



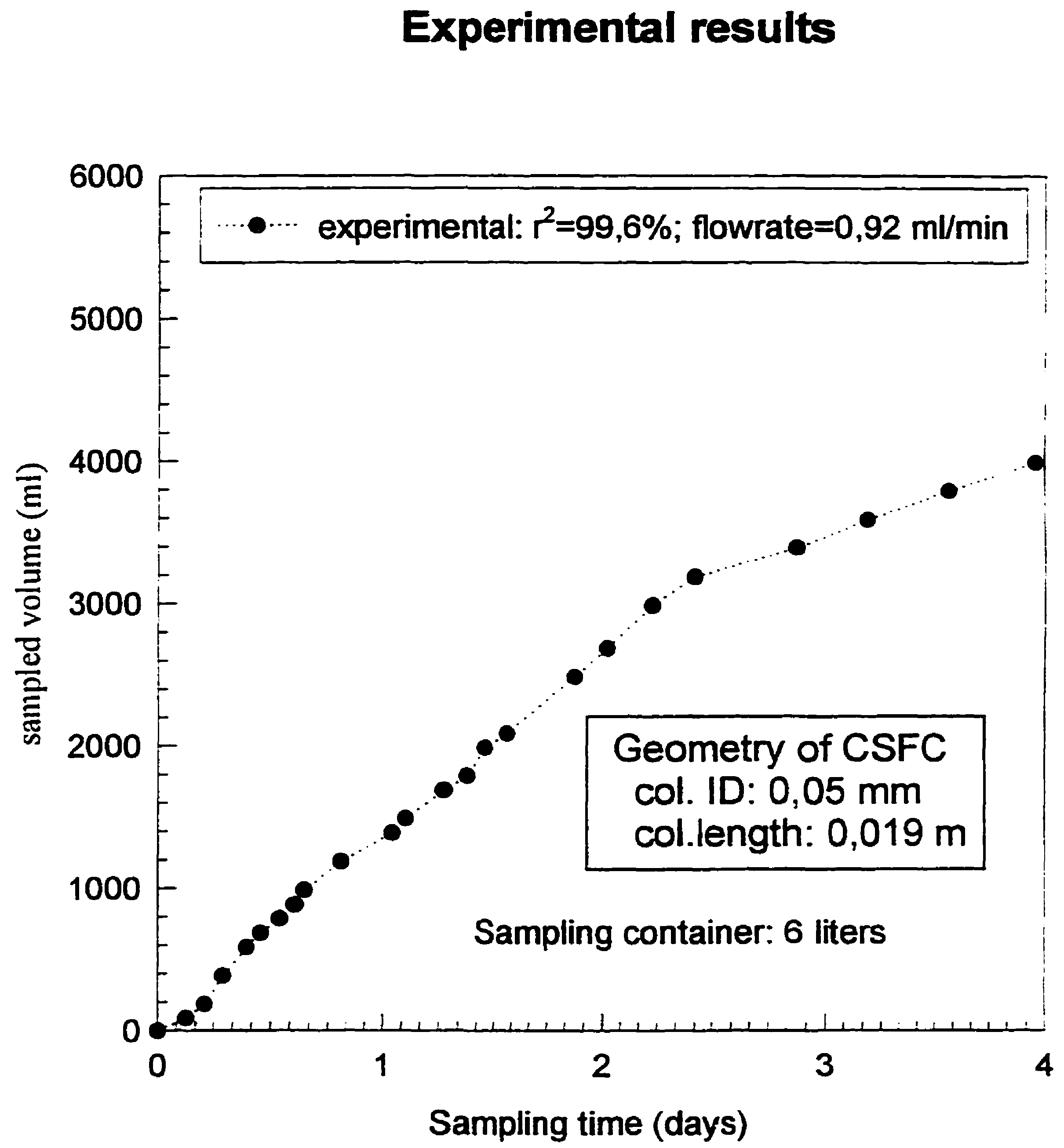
```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 0.982
Naphthalene                   Compound: 53 of 54    Standard Deviation: 9.858
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



```
Calibration Plot (Ext Stds)   Filename: VMIXLOWP    Correlation  Coeff: 1.000
1,2,3-Trichlorobenzene        Compound: 54 of 54    Standard Deviation: 3.660
(Peak Area of Sample) vs (Amount of Sample Injected)                (Lin|Lin)
```



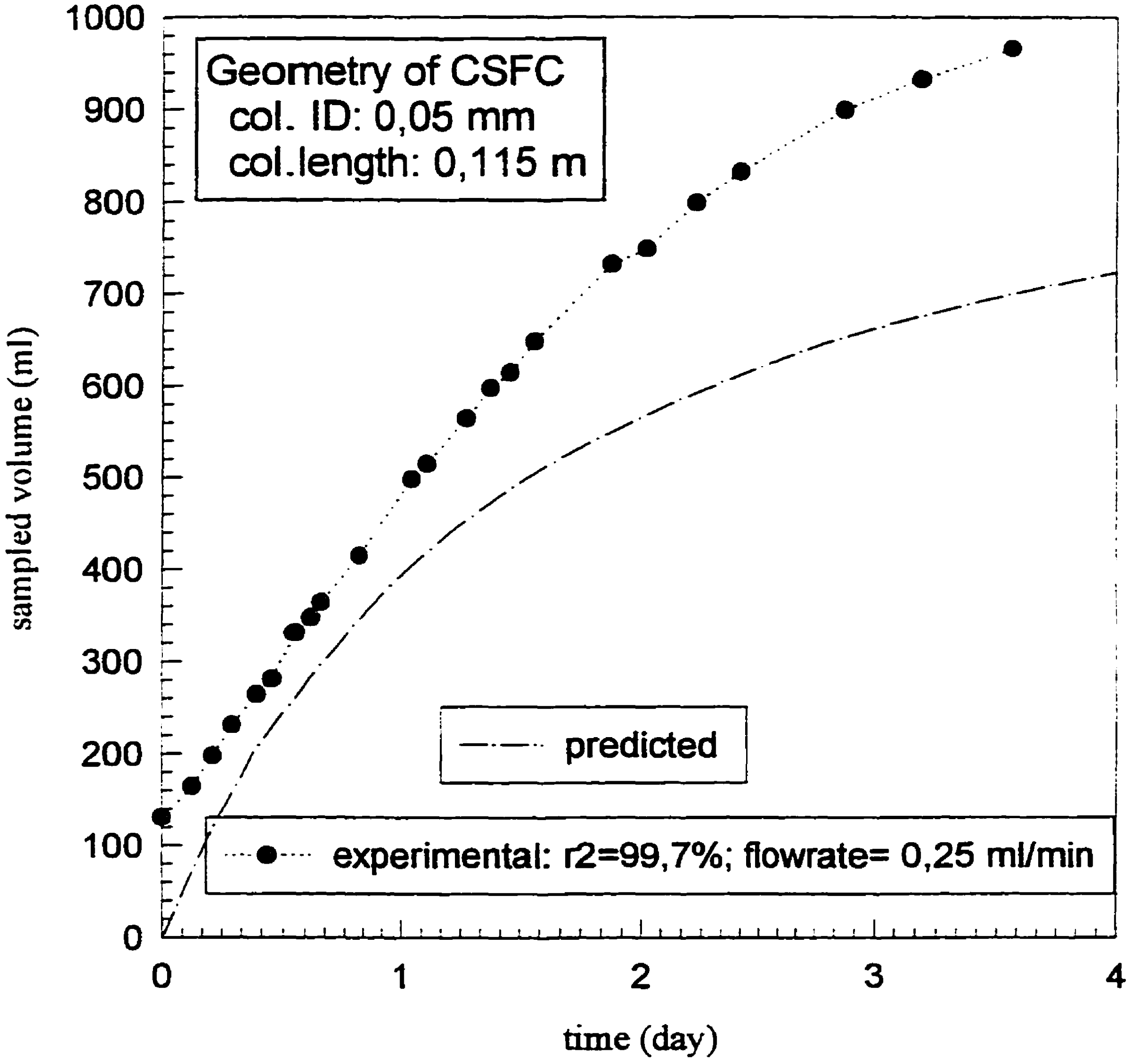
APPENDIX-3: Experimental results for sampling dynamics



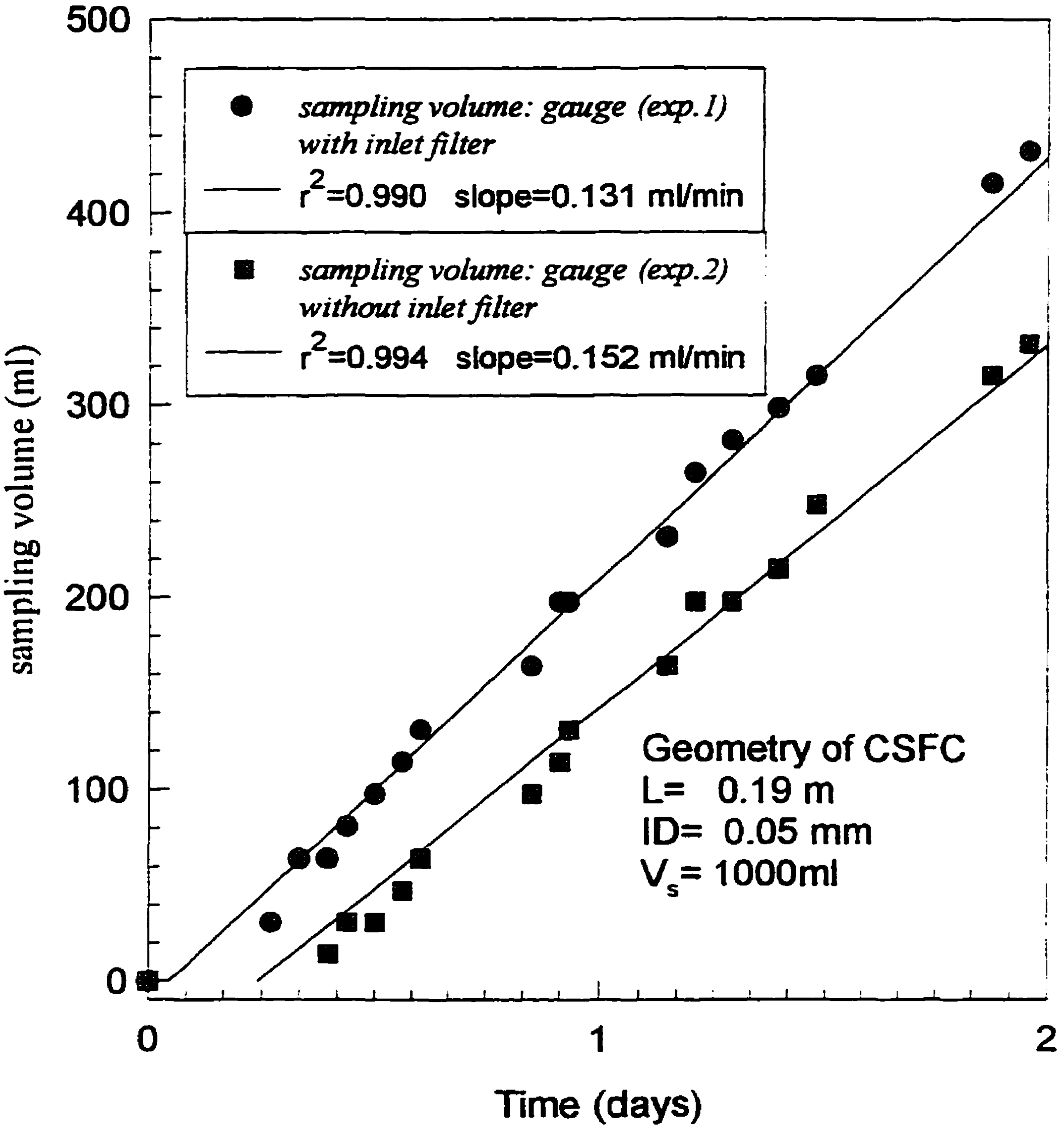
Experimental results

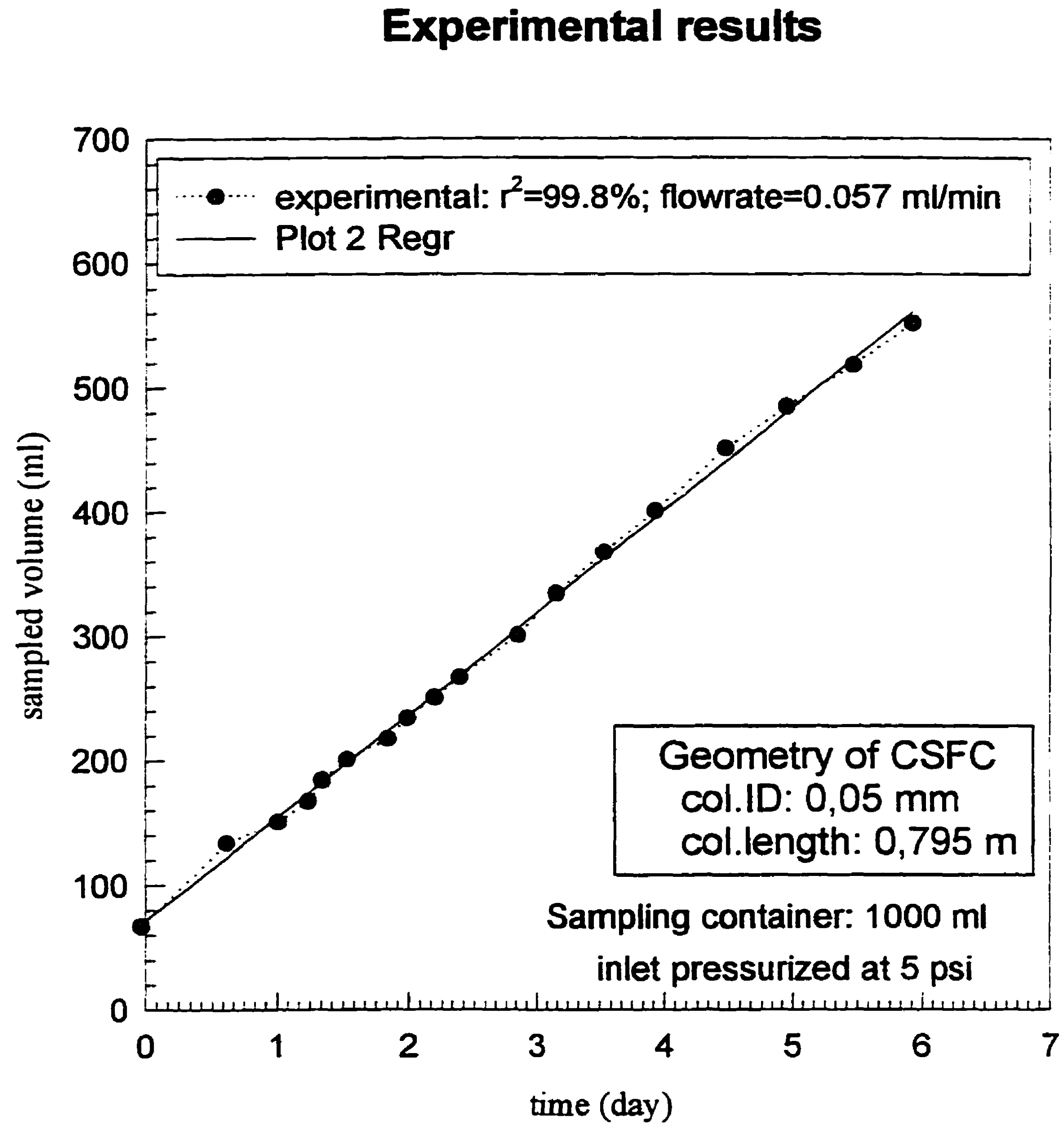
24 hours sampling profile with 1 liter vessel

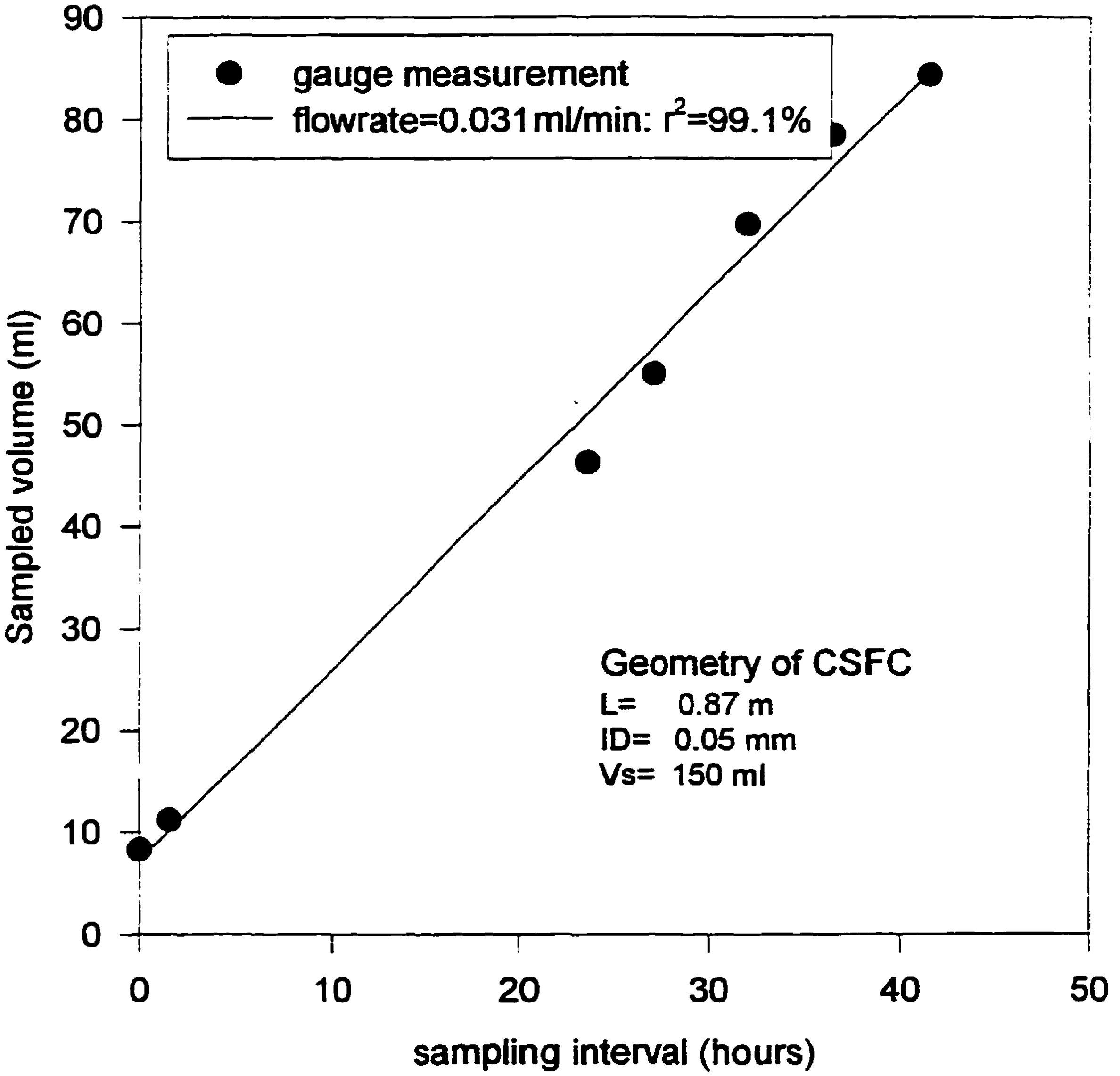
repeated experiment with previously used CSFC



