Compound Specific Isotope Ratio Analysis in Vapour Intrusion Studies using Waterloo Membrane Sampler (WMS)

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

ABSTRACT

Compound specific isotope analysis (CSIA) has been used extensively for fingerprinting applications and for the evaluation of the degradation processes in organic contaminant studies in groundwater. Recently, an increase in academic interest on the potential applications of CSIA in vapour intrusion has been observed, and various studies have been conducted. A key challenge of this research is the development of analytical protocols for CSIA that handle very low concentrations of organic compounds typically found in indoor samples. A sampling device capable of gathering enough mass for CSIA has to be tested for field applications. In this research the Waterloo Membrane Sampler (WMS), a permeation-type passive sampler that has been successfully used in numerous studies, is presented as a potential device for this purpose. Indeed, the WMS has been successfully applied in the quantitation of volatile analytes in indoor and outdoor air, as well as soil-gas matrices. The objective of this research was to evaluate the applicability of the WMS for CSIA in vapour intrusion studies. Analyte amounts sufficient for CSIA were collected when using thermal desorption to introduce the sample into the gas chromatography-isotope ratio mass spectrometry system (TD-GC-IRMS). The TD-GC-IRMS was employed to determine the stable carbon isotopic composition ($\delta^{13}C$) of three model analytes: hexane, benzene and trichloroethylene, which were contained in a standard gas mixture. In order to determine whether isotopic fractionation occurred during the exposure, measures of $\delta^{13}C$ were taken for individual compounds found in both the standard gas (active sampling) and in the gas permeating through the PDMS membrane into the sorbent (passive sampling). Various WMS were exposed to the standard gas for 3, 6, 12, 24, 48, 96 and 192 hours. Variations of the isotopic carbon composition for each analyte were measured versus time, amount of analytes

sorbed and exposure temperature. Results obtained in all studies indicate good reproducibility with a standard deviation within the accepted analytical error of ± 0.5 ‰. All sampling processes introduced small isotopic fractionation; however, the degree of fractionation remained practically constant and independent of sampling time, mass adsorbed and temperature, therefore could be accounted for. The new method developed was applied in a field study, where the results obtained were compared with solvent base active sample collection and analysis. Results obtained demonstrated good data reproducibility. This indicates that CSIA coupled with WMS could be a valuable tool in environmental forensics field.

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I am dedicating this thesis in the memory of my mother.

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LIST OF ABBREVIATIONS

CSIA	Compound Specific Isotope Analysis
EPA	Environmental Protection Agency
EA-IRMS	Elemental Analyzer Isotope Ratio Mass Spectrometry
FID	Flame Ionization Detector
GC-FID	Gas Chromatography - Flame Ionization Detector
GC-IRMS	Gas Chromatography - Isotope Ratio Mass Spectrometry
IAEA	International Atomic Energy Agency
IRMS	Isotope Ratio Mass Spectrometry
HPLC-IRMS	High Performance Liquid Chromatography - Isotope Ratio Mass Spectrometry
LCD	Liquid Crystal Display
LDPE	Low Density Polyethylene
LTPRI	Linear Temperature Programmed Retention Index
MS	Mass Spectrometry
MSDS	Material Safety Data Sheet
nA	Nanoampere
NERI	Northeast Research Institute
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCE	Tetrachlorethene
PDMS	Polydimethylsiloxane
PID	Photoionization Detector
P&T	Purge and Trap
PSG	Passive Soil Gas Sampler
PTFE	Polytetrafluoroethylene
SPME	Solid-Phase Microextraction
SPMD	Semipermeable Membrane Device
SVOC	Semi-volatile Organic Compound

TD-GC/MS	Thermal Desorption - Gas Chromatography/Mass Spectrometry
TPH	Total Petroleum Hydrocarbons
TWA	Time-Weighted Average
VOC	Volatile Organic Compound
VPDB	Vienna Pee Dee Belemnite
WMS	Waterloo Membrane Sampler

1. INTRODUCTION TO ISOTOPES

Isotopes are atoms that contain an equal number of protons but different numbers of neutrons. [1] The word *Isotope* is derived from the Greek words *isos* (meaning equal) and *topos* (meaning place).[1] Isotopes occupy the same location in the periodic table; for a given element, all isotopes maintain the same chemical properties.[1] While some elements have many isotopes, others have just one.[1]

There are two types of isotopes: radioactive and stable. Radioactive isotopes, also called radioisotopes, have unstable nuclei and spontaneously disintegrate and disperse extra energy by discharging radiation as alpha, beta and gamma rays.[2] This results in the formation of a new element.[3] On the other hand, stable isotopes are characterized by stable nuclei and do not decay into another isotope; however, they could originate from a radioactive isotope. Natural occurrence of stable isotopes is dependent on environmental conditions.[4] While most elements have at least two stable isotopes, twenty one elements are considered pure by only having one isotope.[5] For this research, carbon isotopes were chosen for experimentation. They will be further discussed in the next Section.

1.1 CARBON ISOTOPES

A carbon isotope is expressed as ^{A}C, following a conventional short notation, where A represents the atomic mass (the sum of neutrons and protons) followed by the element symbol.[6] Although many carbon isotopes exist, only three occur in nature. Of these, ^{12}C and ^{13}C are stable

isotopes, while ^{14}C is a radioactive isotope. Their distribution ratios found in the environment are 98.93%, 1.07% and 2×10^{-10} % for ^{12}C, ^{13}C and ^{14}C, respectively.[6]

Generally speaking, lighter isotopes of the same element have different properties than heavier isotopes.[7] Heavier isotopes are characterized by greater atomic masses due to their additional neutrons. As a result, their properties differ: lighter isotopes diffuse faster, occupy larger molar volumes, and form less stable chemical bonds.[6] As well, it is central to note other important characteristic of the isotopic processes that naturally occur in nature. An important aspect of isotopic behavior was observed by Craig in 1953. In the course of his research, Craig noted that different biochemical processes modify the equilibrium among the carbon isotopes in nature.[8] Indeed, different environmental processes such as diffusion, microbial transformation, photosynthesis and evaporation favor one isotope over another, which in turn leads to stable isotopic fractionation.[6] More detailed information about this subject can be found in Section 1.3.

As a result of their differences in mass, isotopes can be separated by mass spectrometry. This analytical detection method is used to trace various changes in the environment. The isotopic ratio of an element is denoted as R, which is defined as the ratio of heavier to lighter isotopes (e.g. for carbon, $R=^{13}C/^{12}C$).[6] However, reporting just R is impractical and results are too small, therefore another approach of expressing the isotopic ratio is used.[6] In this approach, the R value is compared to an international standard, and only the deviation from the standard is reported.[6] The variations of the stable isotope are noted as delta (δ), and expressed in parts per thousands (‰, per mil).[6] For carbon, R values are determined for both sample and standard by mass spectrometry, and δ is calculated using the following equation:

$$\delta^{13}C = \frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample} - \left(\frac{^{13}C}{^{12}C}\right)_{standard}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} \times 1000 \qquad \text{[per mil]}^{6} \quad (1)$$

The international reference material used for carbon is the internal calcite structure of the fossil *Belemnitella americana* from the Cretaceous Pee Dee Formation in South Carolina, renamed later as Vienna Pee Dee Belemnite (VPDB) by the International Atomic Energy Agency (IAEA). This carbon isotope has a delta value of $(^{13}C/^{12}C)_{VPDB} = 0.011237$.[6] In this equation, a positive delta value indicates that the sample is enriched in heavier isotopes, while a negative value indicates that the sample is depleted in heavier isotopes relative to the standard.