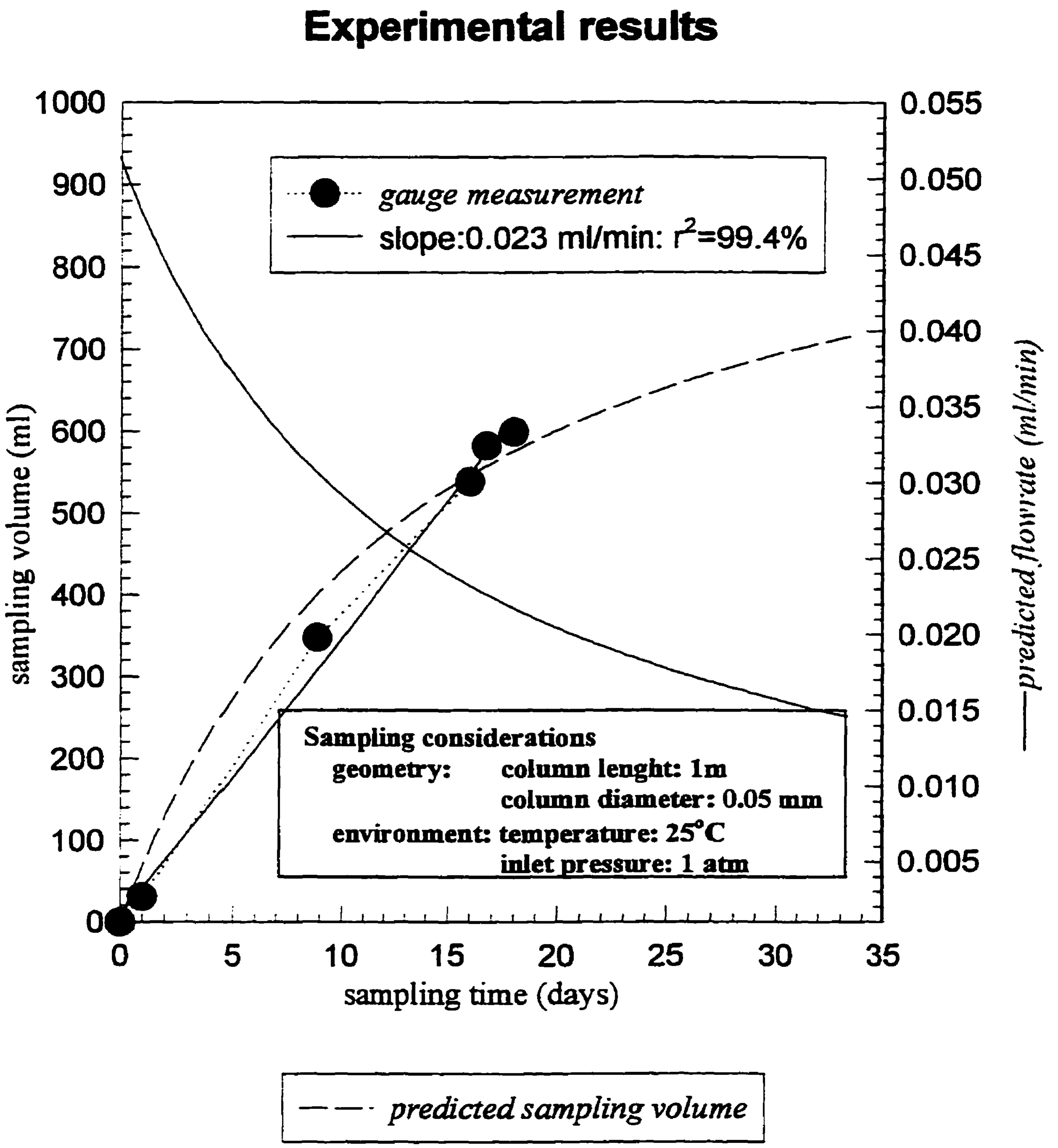
Experimental results



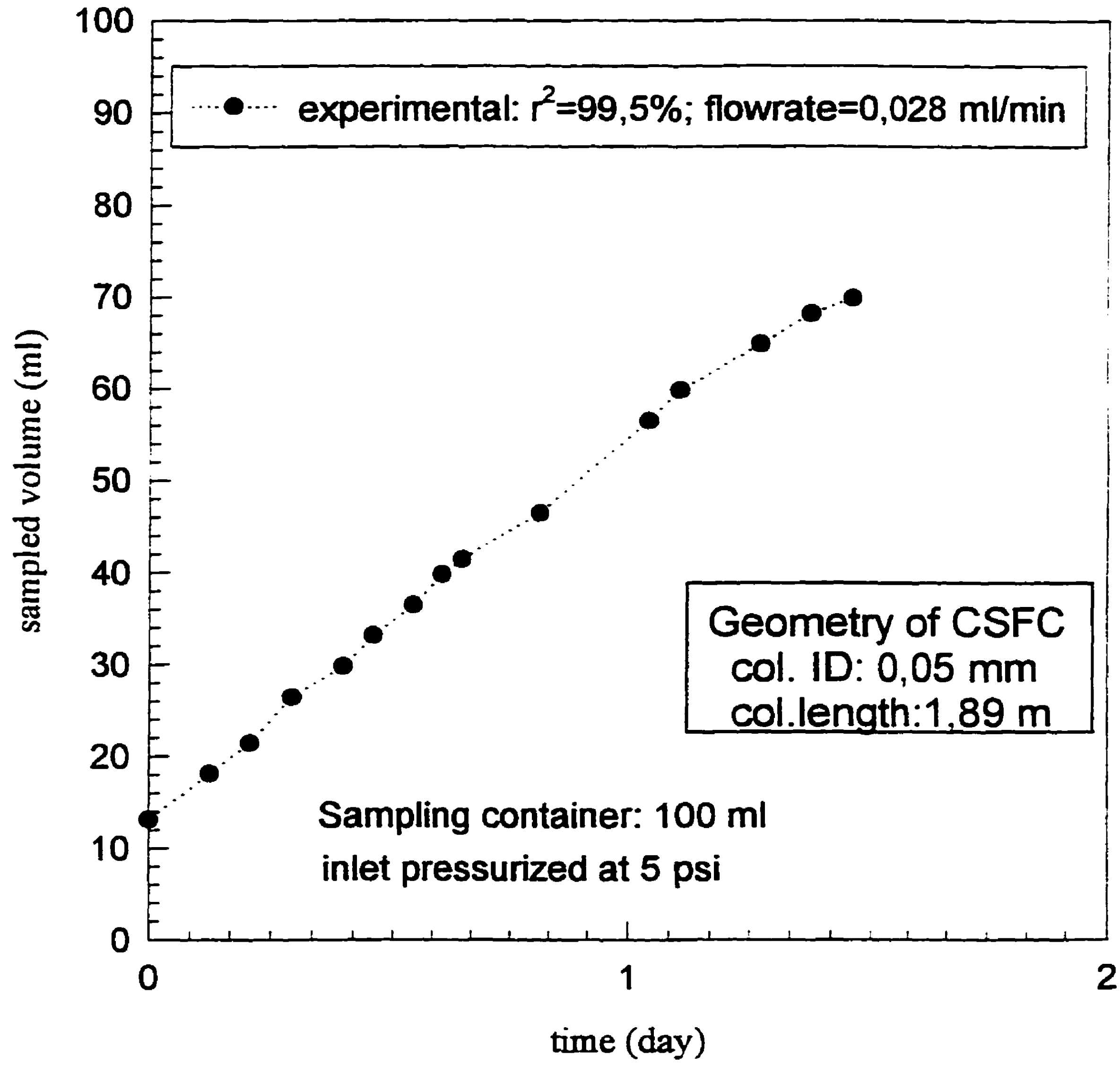

Experimental results
experimental: r^2=99.8%; flowrate=0.057 ml/min
Plot 2 Regr
Geometry of CSFC
col.ID: 0,05 mm
col.length: 0,795 m
Sampling container: 1000 ml
inlet pressurized at 5 psi
sampled volume (ml)
0
100
200
300
400
500
600
700
time (day)
0
1
2
3
4
5
6
7

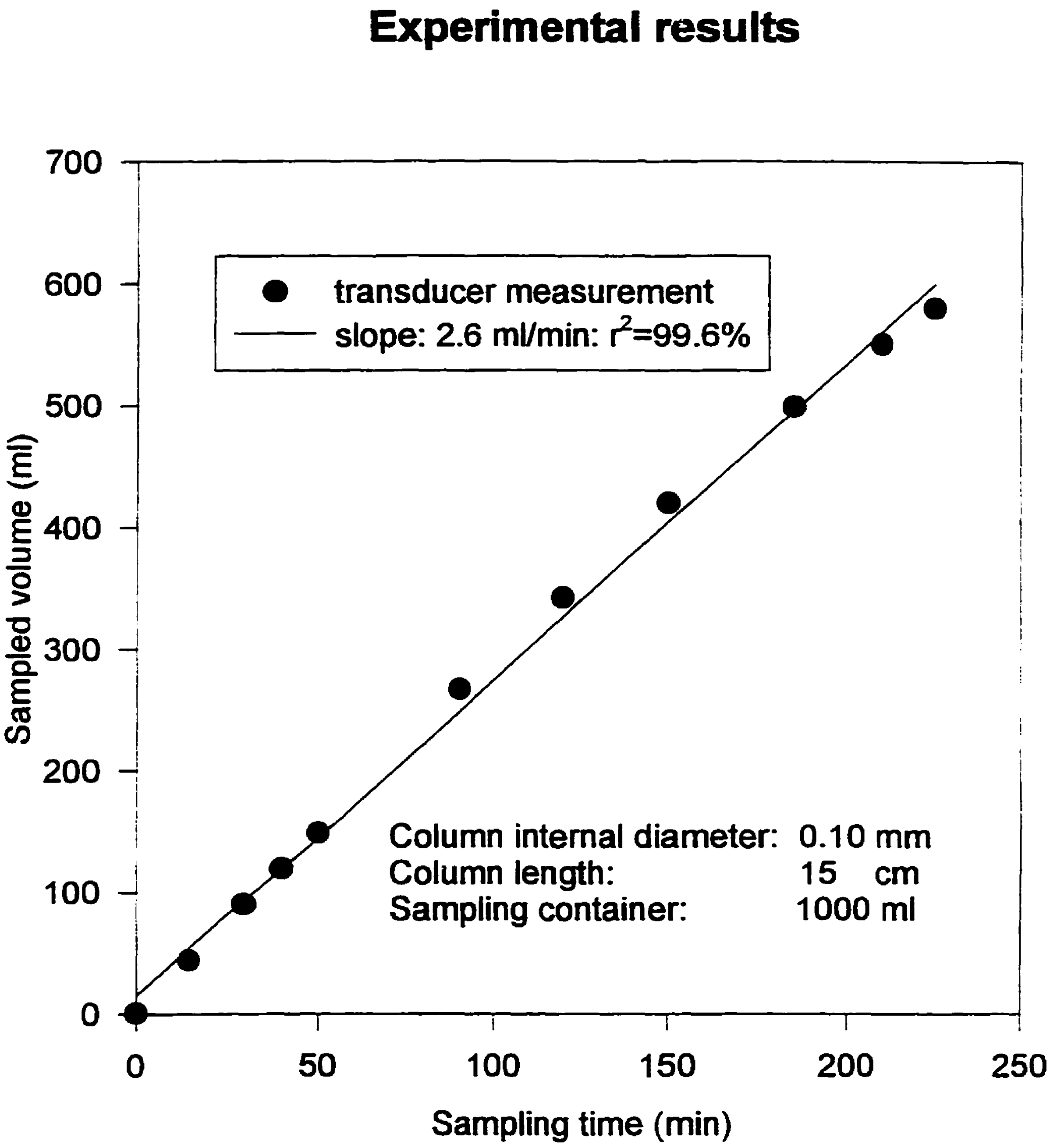


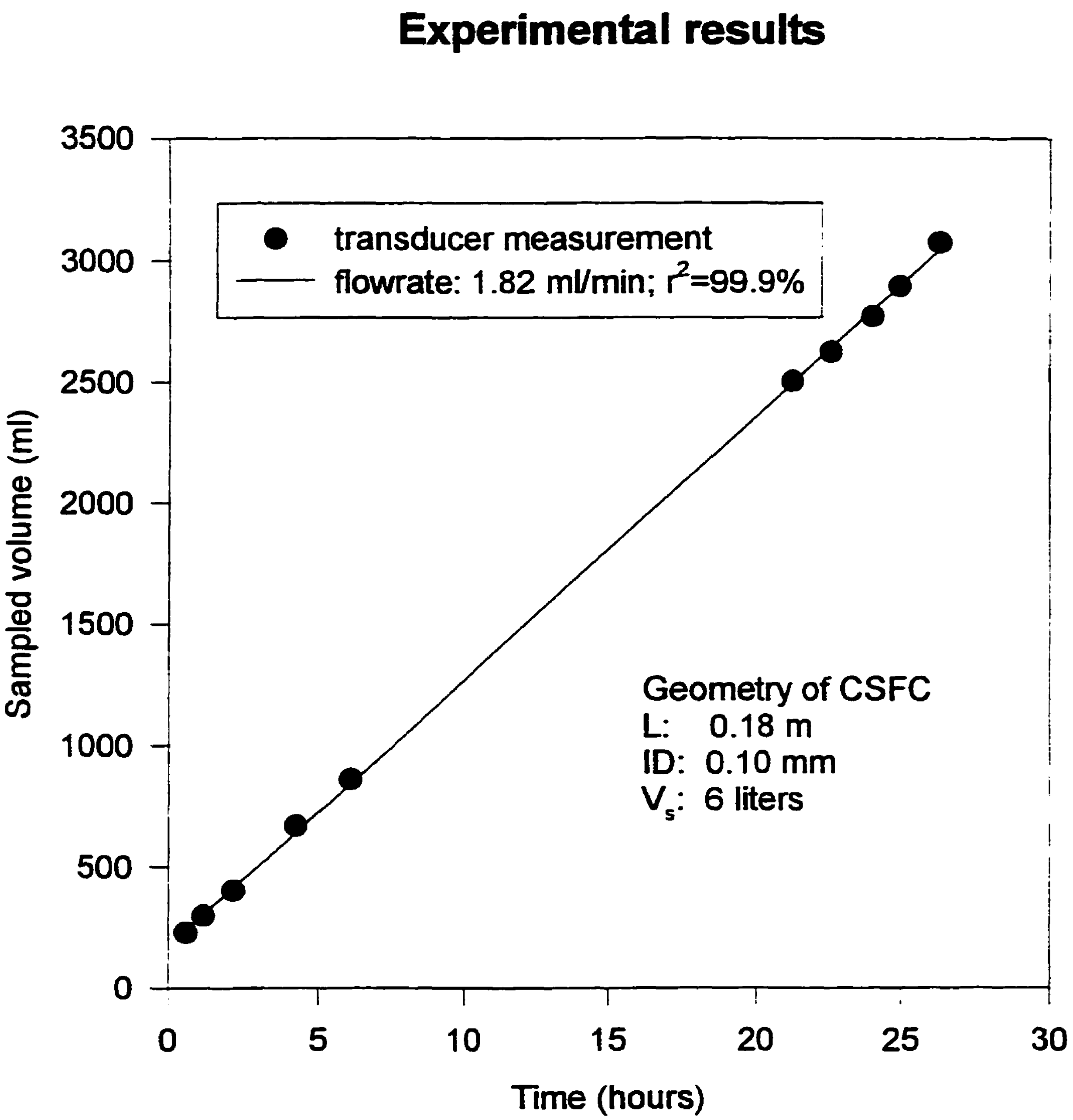
Experimental results

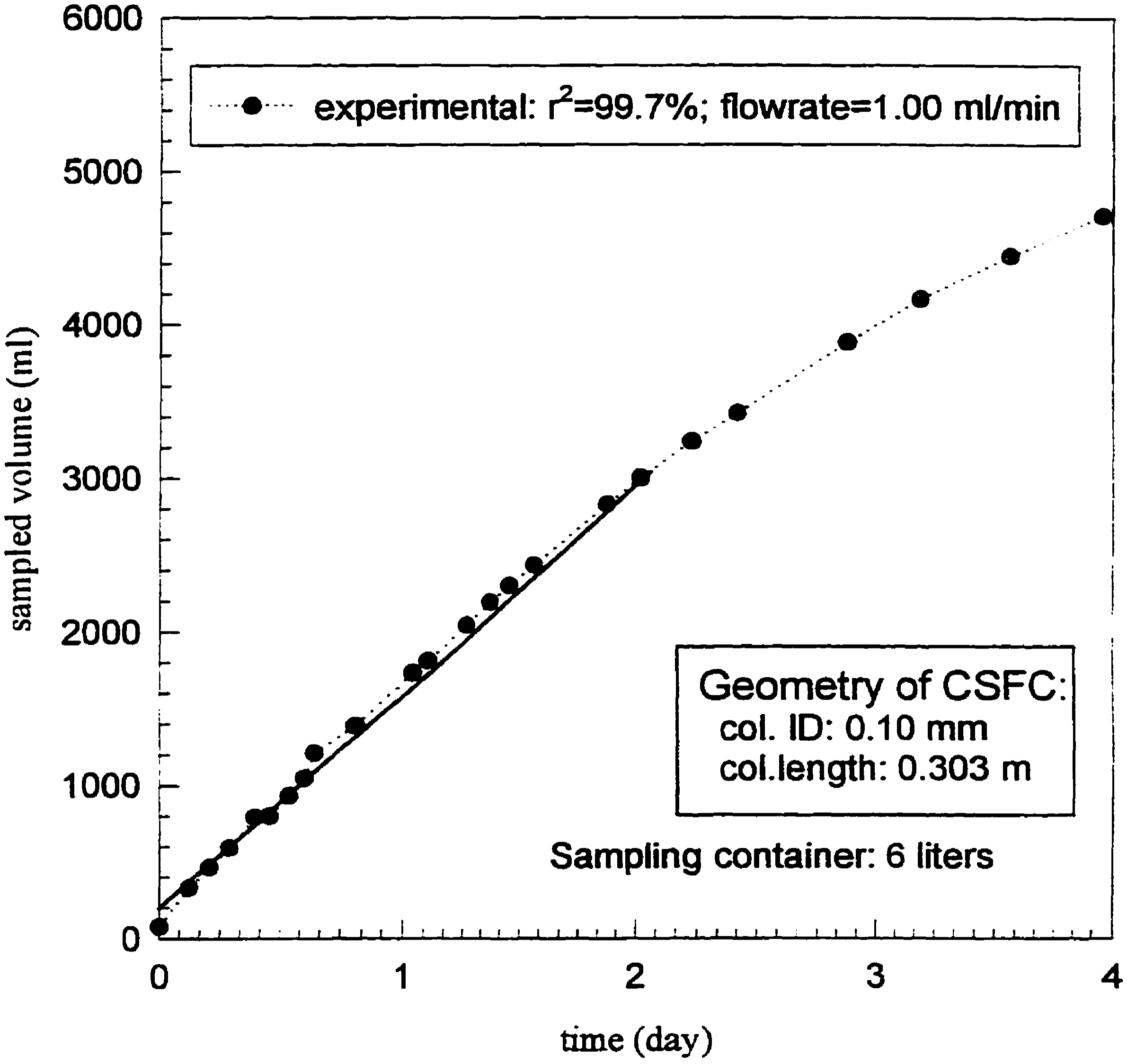

Experimental results
gauge measurement
slope:0.023 ml/min: r^2=99.4%
sampling volume (ml)
0
100
200
300
400
500
600
700
800
900
1000
predicted flowrate (ml/min)
0.005
0.010
0.015
0.020
0.025
0.030
0.035
0.040
0.045
0.050
0.055
sampling time (days)
0
5
10
15
20
25
30
35
Sampling considerations
geometry: column lenght: 1m
column diameter: 0.05 mm
environment: temperature: 25°C
inlet pressure: 1 atm
predicted sampling volume

Experimental results

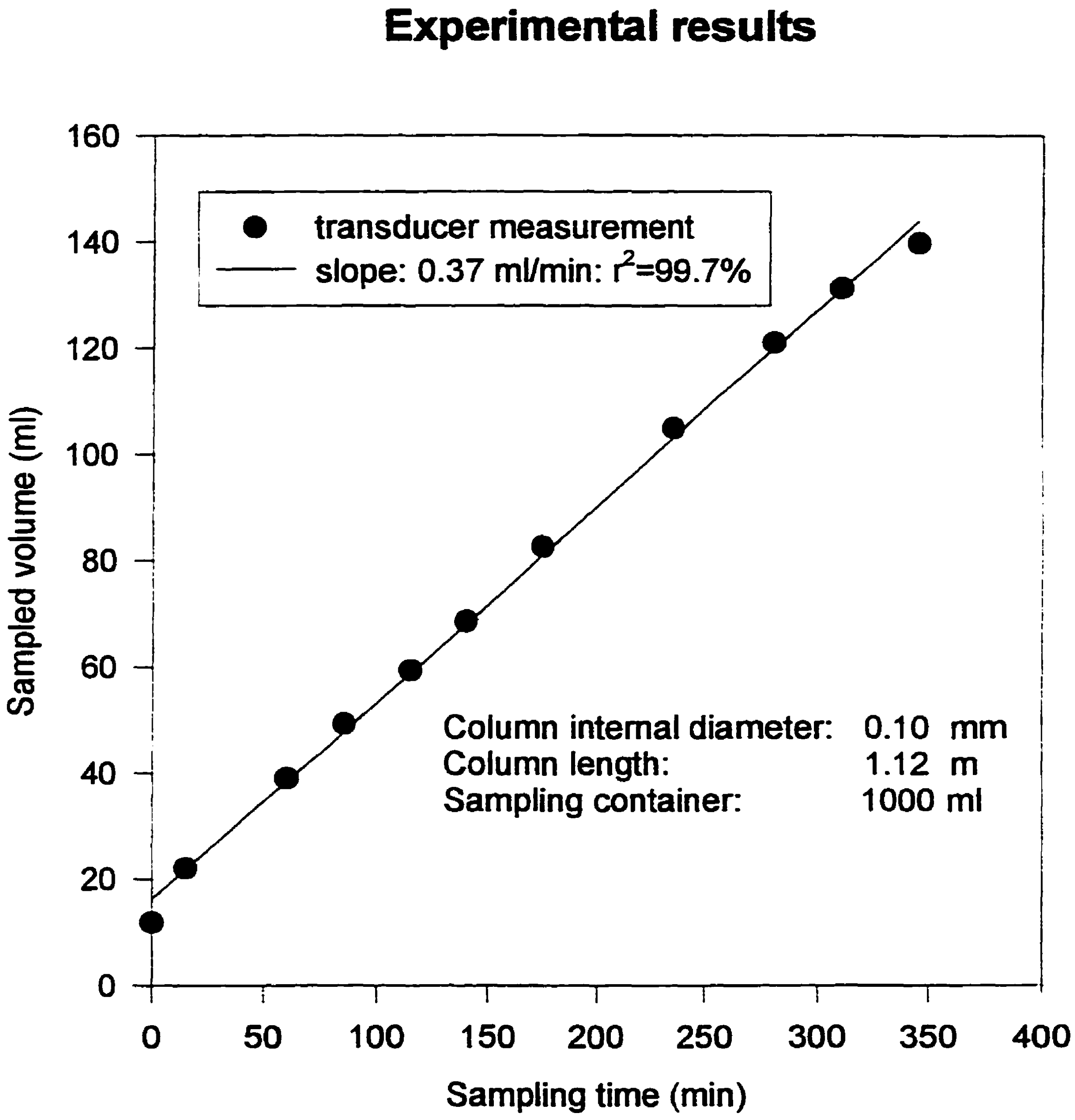



Experimental results
● transducer measurement
—— slope: 2.6 ml/min: r2=99.6%
Column internal diameter: 0.10 mm
Column length: 15 cm
Sampling container: 1000 ml
Sampled volume (ml)
0
100
200
300
400
500
600
700
Sampling time (min)
0
50
100
150
200
250


Experimental results
● transducer measurement
flowrate: 1.82 ml/min; r²=99.9%
Geometry of CSFC
L: 0.18 m
ID: 0.10 mm
V_s: 6 liters
Sampled volume (ml)
0
500
1000
1500
2000
2500
3000
3500
Time (hours)
0
5
10
15
20
25
30

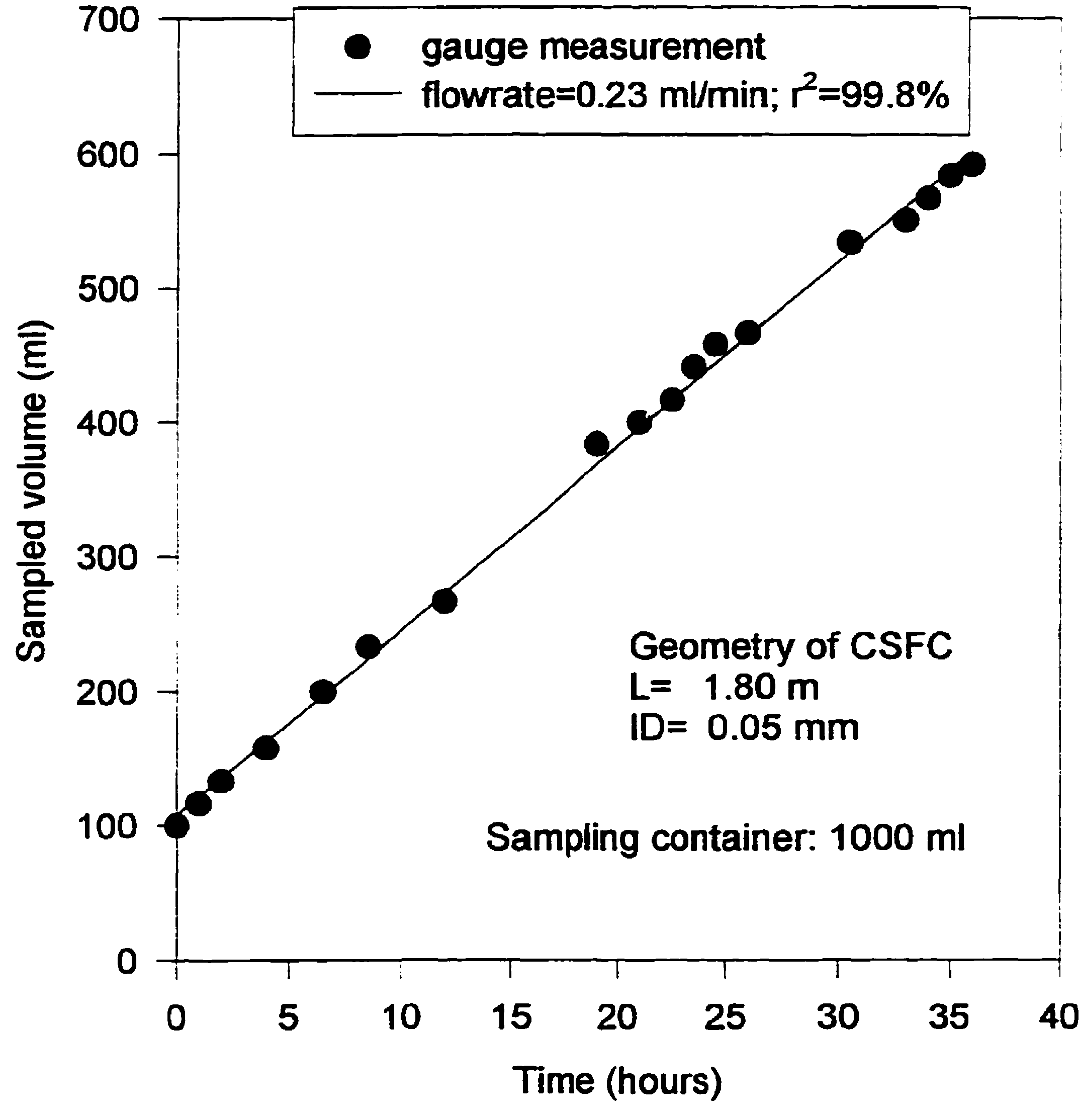


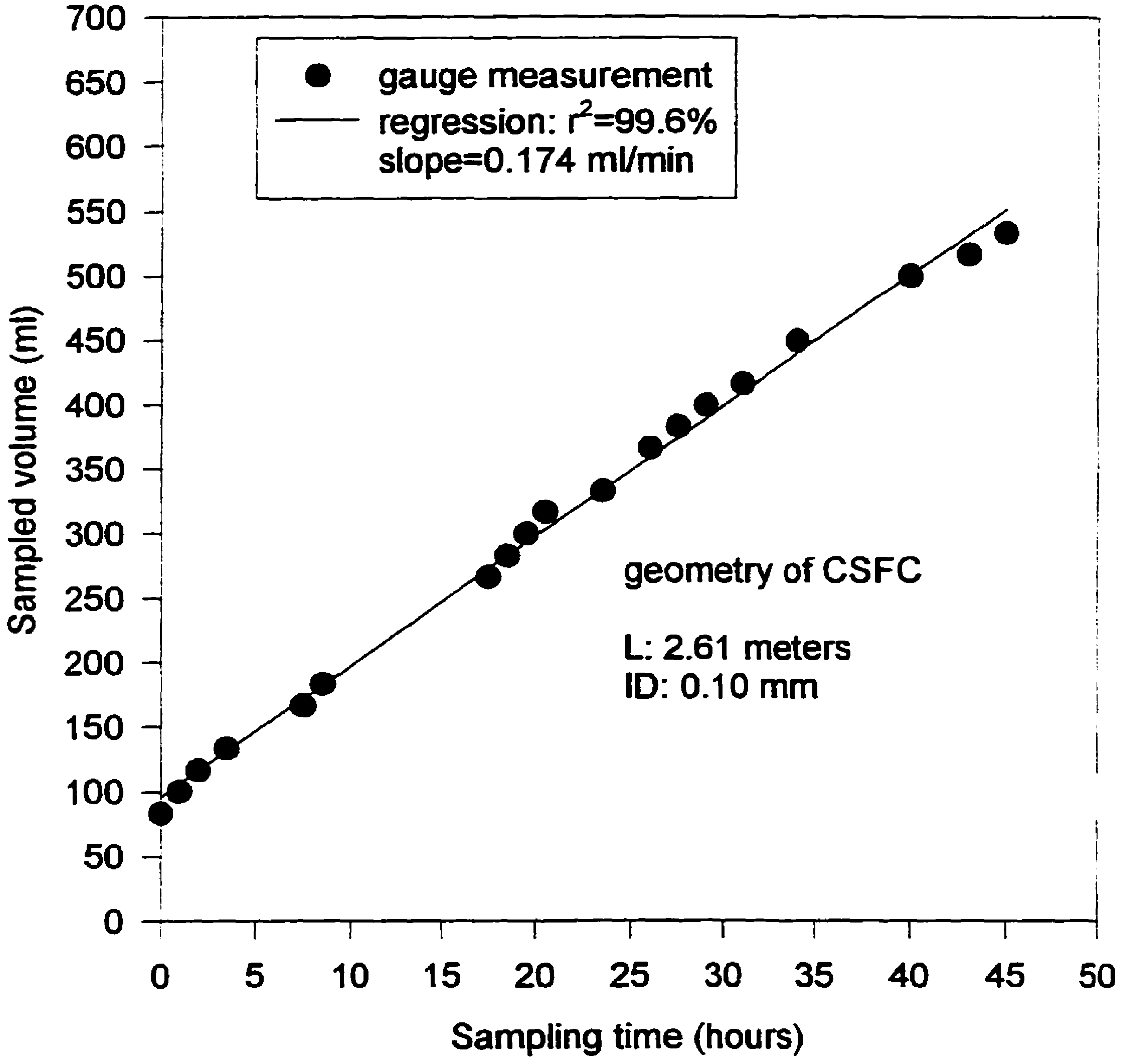
Experimental results