Variations of stable isotopes found in nature have been used extensively in environmental pollution studies. For example, this versatile technique has been applied in the identification of different sources of pollution, and in the determination of the origin of specific compounds.[6] It has also been used in the evaluation of aerobic or anaerobic processes in contaminants, and in the analysis of abiotic and/or biotic processes in pollutants during transportation from the source.[6] Additionally, this technique can be used in other notable ways: to measure isotopic fractionation, in the creation of numerical models used to forecast the impact of contaminants, and in the analysis of natural or polluted media.[6]

1.2 ISOTOPE RATIO MASS SPECTROMETRY

Stable isotope measurements are based on mass spectrometry. However, none of the regular mass analyzers such as quadrupoles, time-of-flight or ion traps have the accuracy sufficient to detect the small changes of stable isotopes composition in the environment.[9] Nevertheless, they can be used for isotopic measurements when combined with isotope dilution.[9] Isotope dilution is an analytical method defined by Rodriguez-Gonzalez et al. as "the technique based on the measurement of isotope ratios in samples where its isotopic composition has been altered by the addition of a known amount of an isotopically enriched element".[10] The instruments employed in the determination of natural isotopic abundances are named isotope ratio mass spectrometers (IRMS). The first IRMS was developed by Alfred Nier in 1947.[11] There are five important parts that form an IRMS: a system for sample introduction, an ionization source for creating ions, a magnetic sector analyzer where ions are accelerated and separated by their mass to charge ratio, a Faraday-collector detector array, and a computer system for data acquisition.[9] Schematic representation of an IRMS is given in Figure 1.

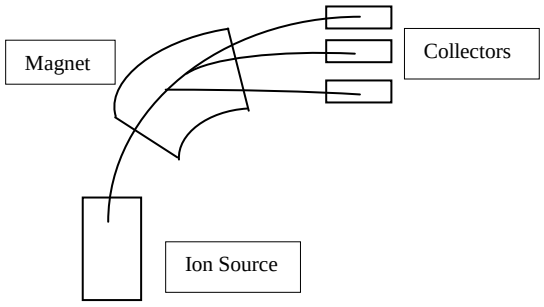

Figure 1. Schematic diagram of an IRMS (adapted from reference 6)

Three types of interfaces are used frequently in IRMS: elemental analyzers (EA-IRMS), gas chromatographs (GC-IRMS) and high performance liquid chromatographs (HPLC).[9]

1.2.1 Elemental Analyzer - Isotope Ratio Mass Spectrometry

Elemental analyzer IRMS is a method that performs carbon, nitrogen and sulfur isotope determinations for the whole sample with no prior separation, and with no information on each individual compound present in the sample.[6,9] For analysis, the sample being tested is placed inside a silver capsule, which is then released into a furnace maintained at 1030-1060 °C.[6] In order to assure fast and total combustion, an oxygen pulse reaches the furnace at the same time.[6] After the combustion step, the resulting sample is then treated in accordance with the type of isotope being analyzed.[9] In carbon applications, the sample is sent to a reduction chamber where nitrous oxides are transformed into N_2 and extra oxygen is eliminated.[9] Next, once water is eliminated through a chemical trap, the sample is separated into CO_2 and N_2 by GC and further analyzed by IRMS.[9]

1.2.2 Gas Chromatography - Isotope Ratio Mass Spectrometry

Using HPLC or GC method in the separation of the analytes before IRMS measurements allows for the analysis of isotope ratios of compounds in complex mixtures. Compound specific isotope analysis refers to the method developed by Mathew and Hayes in 1978 that uses GC and IRMS together in the determination of isotope ratios in a specific compound.[12] In the first step of this method, the sample is injected into the GC, where the GC column separates the components.

Then, helium, as the carrier gas, transports the separated sample into the combustion furnace, where the compounds are mineralized to CO_2, N_2 and H_2O using a narrow-bore reactor tube. These tubes can be packed with Cu oxide pellets or a mixture of copper/nickel/platinum wires.[6] Automatic reoxidation of the wire system with O_2 is needed to increase its capacity.[6] In order to obtain accurate measurements, water from the combustion process is removed by using an H_2O trap.[6] The gas is then transferred to IRMS for ionization, where the resulting ions are separated by masses and measured by IRMS.[6] Figure 2 displays a schematic representation of a GC-IRMS system.

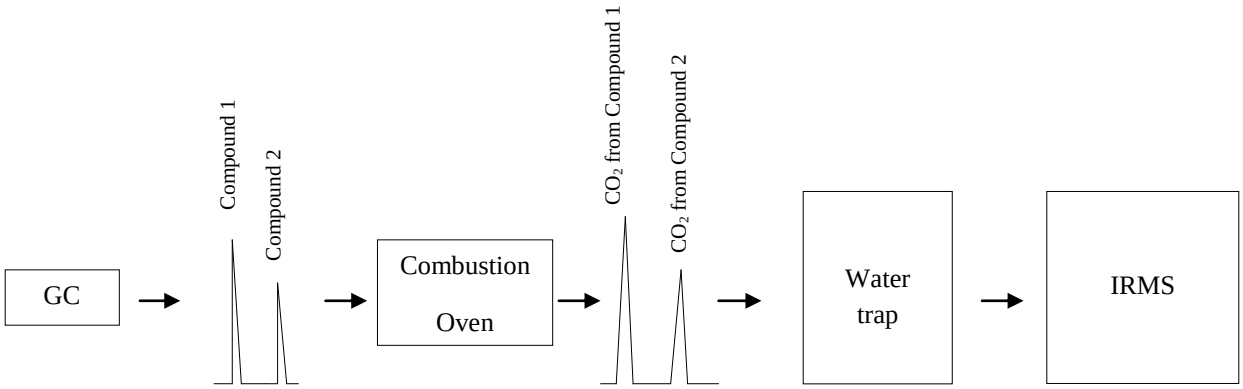

Figure 2. Schematic representation of GC-IRMS (adapted from reference 13)

It is important to note that limitations of the CSIA method include the need for large sample mass required for analysis and the necessity of baseline separation of the analytes in the GC.[6]

1.2.3 High Performance Liquid Chromatography - Isotope Ratio Mass Spectrometry

HPLC-IRMS is a relatively new technique mainly used for carbon applications. It was first introduced in 2005 by Mohammadzadeh.[6,9] In this method, wet oxidation is used to change organic compounds into CO_2 gas.[6,9] This transformation takes place in an oxidation reactor, where a membrane exchanger is used to separate CO_2 from other gases. Next, a gas-permeable membrane transports CO_2 gas into a helium stream. After water is eliminated by a semi-permeable membrane, CO_2 is sent directly into the IRMS for further analysis.[9] For this application, the required mass used in sampling is larger than the mass used in GC-IRMS.[6]

1.3 COMPOUND SPECIFIC ISOTOPE ANALYSIS

CSIA is an important tool in many areas of research due to its ability to determine the abundance of stable isotopes in a given sample. It can be applied for a series of isotopes: hydrogen ($^{2}H/^{1}H$), carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), oxygen ($^{18}O/^{16}O$; $^{17}O/^{16}O$) and chlorine ($^{37}Cl/^{35}Cl$).[14] The CSIA method has been noted to be of growing interest in a variety of fields, such as food research, pharmaceutical studies, doping tests, biochemistry and biomedical applications, archaeology, geochemistry and environmental chemistry.[15,16] In environmental pollution studies, it differentiates between sources of contaminants with distinct isotopic composition and analyzes their transformation reactions in the environment.[17] As a fingerprinting application, it is used for example to differentiate between different manufacturers of the same volatile organic compounds (VOC).[16] Various studies have been performed for chlorinated solvents; benzene, toluene, ethylbenzene and xylenes (BTEX), polycyclic aromatic hydrocarbons