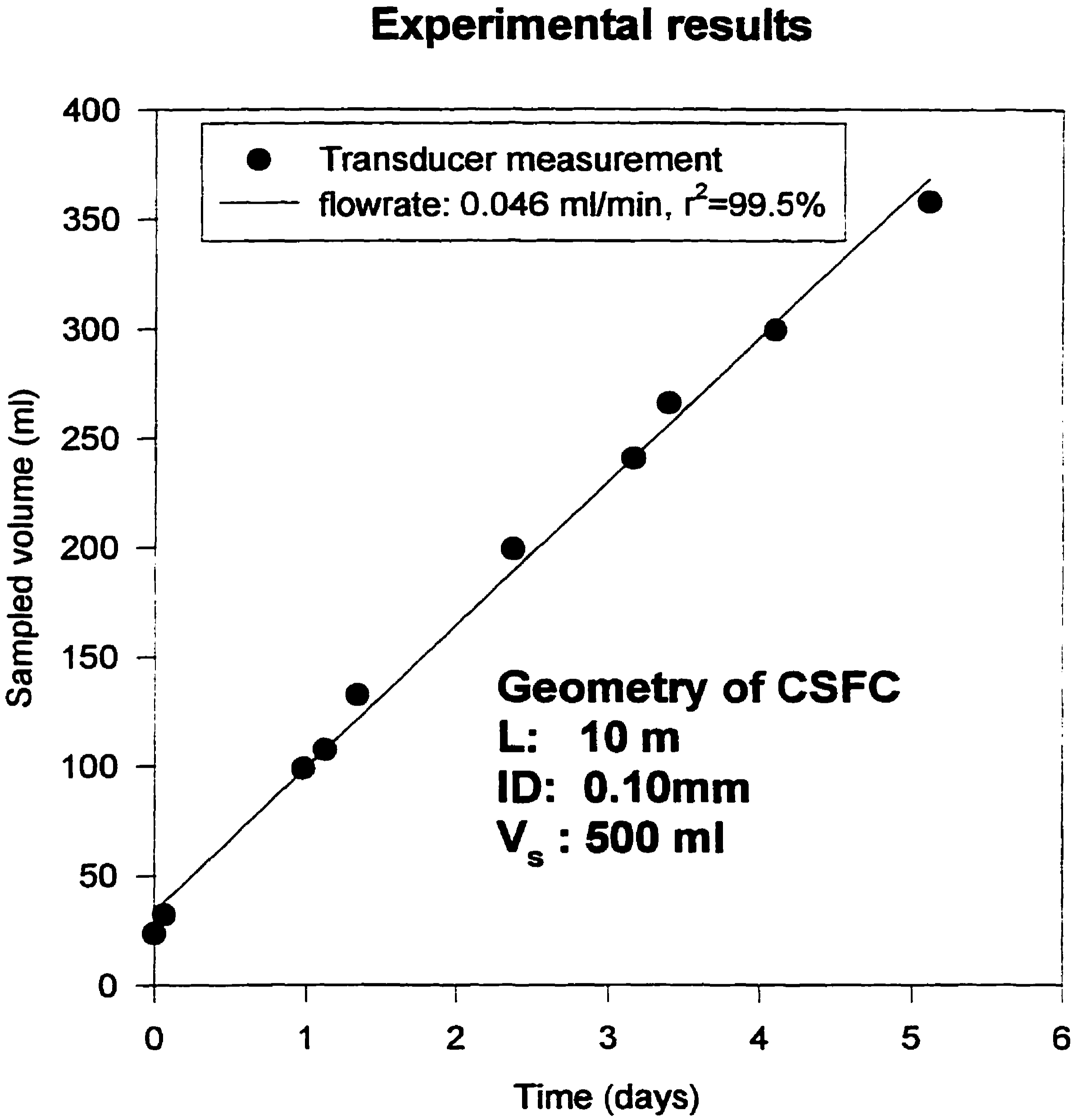
Experimental results

Experimental results





Experimental results


Experimental results
● Transducer measurement
flowrate: 0.046 ml/min, r^2=99.5%
Geometry of CSFC
L: 10 m
ID: 0.10mm
V_s : 500 ml
Sampled volume (ml)
0
50
100
150
200
250
300
350
400
Time (days)
0
1
2
3
4
5
6

APPENDIX-4: Validation studies from an external laboratory

LONG TERM TIME INTEGRATED SAMPLING CANISTER

1. Introduction

The Summa passivated canister has been used extensively with success for the collection of grab samples for trace organics in air. More recently, a flow controller has been developed that allows the collection of time integrated samples into the canister. The operation of the controller is based upon the use of a restricted orifice that can be designed