(PAHs), n-alkanes, polychlorinated biphenyls (PCBs) and methyl-tert butyl ether (MBTE).[16] These studies have demonstrated that different isotopic signatures can exist depending on the production process, producers and raw materials.[16] Additionally, CSIA can provide information related to isotopic behaviour due to environmental processes such as dissolution, volatilization, sorption and degradation.[6] Experiments have determined that volatilization and dissolution of organic compounds generally do not cause a representative change in their isotopic composition; however, volatilization could cause an indicative isotopic fractionation when a high amount of pollutant is lost.[16] Also, laboratory studies indicated that isotopic fractionation occurs when a pollutant undergoes aerobic, anaerobic or abiotic changes.[16]

Hoefs defines the isotopic fractionation process as "the partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios".[5] There are two main types of isotopic fractionation: kinetic and equilibrium. Kinetic fractionation is irreversible, and is related to unfinished processes such as evaporation, dissociation reactions, biologically mediated reactions and diffusion.[5] It is the result of the chemical reaction rate sensitivity to atomic mass.[5] In equilibrium fractionation, on the other hand, the "isotope exchange" reactions take place where the isotope dispersion is in between two or more chemical substances, phases or distinctive molecules.[5] CSIA is used to determine which processes are responsible for fractionation and to what extent they affect the contaminant.[6] Indeed, studies have demonstrated the applicability of CSIA in field contamination analysis to assess the part responsible for the pollution.[16] Field applications include the analysis of site, soil and groundwater contamination, accidental spills, and underground storage tank leaks.[17] Additionally, recent studies have applied CSIA in the evaluation of biodegradation and source identification.[16]

New areas of research for CSIA include vapour intrusion studies and indoor sources of VOCs for fingerprinting investigations. Not many publications have been published on this

subject however, and the few related studies that can be found have all used preconcentration of VOCs on adsorbents or cryogenic traps.[17] In one particular review, numerous measurement techniques were mentioned for isotopic ratio of VOCs at very low concentrations.[18] Of interest, a recent study has developed a new CSIA method that uses adsorbent tubes to obtain sufficient mass for analysis; it was used to determine the presence of tricholorethene and tetrachlororethene in vapour intrusion and indoor sources.[19]

1.3.1 Vapour intrusion

Vapour intrusion can be defined as the migration process of volatile chemicals from contaminated groundwater or soil into an overlying building. Volatile chemicals are known to emit vapours that can migrate through the floors and wall cracks into indoor air spaces. The ingress of VOCs occurs through advection or diffusion. As a result of vapour intrusion, indoor air quality is affected and can result in the occurrence of health problems associated with breathing in contaminated air. When vapour intrusion occurs, the concentrations of chemicals found are generally very low (0.001 to 0.01 mg/m^3 range). As a result, sampling and CSIA analysis of the analytes at such low concentrations can be a very challenging process.

Generally, the one question that must be answered in vapour intrusion is related to its origin: is it linked to an in-situ source or is it related to vapour migration from a contaminant plume? To determine if CSIA can be applied to the analysis of the source of vapour intrusion requires an understanding of the processes that can change the isotopic composition of the vapour during the transportation of samples. A particular challenge of using CSIA in vapour intrusion studies is obtaining a sufficient analyte mass for isotope analysis. A variety of methods are available for soil gas collection; they are described in the next Section.

2. SOIL GAS SAMPLING TECHNIQUES

Two basic methods can be applied when collecting soil gas contaminants: active and passive sampling.[20] Active sampling is based on collecting a sample by "pulling" vapours from a probe inserted in the soil into an analytical device.[21] Equipment used in active sampling of soil gas includes air-tight syringes, Tedlar® bags, glass bulbs, hand-held direct measurement devices (e.g. Photoionization Detector (PID)) and flux chambers.[21] Some active sampling methods require a pump for sample collection; such devices can be expensive. Training of personnel is another important requirement, as some active sampling device designs make sample collection very challenging in certain structure types.[21] As well, sample collection times are typically short (not exceeding 48 hours) and do not allow the determination of the average concentration of a contaminant over a longer period of time (time-weighted average concentration - TWA).[21] Due to these disadvantages associated with active sampling, passive sampling is more suitable for vapour intrusion applications.

Passive sampling is defined as "any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media".[22] Unlike active sampling, passive sampling does not need power or complicated designs; passive sampling requires little training for deployment, and it conserves the analytes against transformations.[23] It can be used to determine the presence of analytes in water, air and soil samples.[23] Additionally, due to longer exposure times typically used with passive sampling, TWA concentrations can be easily determined. The main disadvantage of passive sampling is the need to calibrate the device for each analyte when quantitative results are desired. The next Section presents the main devices used as passive samplers for soil gas contaminant determinations.

2.1 PASSIVE SAMPLERS USED IN SOIL GAS ANALYSIS

2.1.1 PETREX Sampler

The PETREX sampler is a soil gas analysis device developed by the Northeast Research Institute (NERI).[20] As presented in Figure 3, this type of sampler consists of two or three activated carbon adsorption elements which are fused to ferromagnetic wire collectors assembled in a glass tube.[24] The samplers are buried (30 to 45 cm) in the soil with the open end down, and exposed for periods ranging from overnight to 2-3 weeks to the soil gas.[25] During sampling, analyte vapours diffuse through the open end and into the activated carbon sorbent.[25] Next, analytes collected by the sampler are thermally desorbed and analyzed by MS or by GC-MS.[20,26] Because of the sampler design, data obtained is expressed in ion flux counts that are proportional to the pollutant concentrations in the collecting medium.[25,20] This method is used for the determination of a large range of VOCs and semi-volatile organic compounds (SVOCs).[20]

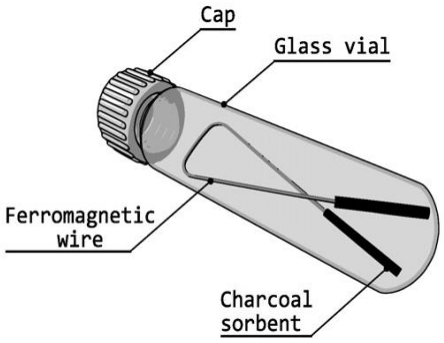

Figure 3. Design of a PETREX sampler[24]

2.1.2 GORE SORBER Sampler

The GORE SORBER module design is schematically presented in Figure 4. It is equipped with two or more sorbers (separate sorbent units) where each sorber contains an equal amount of sorbent material (polymeric or carbonaceous resins).[20,24] These sorbents have hydrophobic properties and affinity to a broad range of VOCs and SVOCs.[24] They are sheathed in a vapour-permeable retrieval cord made of inert, hydrophobic, microporous GORE-TEX® expanded polytetrafluoroethylene (PTFE).[27] The microporous structure of PTFE prevents contamination of the sorbent with soil and water, while facilitating vapour movement through the membrane and onto the sorbent.[27] The device is approximately 30 cm in length and allows for insertion of more sorbers into the module.[24] It can be used to collect both organic and inorganic compounds covering a volatility range from C_2 to C_{20}.[28] The samplers are stored in glass vials and are deployed in 1-2 cm diameter holes at a depth of 50-100 cm.[20] The analytes collected are analyzed by thermal desorption using gas chromatography-mass spectrometry (TD-GC-MS).[20] This method is mainly used for screening and contamination mapping. It produces semi-quantitative results at best.