and configured for continuous sampling over various intervals of specified time. Figure 1 provides a diagram of the overall configuration of time integrated sampling device as currently being used.

The flow controlling device simply connects to the canisters through standard Swagelok fittings. The device is equipped with a pressure gauge which allows the monitoring of the pressure during sampling process. The flow controller is housed within a hollow stainless steel enclosure which has standard Swagelok fittings welded for attachment of the various functional elements. A 0.5 μm stainless steel fritted filter is attached to the inlet of the flow controller to prevent particulates from entering the small orifice of the controller. The device can be configured with any size canister, and the orifice can be easily configured to collect samples for various time intervals that may be needed based upon sampling objectives. The device can be configured for collection of samples in a linear manner for hours, days, weeks, and even months if necessary.

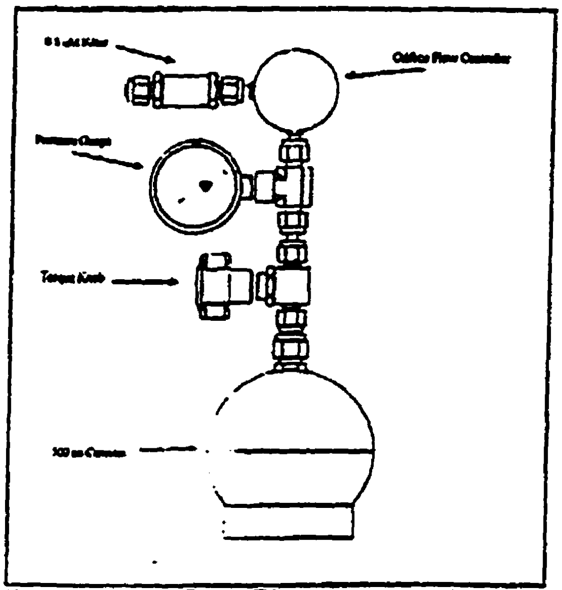


Figure 1 Long Term Time Integrated Sampling Canister Assembly

Boeing Analytical Services has been working cooperatively in the applications development and verification of the device with McGill University in Canada over the last year. The basic description and functionality of the device was first published at the *Symposium on the Measurement of Toxic and Related Air Pollutants* in May 1996 at Research Triangle Park, North Carolina. A copy of that paper is attached to this summary report for review.