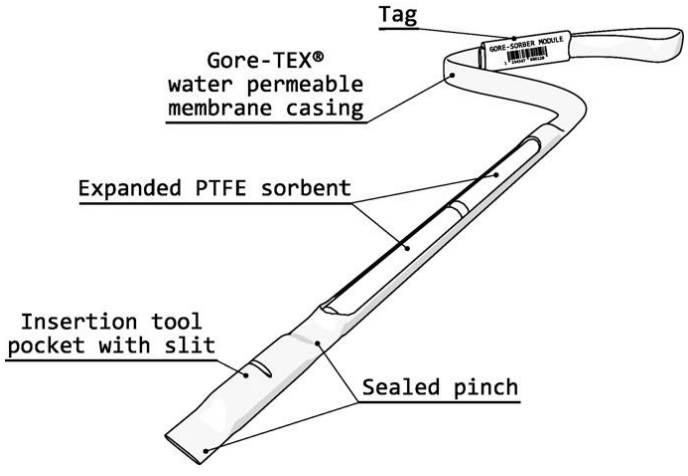

Figure 4. Design of a GORE SORBER sampler.[24]

2.1.3 Passive soil gas sampler (PSG)

The PSG sampler was developed by Beacon Environmental Services in 1988.[29] It consists of a 7 mL screw-top glass vial with two sets of hydrophobic adsorbent cartridges inside.[29] The exposure period of this sampler varies between 3 and 14 days.[29] The vial has a wire around it for easy retrieval from the soil.[20] The device can be used in the detection of approximately 40 compounds, including total petroleum hydrocarbons (TPH).[29] Analytical testing of the collected samples is being done by TD-GC-MS following EPA procedures.[29] This sampler can be used to detect contamination sources as well as for onsite screening.[29]

2.1.4 Solid-phase microextraction (SPME)

SPME technique was first introduced by Pawliszyn et al.[30] It is a simple method used to extract analytes from different matrices without using a solvent. Its main component is a silica fiber coated with a stationary phase, attached to the base of a syringe with a fixed metal needle.[31] The device is schematically presented in Figure 5.

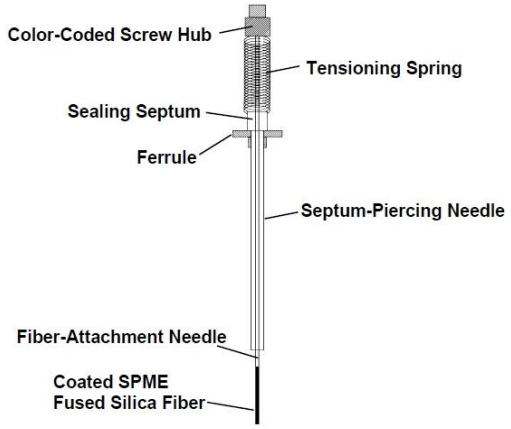

Figure 5. Design of a SPME sampler[32]

During sampling, the fiber is extended outside the needle and exposed to the tested environment. After exposure has been completed, the fiber is retracted back into the needle and the needle is introduced into a hot GC inlet. The fiber is then extended inside the hot injector liner for thermal desorption of the analytes from the coating. The analytes are transferred into a GC column for separation. A headspace SPME method followed by GC-MS analysis was developed by Hawenga and Rohwer and has proven to be a fast and sensitive technique for screening soil samples contaminated by polycyclic aromatic hydrocarbons (PAH) containing up to four rings in their structures.[33] For this method, the soil sample was transferred into sealed vials, and after thermal equilibrium had been reached, the SPME fiber was exposed to the headspace above the soil. Once the exposure was completed, the fiber was inserted in the GC injector for thermal desorption and GC-MS analysis.[33] SPME is a versatile technique that can be used for sampling air, water, soil and sediment.[20] It is applicable to many VOCs and SVOCs, including pesticides, herbicides, organometallic compounds and amines.[34]

2.1.5 Semipermeable membrane device (SPMD)

SPMD was introduced by Huckins et al. in 1990.[35] The sampler consists of a sealed, lay-flat, low density polyethylene tube (70 – 90 μm wall thickness) that contains triolein inside.[36] It has wide applicability in identification and quantitation of a variety of non-polar and some polar organic contaminants in water and air.[37] A few applications to solid environment have been reported as well.[37] Exposure time is usually from 14 to 30 days.[37] Because SPMD samplers are easily contaminated when exposed to environmental conditions, it is important to follow proper handling methods during deployment and retrieval from the exposure medium.[37] SPMD was used

for the determination of bioavailability of contaminants in sediment samples. It allowed the detection of PAHs and polychlorinated biphenyls (PCBs).[38] SPMD is most commonly used in conjunction with GC-MS and GC-FID in the identification and quantification of analytes of interest.[33]

2.1.6 Waterloo Membrane Sampler (WMS)

The Waterloo Membrane Sampler is a passive sampler designed by our group. It is based on a 1.8 mL or 1.5 mL standard crimp-top chromatographic autosampler vial that is partly filled with a sorbent and sealed with a polydimethylsiloxane (PDMS) membrane replacing the standard septum. Figure 6 presents the design of the standard version of the device using a 1.8 mL vial.

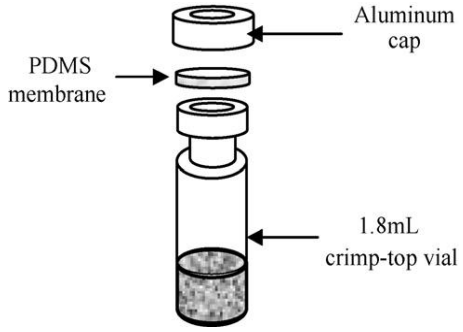

Figure 6. Waterloo Membrane Sampler design[26]

The PDMS membrane used in this device is prepared in the laboratory using spin coating technique. It has a nominal thickness of 100 μm and is cut to size to fit the vial. The structure of PDMS is presented in Figure 7. Dichlorodimethylsilane $(Si(CH_3)_2O)_n$ is the repeating unit in the polymer. PDMS is a highly hydrophobic polymer with a density of less than 1.0 kg/m^3.[39] It is a rubbery type polymer with a low glass transition temperature of -127 °C, which permits the long polymer segments to move at very low temperatures. This allows PDMS to have the lowest diffusivity selectivity for permeation of all polymers.[39,40]

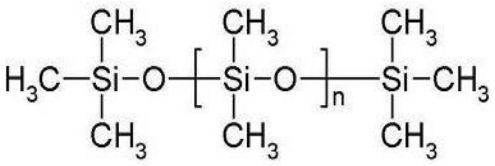

Figure 7. PDMS structure

Depending on the sensitivity required, the WMS sorbent used can be Anasorb® 747 (suitable for solvent desorption) or Carbopack B®, which is used with thermal desorption. Figure 8 illustrates the steps involved in the fabrication of the WMS sampler.

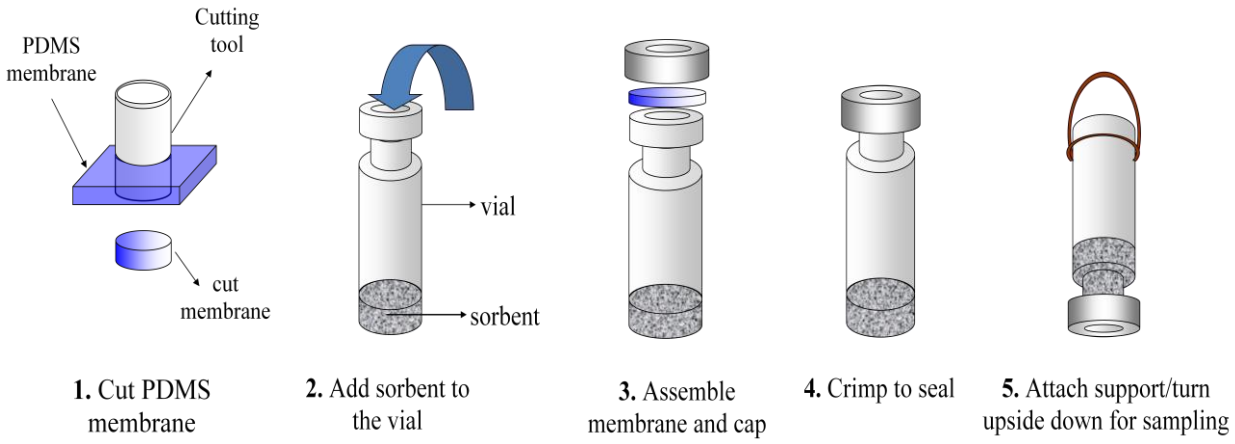

Figure 8. Fabrication of WMS[41]

The passive sampling techniques described above are among the most commonly used for soil gas applications. PETREX, GORE-SORBER and PSG samplers are used to gain information on contamination from a qualitative point of view (site-screening), while SPME, SPMD and WMS samplers can be used to quantify the concentrations of the analytes of interest.[20] Since WMS was used in this research project, it is described in more detail in the next Section.

3. WMS

3.1 THEORY OF WMS

WMS is a permeation-type passive sampler where the transfer of analytes between the sample medium (air) and collecting medium (sorbent) is performed through a polymer membrane.[41]

Applying Fick's first law of diffusion to permeation-type samplers, the following equation is obtained:

$$\frac{M}{t} = D\,\frac{A}{L_m}\left(C_{ma} - C_{ms}\right) \quad (2)$$

Where M (kg) is the mass of the analyte collected by the sampler in time t (min), D is the molecular diffusion coefficient of the analyte in PDMS (cm^2/min), A is the surface area of the membrane (cm^2), L_m is the membrane thickness (cm), C_{ma} is the concentration of the analyte on the membrane surface exposed to air (kg/cm^3) and C_{ms} is the concentration of the analyte on the membrane surface in contact with the sorbent (kg/cm^3).[41] Because the sorbent acts as a sink that removes the analyte vapours that emerge from the membrane at the interface between the sorbent and the polymer membrane, the concentration of the analytes at this interface is approximately zero:[41]

$$C_{ms} \approx 0 \quad (3)$$

At a specific temperature, the relationship between the concentration of the analyte in the air (C_0) and C_{ma} is given by equation 4:

$$C_{ma} = KC_0 \quad (4)$$

where K is the partition coefficient of the analyte between the air and the membrane (dimensionless), and C_0 is the concentration of the analyte in the air (kg/cm^3).[41]

At constant temperature, L_m, D, K and A are constant and can be replaced by a new constant k :

$$k = \frac{L_m}{DKA} \quad (5)$$

where k is the calibration constant of the sampler.[41] Equation 5 illustrates the dependence of the calibration constant on the sampler geometry through L_m and A, and on permeability P of the polymer towards a specific analyte through the product DK (cm^2 min^{-1}).[41]

From equations 2, 3, 4 and 5, the concentration of the analyte in the sample is calculated through the following equation:[41]

$$C_0 = \frac{kM}{t} \quad (6)$$

In order for this sampler to be used for quantitative field applications, calibration is required before the exposure. Calibration involves the determination of the calibration constant, which is done by using a standard test gas atmosphere with a known and controlled analyte concentration for a predetermined exposure time, followed by the determination of the mass of the analyte collected by the sampler using chromatographic methods.[41]

The permeation process, i.e. the transfer of the analytes from the sampled medium (which can be air or water) to the collecting medium (sorbent) through the membrane involves three steps: dissolution of the analyte vapours in the polymer, diffusion through the polymer membrane

and release of the analytes vapour inside the sampler.[42] The permeability coefficient *P* of a molecule in the polymer membrane is defined as the product of the diffusion coefficient *D* and the partition coefficient *K*:[41]

$$P = DK \tag{7}$$

By substituting *P* from equation 7 into equation 5, equation 8 is obtained:

$$\frac{1}{k} = \frac{PA}{L_m} \tag{8}$$

Equation 8 presents the relationship between the partition coefficient and the calibration constant.[41] In gas chromatography, the retention characteristics of an analyte are a function of the analyte partition coefficient between the carrier gas and the stationary phase. Linear temperature programmed retention indices (LTPRI) and the partition coefficient are related together through the following equation:[41]

$$\ln K = N(LTPRI) + Q \tag{9}$$

In equation 9, *N* and *Q* are constants.[41] With the assumption that *D* is varying insignificantly compared to *K*, the following relationship between *k* and *LTPRI* results:[41]

$$\ln k \propto -LTPRI \tag{10}$$

From equation 10, ln k is directly related to LTPRI, and this relationship is used in evaluation of the calibration constants of analytes whose identities are unknown.[41]

3.2 PREVIOUS RESEARCH

Calibration constants for 41 compounds belonging to different chemical classes were determined experimentally for WMS. The analytes included n-alkanes, aromatic hydrocarbons, alcohols, esters and chlorinated compounds.[41] Seethapathy determined the relationship between the calibration constants of the analytes and their linear temperature-programmed retention indices in PDMS-coated GC capillary columns.[41]

The effect of environmental factors such as temperature, linear velocity of air and humidity on the uptake rates of WMS were studied, and it was determined that an increase in temperature decreases the uptake rates for the sampler; a linear flow velocity below 0.35 m/s has a significant effect on the uptake rate, while the humidity level has no significant effect on the uptake rate.[41] Indoor air exposures and soil gas sampling were performed using the WMS sampler, and results demonstrated good reproducibility when compared with other devices for analyte collection.[41] For example, for soil-gas sampling and analysis, WMS performance was compared with the Gore sampler and Summa canister sampling methods.[41] Overall, the new device has significant advantages: low cost, low maintenance requirements and ease of use.

3.3 RESEARCH OBJECTIVE

The objective of this thesis was to evaluate the suitability of WMS to environmental forensics based on CSIA. This has been done by employing WMS samplers under controlled conditions to measure the carbon isotope composition ($\delta^{13}C$) of a series of analytes that were contained in a standard gas mixture. In order to determine if isotopic fractionation occurred

during exposures, $\delta^{13}C$ was determined for each individual compound for the standard feeding gas and for the gas that permeated through the PDMS membrane into the sorbent. The values for $\delta^{13}C$ obtained represented no fractionation when differences between the results obtained for the two matrices were statistically insignificant.

The procedure was modified by adding thermal desorption to overcome the main limitation of CSIA, viz. the requirement for a large analyte mass. In addition, the effects of various parameters such as time of exposure, amount collected and exposure temperature were studied, and the method was tested in a field application.

Thus far, one study evaluated the permeation of formaldehyde from an aqueous solution through a commercial PDMS membrane and results showed an isotopic fractionation of 1.0026± 0.0003.[43]

4. EXPERIMENTAL PROCEDURE

4.1 MATERIALS

4.1.1 Chemicals

The test analytes used in the study were hexane, benzene, and trichloroethylene, representing n-alkanes, aromatic hydrocarbons and chlorinated hydrocarbons, respectively. These chemical classes are typically found in vapour intrusion studies. High purity analytical grade chemicals were procured from Sigma-Aldrich, Canada. A standard gas mixture was generated using a gas cylinder purchased from Scott Specialty Gases, USA. In the gas cylinder, each compound had a concentration of 100 ppm in nitrogen.

4.1.2 WMS

WMS was described in Section 2.1.6. The sorbent used in the experiments was Carbopack B® (180 mg, 60/80 mesh) purchased from Sigma-Aldrich, Canada. PDMS membrane was prepared in our laboratory by mixing silicone elastomer base with silicone elastomer curing agent and by using spin coating technique. The raw materials for PDMS membrane were procured from Dow Corning, USA as SYLGARD® 184 SILICONE ELASTOMER KIT. The precision spin coater, Cee® model 200X, was purchased from Brewer Science, Inc. The spin process was run for 60 seconds at 624 rpm speed. The thickness of the PDMS membrane produced was controlled through weighing of a random sampling of membranes cut to the desired size, with the target weight being 8.0 ± 0.5 mg for the sampler based on the 1.8 mL vial.