Since a US patent application has been submitted for the device, the details of the device configuration cannot be discussed at this time. This report will however summarize the operating characteristics and results of pre-flight verification testing before shipment to the Russian Space Station Mir.

2. Sampling Dynamics

Pressure equilibration across a restricted orifice is a well defined phenomenon based upon fundamental laws of fluid dynamics and gas kinetics. Figure 2 illustrates the pressure equilibration curve of a 500 cc canister equipped with a flow controller designed to collect a one week (7 days) sample.

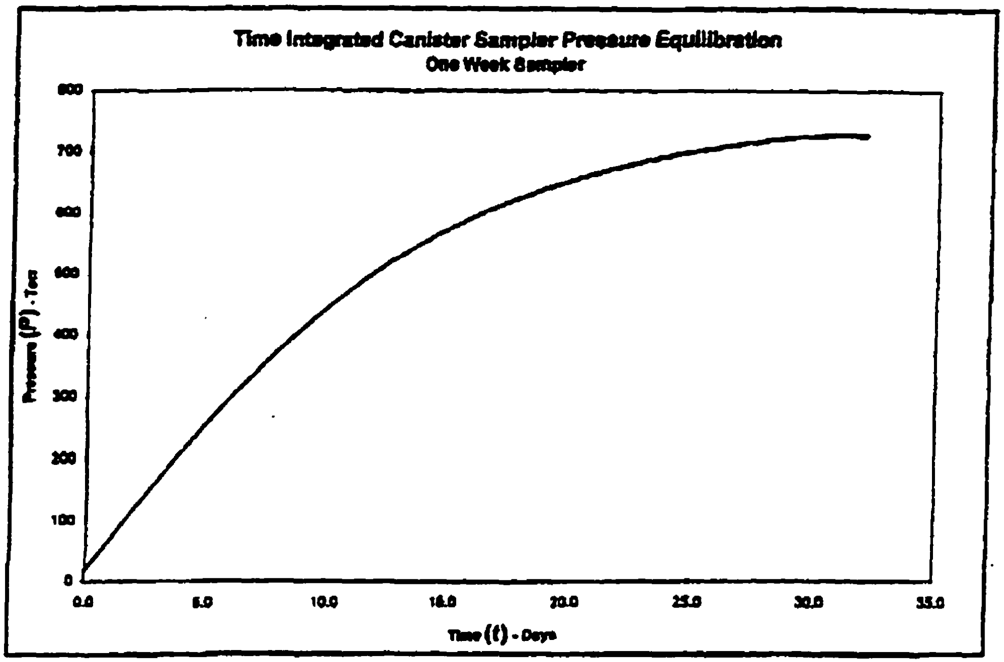


Figure 2 Pressure Equilibration Curve for A One Week Sampler

As illustrated in Figure 2, the pressure equilibration process begins in a reasonably linear fashion, and the process becomes very slow as the ΔP between the canister and the ambient environment becomes small. The above curve for the overall time interval of thirty three days fits a fifth order polynomial with a correlation coefficient (R^2) greater than 0.9999. As the pressure in the canister approaches the ambient pressure of the sampling environment, the curve flattens out and actually fluctuates up and down with the fluctuation of the ambient pressure. It appears that the sampling rate in Figure 2 is linear in the initial part of the pressure equilibration process. In Figure 3, the same data from Figure 2 is processed for the time interval of one week.

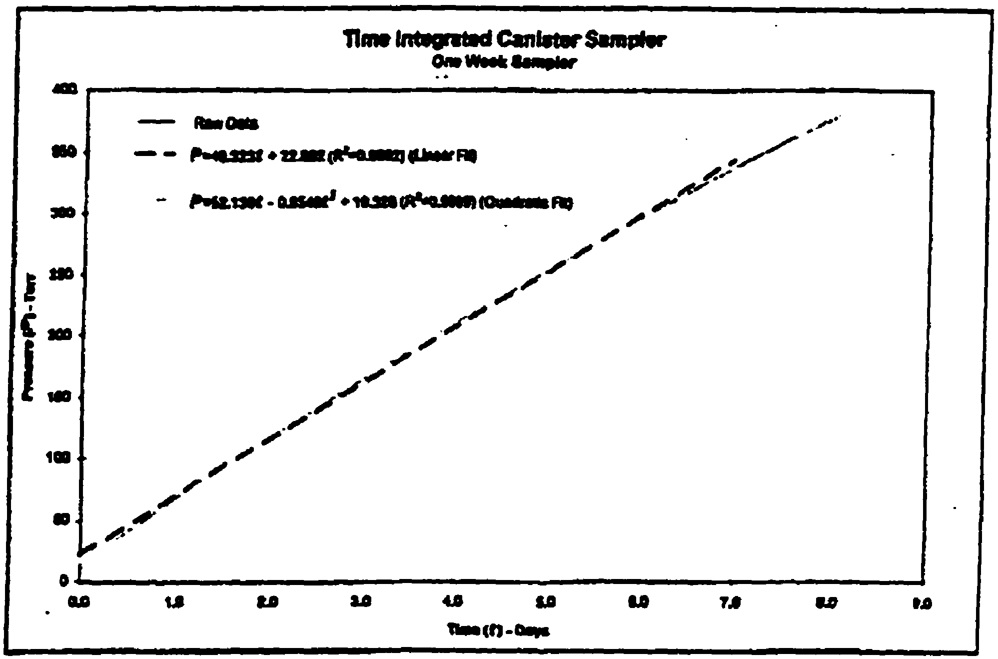


Figure 3 Time Integrated Sampler Configured For Seven Days (Processed for 50% Volume of the Canister)

As can be seen from Figure 3, the rate of sample collection within the 7 day sampling interval is very close to the linear approximation. The linear regression of the data over the seven day time interval provides a correlation coefficient of 0.9992. In essence, the slight difference from the linear approximation and the raw data is far beyond the statistical variation expected from the trace contaminant analytical methods.

Figure 4 below also illustrates similar data for a flow controller configured for a 48 hour sampling interval. Figure 4 appears to demonstrate slightly more deviation from the linear approximation than Figure 3 for the one week sampler. In actuality, this is not true because the linear estimate was processed to a smaller ΔP. In Figure 4, the data is processed for a time interval that represents the canister equilibrating to 60 percent of the ambient environmental pressure rather than the 50 percent for the one week sampler in Figure 3. In both cases, the deviation from linearity could not be determined from trace contaminant analytical methods, but obviously you get the best approximation for linear sample collection when collecting about 50 percent of the volume of the canister.

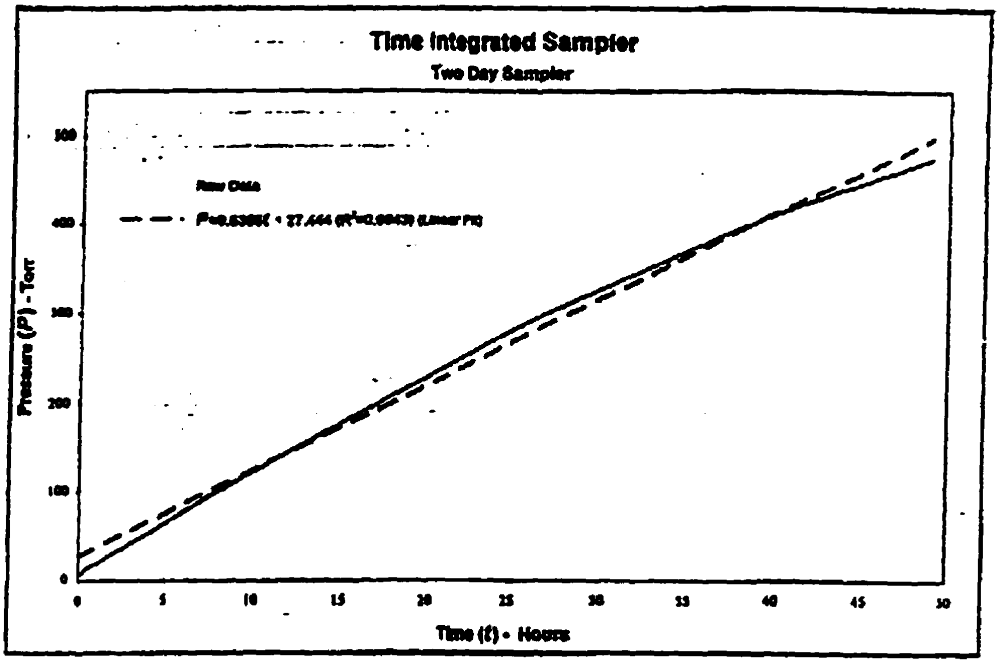


Figure 4 Time Integrated Sampler Configured For Two Days (Processed for 60% Volume of Canister)

Another important aspect to the application of the time integrated canister involves the effect of the changing ambient environmental pressure on sampling accuracy. The data from the charts illustrate that the sampling rate is essentially constant as long as the canister pressure (or volume) is less than 50 to 60 percent of the ambient pressure (or volume of canister) of the environment being sampled. Therefore, pressure changes in the range of ±50 mm expected within a spacecraft environment will have no measurable impact on the rate of sampling and the quality of the quality of the data obtained.