4.2 INSTRUMENTATION

4.2.1 Thermal desorption unit

Thermal desorption was performed using an ATD 400 Thermal Desorber (Perkin Elmer) equipped with a carousel that holds up to 50 TD tubes. The TD tube containing the sample was sealed with caps and installed on the ATD carousel.[44] After one turn, the TD tube was sealed in the carrier gas stream.[44] A leak test was performed to assure that the TD tube was in the right position.[44] Next, the sample inside the tube was heated to a predetermined temperature and for a predetermined time using a stream of inert gas for analyte desorption from the sorbent.[44] Following desorption, volatile compounds were sent to a cold trap before they were transferred through a hot transfer line into the GC column.[44] ATD 400 is an automated system with 3 modes of operation controlled by a keyboard and Liquid Crystal Display (LCD).[44] The keyboard and LCD allowed all the variables in the thermal desorption process to be set.[44] From the three modes that the ATD 400 could be set to, in this study only Mode 1 and Mode 2 were used. They are described in the next two Sections.

4.2.1.1 ATD 400 Mode 1

Mode 1 is the tube conditioning mode. TD tubes were heated to a predetermined temperature and impurities from the sorbent were removed leaving the tube clean. The cold trap was not involved in the process.[44] The conditioning time was 3 minutes, and temperature was set at 250 °C.

4.2.1.2 ATD 400 Mode 2

Mode 2 is a two-stage desorption mode. In this mode, after the leak test was performed, the TD tube was purged of air by a flow of inert gas, and then heated to the desorption temperature for a predetermined time (primary desorption).[44] During the heating process, the volatiles liberated from the sorbent were sent to the cold trap.[44] At the end of the first stage, the cold trap was heated and the analytes were transferred to the GC for further analysis (secondary desorption).[44] For this research, the first desorption temperature was held for 1.5 minutes at 250 °C, and after 65 seconds of purging the TD tube, the volatile chemicals were sent to the cold trap set at -30 °C. In the second desorption, the cold trap was heated to 280 °C and the sample from the trap was sent through a heated line directly into the GC column.

4.2.1.3 ATD 400 flows

As mentioned in the previous Section, volatile analytes from the TD were sent directly into the GC column, and in this case, the GC flow was controlled by the TD unit. For this study, single split operation was selected for the ATD 400 unit with ~10 % of the sample from the TD tube reaching the GC column. The flow settings used for the thermal desorber in the experiments are presented in Table 1. They were set using an electronic flow meter (ADM2000 Universal Gas Flowmeter) purchased from Agilent Technologies, USA.

Table 1. TD flows

Column flow	**1 mL/min**
Primary desorption flow	**50 mL/min**
Secondary desorption split flow	**10 mL/min**

4.2.1.4 TD tubes

TD stainless steel tubes (90 mm long and 6.35 mm outside diameter) purchased from Perkin Elmer, Canada, were manually filled with Carbopack B® sorbent (0.2 g). The TD tubes were capped with PTFE caps and glass wool plugs were used with minimal compression at both ends. TD tubes were conditioned using the thermal desorption instrument described in Section 4.2.1.1.

4.2.2 GC-IRMS

The Mode 2 method developed for TD was carried out on an Agilent 6890 GC equipped with a 60 m x 0.32 mm x 1.0 µm RXI-1MS column (Agilent Technologies Inc.). The GC oven temperature was held isothermally at 40 °C for 5 min, then ramped to 125 °C at 20 °C/min and held for 1 min, followed by a secondary temperature ramp to 250 °C at 30 °C/min and held for 1 min. The flow of the carrier gas through the GC was controlled by the TD unit as shown in Table 3. The separated compounds eluting from the GC column were transferred to the IRMS for carbon isotope analysis. The IRMS used in the study was a Micromass IsoPrime (Micromass UK Ltd.) mass spectrometer equipped with MassLynx software. The analytical instrument employed in $\delta^{13}C$ determinations for the chemicals used in the study was the TD-GC-IRMS located in the

Environmental Isotope Laboratory at the University of Waterloo. A picture of this setup is presented in Figure 9.

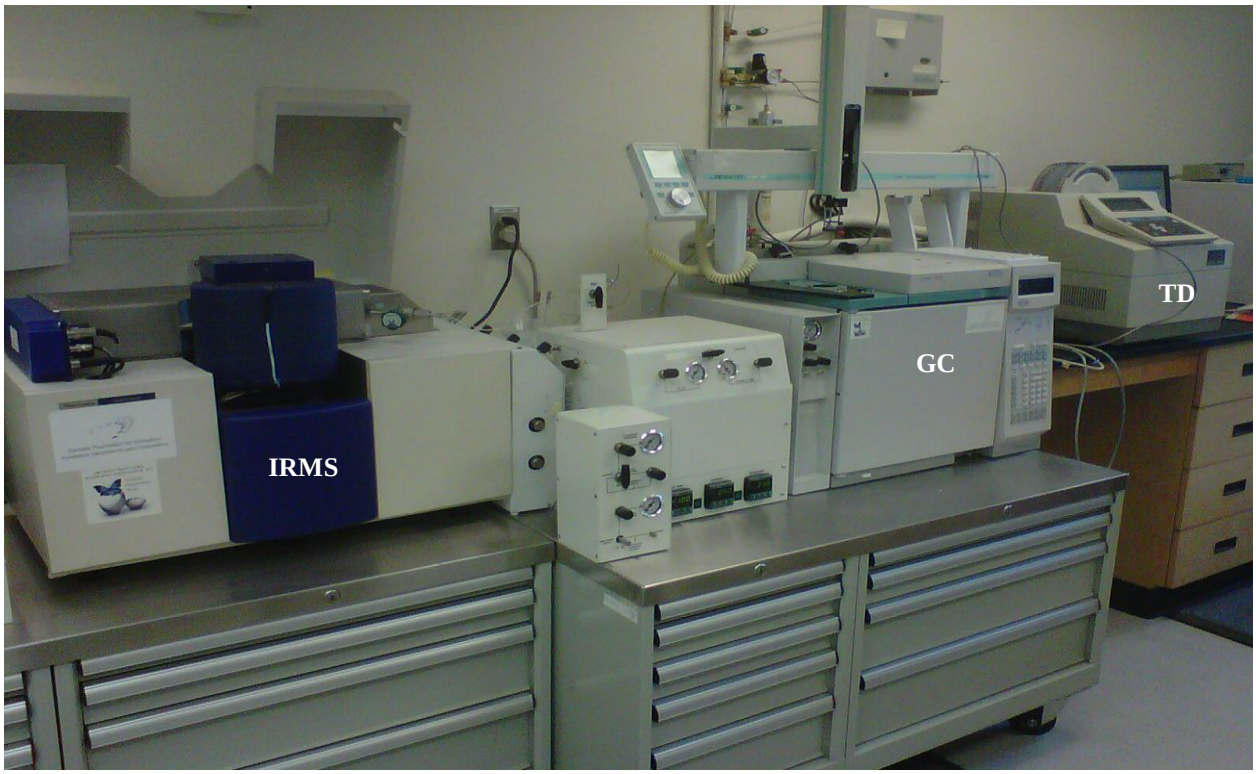

Figure 9. TD-GC-IRMS system used in the study.

4.2.2.1 Carbon isotope ratio determination

The $\delta^{13}C$ values were calculated by integration of the 44, 45 and 46 m/z ion currents of the peaks resulting from combustion of the separated compounds to CO_2 and H_2O. These ion masses correlate to the following CO_2 isotopologue masses (identical molecules with different isotopic composition): 44 for $^{12}C^{16}O^{16}O$, 45 for $^{13}C^{16}O^{16}O$ and $^{12}C^{16}O^{17}O$, and 46 for $^{12}C^{16}O^{18}O$, $^{13}C^{16}O^{17}O$ and $^{12}C^{17}O^{17}O$.[6] In order to obtain accurate results for the $^{13}C/^{12}C$ ratio, mass 45 has to

be corrected for the presence of $^{12}C^{16}O^{17}O$.[6] Furthermore, for $^{18}O/^{16}O$ ratio determination, one has to take into consideration what types of isotopologues mass 46 contains.[6] The analytical instrument measures two types of mass ratios: 45/44 and 46/44, but there are three unknowns to be determined: $^{12}C/^{13}C$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios.[6] In this case, one more equation is required and is represented by a relationship between ^{17}O and ^{18}O presuming that these two isotopes are proportionally fractioned in all processes. In 1957 Craig introduced the two most used correction equations:[45]

$$\delta^{13}C = 1.0676\ \delta\ (45/44) - 0.0338\ \delta^{18}O \quad (8)$$

$$\delta^{18}O = 1.0010\ \delta\ (46/44) - 0.0021\ \delta^{13}C \quad (9)$$

Where: δ (45/44) is the ratio of the amount of CO_2 of molecular weight 45 over the amount of CO_2 of molecular weight 44, δ (46/44) is similar for molecular weight of 46 over 44, $\delta^{13}C$ is calculated using Equation 1, and $\delta^{18}O$ is calculated using a similar equation as Equation 1 only for the $^{18}O/^{16}O$ isotope ratio for the sample and the standard, respectively. Equations 8 and 9 were used by the IRMS MassLynx software for delta value corrections in carbon isotopic determinations.[45]

4.2.2.2 Uncertainty in carbon isotope analysis

Because the international standard material used for calibration is not available in large amounts, laboratories designated for carbon isotopic ratio determinations are using pure CO_2 reference gas.[46] This pure reference gas is calibrated against the international standard and in this way becomes an internal laboratory standard.[46] By using this approach, the laboratories are

developing their own standard materials.[46] To obtain high precision and accuracy in regards to the international standard and the internal CO_2 standard, the isotopic composition of the materials used as standards was determined using EA-IRMS.[46] Internal laboratory standard values for the analytes used in this study are presented in Table 2.

Table 2. $\delta^{13}C$ values for standard chemicals used in the studies [‰].

Standard	**$\delta^{13}C$ [‰]**
Hexane	-27.1
Benzene	-28.4
TCE	-31.4

CSIA is capable of measuring the $\delta^{13}C$ values of the analytes in a complex mixture in one analysis, even though each compound is present in the sample at different levels of concentrations.[46] Certain adjustments in oven temperature, split ratios and flow rate can be made so that the sample concentration is in the linear range of the instrument.[46] In GC analysis, the response to the compound analyzed depends linearly on its concentration within the linear portion of the dynamic range of the detector (the higher the concentration, the higher the peak height/area). On the other hand, in CSIA measurements using IRMS, linearity refers to the fact that the carbon isotopic ratio value obtained ($\delta^{13}C$) should always be the same regardless of the quantity of the analyte injected.[46] For $\delta^{13}C$ measurements in IRMS, the acceptable total uncertainty value is 0.5 ‰.[46,47] Linearity tests obtained in this study for the standard compounds used, as well as the total uncertainty values obtained, will be presented in the next Section.

4.3 TD-GC-IRMS CALIBRATION

TD-GC-IRMS calibration was performed by preparing a standard gas mixture containing all three compounds of interest in a Tedlar bag filled with air. The volumes of the standards injected were 1 µL hexane, 1 µL benzene and 3 µL TCE. The delta values for internal laboratory standards used are presented in Table 3. Concentrations of the chemicals in the Tedlar bag remained constant and different standard gas mixture volumes were injected directly into the TD tubes. Calibration experiments were done with the same setup for TD and GC-IRMS as described in Sections 4.2.1.2 and 4.2.2. Prior to injection, the TD tubes were conditioned as specified in Section 4.2.1.1. A five-point calibration curve was generated and the final $\delta^{13}C$ values for the standards were reported after normalization. Normalization in this case was based on a polynomial regression with the intercept and slope used to correct the measured values to the internal laboratory standards run under the same conditions. This calibration method was used in all experiments in the study.

4.4 EXPERIMENTAL SETUP

The purpose of the experimental setup, which can be seen in Figure 10, was to generate a standard test gas with constant analyte concentrations. The setup allowed the determination of $\delta^{13}C$ for both passive and active sampling. Each standard chemical in the gas mixture inside the cylinder had a concentration of 100 ppm in nitrogen. Nitrogen gas was used to dilute the standard gas mixture, which was delivered to the exposure chamber at controlled flow rates. The flow rate for the standard gas was controlled by a mass flow controller, while the flow rate of the nitrogen gas was controlled by a needle valve. The flow of each gas was adjusted according to the requirements of a given study.

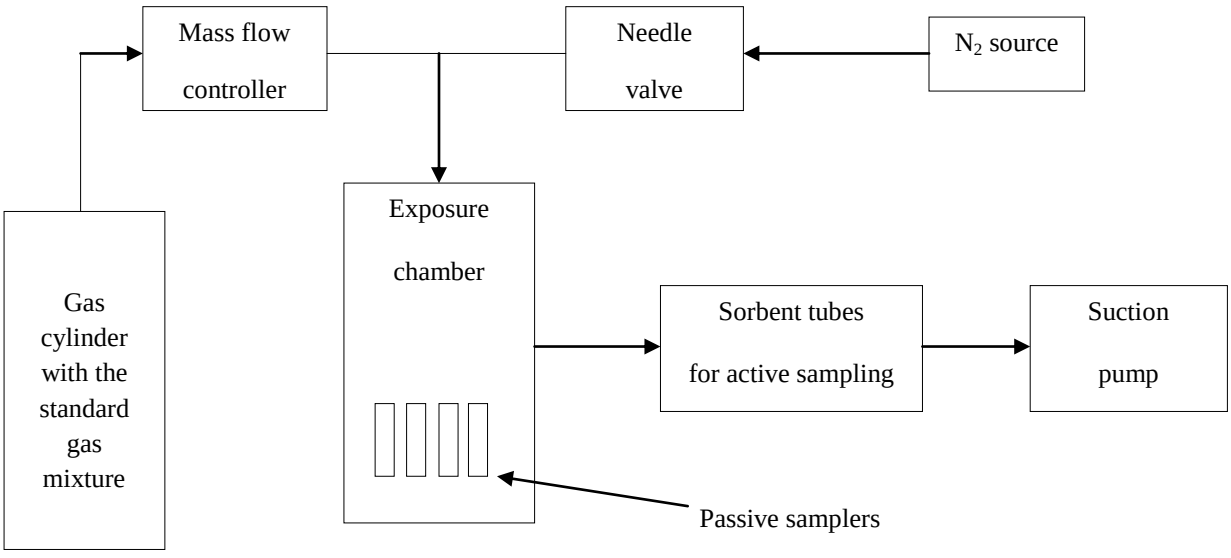

Figure 10. Schematic diagram of the experimental setup.

Prior to each exposure, the chamber was conditioned with the gas mixture for 1 hour. Exposure times for WMS varied depending on the study. The initial time of exposure was calculated using Equation 6. In this equation C_0 was 100 ppm, *k* was determined by Seethapathy

in his thesis for each analyte, and *m* was the detection limit calculated in Section 5.1.[41] During these passive sampling exposures, active sampling was performed using a suction pump (High Flo Gold Series pump) purchased from Canadian Tire, Waterloo, Canada. The flow of the suction pump was measured using a flow meter and different volumes were collected depending on the concentration of the standard gas mixture inside the exposure chamber at the time of sampling. For each exposure, active sampling used TD tubes packed with fresh Carbopack B sorbent, and passive sampling used new WMS fabricated in our laboratory. The effects of three parameters on $\delta^{13}C$ values obtained through passive and active sampling for the three analytes were examined for this thesis: time of sampler exposure, analyte amount collected and exposure temperature. In each experiment, 4 passive samplers were exposed at the same time and 3 TD tubes were used for active sampling. In the end, $\delta^{13}C$ for passive and active methods for the three analytes were measured using the setup for TD-GC-IRMS mentioned in Section 4.2.2 and 4.2.1.2. In the following Sections, experimental setups are described in detail for each study conducted.