3.0 Assessment of Bias Effects of the Time Integrated Sampler

It is important to assess the efficiency of transfer of the flow controller for any potential bias effects for collection of contaminants into the canister. An experiment was conducted by allowing a 500 cc time integrated canister to collect a sample over a period of seven days. The recovery of the compounds were determined from a standard prepared from the same source. The data obtained for non-polar compounds from this experiment is presented in Table 1.

	Percent		Percent
Target Compounds	Difference	Target Compounds	Difference
Freon 12	6.1	Trichloroethene	2.6
Freon 114	9.7	cis-1,2-Dichloropropene	-10.6
Chloromethane	-9.2	Toluene	7.8
Vinyl chloride	8.2	trans-1,3- Dichloropropene	-18.2
Bromomethane	-6.0	1,1,2- Trichloroethane	5.1
Chloroethane	14.3	Tetrachloroethene	2.0
Freon 11	7.4	1,2- Dibromoethane	-7.2
1,1 dichloroethene	15.9	Chlorobenzene	-3.0
Freon 113	5.8	Ethylbenzene	0.0
Methylene Chloride	15.8	m,p- Xylenes	2.2
1,1-Dichloroethane	6.1	o- Xylene	-0.4
cis-1,2- Dichloroethene	4.1	Styrene	-13.3
Chloroform	7.8	1,1,2,2- Tetrachloroethane	-18.6
1,1,1- Trichloroethane	4.1	1,3,5- Trimethylbenzene	-15.9
Carbon Tetrachloride	2.1	1,2,4-Trimethylbenzene	-21.2
Benzene	9.5	1,3-Dichlorobenzene	-25.9
1,2- Dichloroethane	1.5	1,4- Dichlorobenzene	-27.6
1,2-Dichloropropane	2.5	1,2- Dichlorobenzene	-34.3

Table I Summary of Bias Effects of the Time Integrated Cansiter for Non-polar Compounds (7 Day Equilibration)

The average percent deviation from Table 1 is 9.7 with a range of 0.4 to 34 percent. The largest deviations are experienced by the largest molecular weight compounds. This is the same trend that is experienced for dealing with simple transfers of standards between canisters. The last compound slightly exceeded the ± 30% deviation criteria that has been identified as the expected range of acceptability for utilization of the canister method. It appears that the restricted orifice flow controller has little or no effect on the recovery of compounds, but more data needs to be collected under different controlled conditions to make a more definitive statement.

Table 2 summarizes deviations for a variety of polar compounds that were determined in a similar manner. The average percent deviation is 13.7 percent with a range of 1.4 to 32.6 percent. Generally, a larger negative deviation is observed for the polar organic compounds through the flow controller than for the non-polar compounds. This trend in data is also similar to that experienced for these compounds from simply transferring standards from canister to canister. As with the non-polar compounds, more work needs to be conducted under different controlled conditions to better characterize what impact if any that the flow controller has on transfer of polar compounds into the canister.

	Percent
Target Compounds	Difference
Acetaldehyde	-5.0
Pentane	4.8
Ethanol	32.6
Propanal	18.8
Acetone	-11.5
Isopropanol	-1.4
Hexane	-2.5
1-Propanol	-25.5
Butanal	12.0
2-Butanone	-14.5
Ethyl Acetate	-9.5
2-Butanol	22.4
Cyclohexane	-6.3
Heptane	-7.7
1-Butanal	28.7
n-Propyl Acetate	-8.4
4-Methyl-2-Pentanone	-19.5
Octane	-12.9
2-Hexanone	-25.4
Butyl Acetate	4.7

Table 2 - Summary of Bias Effects of the Time Integrated Canister for Polar Compounds
(7 Day Equilibration)

4.0 Vibration Testing

Prior to shipment, all of the flight time integrated canisters were subjected to the spectrum of vibrations according to specifications prescribed by RSC Energia in Table 3 below.

Frequency	Power Spectral Density (g2/Hz, in 120 sec)
20 - 100 Hz	0.02
100 - 200 Hz	0.02 up to 0.05
200 - 500 Hz	0.05
500 - 2000 Hz	0.05 up to 0.025

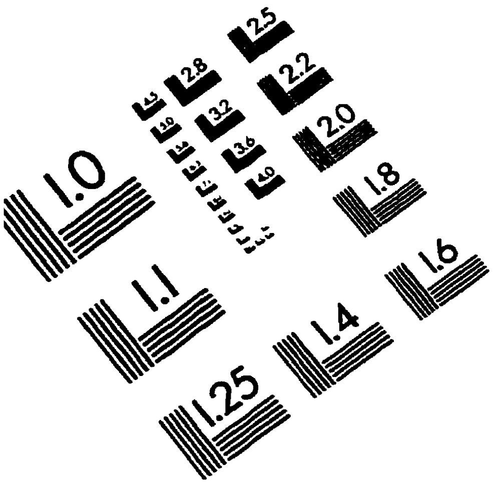
Table 3 Vibration Test Parameters

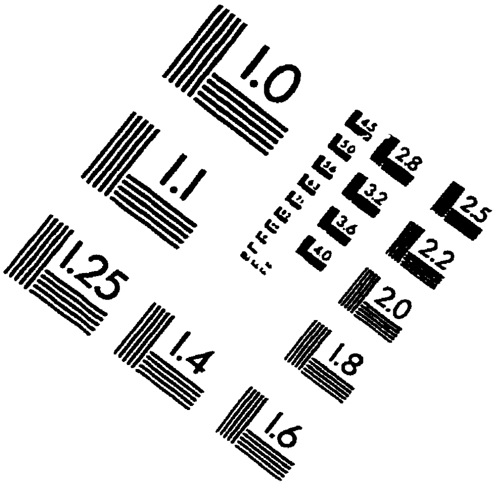
For the Russian Progress module, flight hardware is packed tightly with cotton into various compartments. The vibration test was conducted in such a manner to simulate this environment by packing the flight hardware tightly with cotton towels inside an aluminum box. The vibration tests were conducted for 2.6 minute intervals with the container placed in different positions relative to the forces being applied. After the tests, all evacuated canisters were allowed to start pressure equilibration for two days to detect failures. All of the tested canister equilibrations were noted to be normal and acceptable for flight.

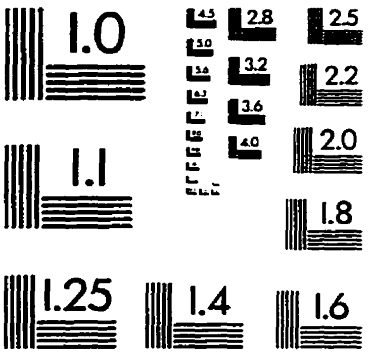
5.0 Summary

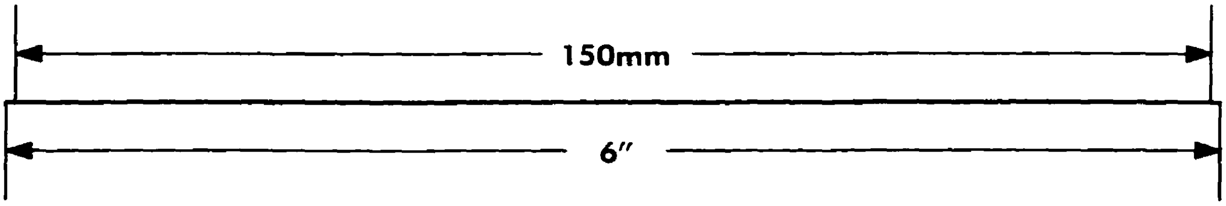
In summary, the new time integrated canister sampling device provides a flexible means for collection of time integrated samples in a linear manner. The device configuration can be easily modified to provide sampling over any defined time interval needed to achieve measurement objectives. The data from initial ground testing indicate acceptable transfer of compounds across the restricted orifice inlet system. All tested canisters survived the vibration tests that covered the full spectrum and intensity of expected vibrations. Evidence obtained to date indicate that the time integrated canisters did survive the launch to Mir and are operating as expected. Further testing and modification of the device is in progress to better characterize operating parameters and optimize performance for future applications.

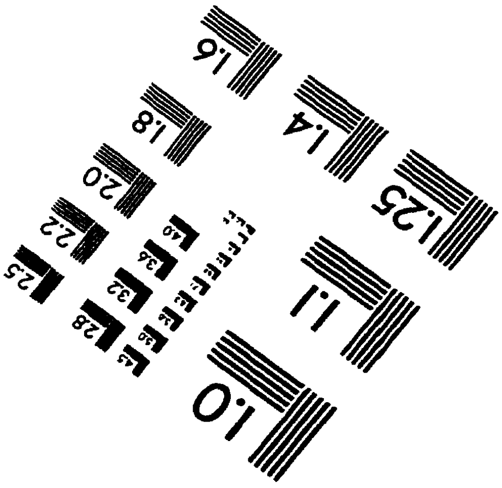
IMAGE EVALUATION TEST TARGET (QA-3)

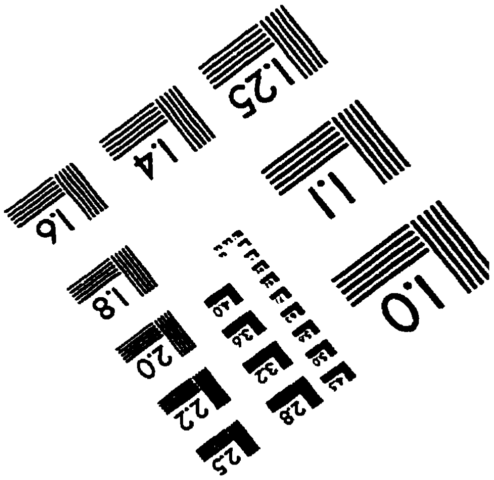












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