4.4.1 Effect of the WMS exposure time on $\delta^{13}C$ of the analytes inside the passive sampler

In this study the experimental setup used was the same as described in Section 4.4. Experiments were performed at room temperature and the concentration in the exposure chamber was adjusted for each exposure time so that the analyte amount collected by the passive sampler was always the same. The times of exposures were 3, 6, 12, 24, 48, 96 and 192 hours, and the corresponding concentrations of the standard gas mixture in the exposure chamber were 6, 3, 1.5,

0.75, 0.375, 0.1875 and 0.09375 mg/m^3. The volumes of the standard gas mixture collected through active sampling were 240, 480, 960, 1920, 3840, 7680 and 15360 mL, respectively.

4.4.2 Effect of the amount of analyte collected by WMS on the δ^{13}C values for the analytes inside the passive sampler

The experimental setup described in Section 4.3 was used to determine the effect of the amount of the analytes collected by the sorbent in the WMS. Experiments were performed at room temperature, and exposure times were 3, 6, 12, 24, 48 and 96 hours. To achieve an increase in the amount absorbed by the sorbent in the WMS, the concentration inside the exposure chamber was constantly maintained at 6 mg/m^3 throughout the experiments. The volume of the standard gas mixture collected by active sampling was 240 mL for each exposure time.

4.4.3 Effect of the WMS exposure temperature on δ^{13}C values of the analytes inside the passive sampler

The experimental setup described in Section 4.4 was modified in order to obtain a lower temperature inside the exposure chamber (Figure 11).

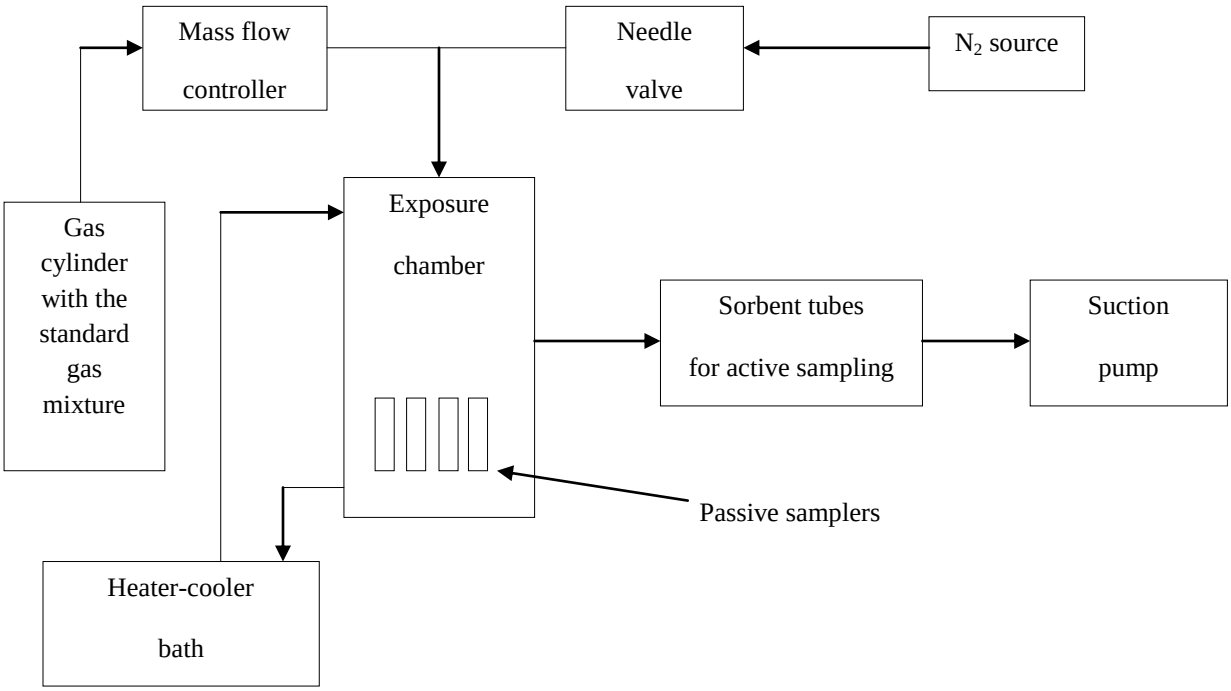

Figure 11. Modified experimental setup.

The modification involved wrapping a thin flexible plastic tube around the chamber and insulating it. The plastic tube was connected to a circulating bath with programmable temperature controller purchased from VWR, USA. The circulating bath temperature was adjusted to 4°C, so that the temperature inside the exposure chamber could reach 12°C and be maintained constant throughout all the experiments. All parameters (time, concentration and volume) were the same as in Section 4.4.1, except that the 192 hour exposure was not performed for this study.

5. RESULTS AND DISCUSSION

5.1 DETECTION LIMIT FOR TD-GC-IRMS

In detection limit determinations for TD-GC-IRMS, the standard gas mixture in the Tedlar bag was prepared as mentioned in Section 4.3, and the same setup for TD-GC-IRMS was used as well. The concentrations of the chemicals in the Tedlar bag were 0.65 mg/m^3, 0.88 mg/m^3 and 4.38 mg/m^3 for hexane, benzene and TCE, respectively. The corresponding masses for each analyte in the Tedlar bag were 655 ng for hexane, 880 ng for benzene and 4380 ng for TCE. The smallest volume of the standard gas mixture injected into the TD tube that produced a minimum acceptable analytical response (signal intensity) expressed in nA (nanoampere) and referred to as "peak height" throughout the study, was 1 mL. The minimum peak height with which $\delta^{13}C$ could be calculated with adequate confidence was 1 nA. The optimum analytical response represented the values obtained for $\delta^{13}C$ that maintained the same precision and reproducibility and for which the calculated standard deviations were within ± 0.5 ‰.[46] The analyte delta values and the analytical response reproducibility (n=5) were tested for 1 mL volume standard gas mixture injected into the TD tube. The results are presented in Table 3.

Table 3. $\delta^{13}C$ and analytical response values obtained for each analyte (n=5) for 1 mL volume of standard gas mixture injected into the TD-GC-IRMS system.

Compound	**Average $\delta^{13}C$ [‰]**	**Std.dev. for $\delta^{13}C$ values**	**Analytical response Peak height [nA]**	**Std.dev. for Peak Height values**
Hexane	-30.9	0.30	1.13	0.20
Benzene	-29.7	0.40	1.96	0.60
TCE	-34.5	0.30	1.66	0.60

The calculated concentration values for each analyte in 1 mL standard gas volume represented the detection limit for TD-GC-IRMS and have the same values as the ones in the Tedlar bag.

MS responses to high concentration samples, which are samples that produce a large volume of CO_2 in the combustion tube, are truncated peaks. Usually a sample with enough CO_2 produces a peak height of 19 nA. Truncated peaks are detrimental to the results produced by the MassLynx software since the software will automatically use truncated peaks instead of the reference gas peak, which has a different $\delta^{13}C$ signature. Because of this, the results obtained are erroneous. To correct these results, truncated peaks must be removed from the chromatogram. Fortunately, the MassLynx software allows for this correction. In this study, a few analytical responses resulted in truncated peaks; they represented analyte concentrations exceeding the upper limit of the analytical instrument response (peak height value of 19 nA). In cases such as these, where the $\delta^{13}C$ obtained was calculated relative to that chemical and not relative to the CO_2 internal standard, truncated peaks were removed and results were recalculated. Throughout the study, in most of the $\delta^{13}C$ measurements the analytical response of the TD-GC-IRMS was adjusted to fall between 2 and 10 nA for the peak heights. Those values were selected in order to assure that the reproducibility and the accuracy of the $\delta^{13}C$ values obtained were maintained. This optimization process was carried out by carefully predetermining the effective amount of sorbent introduced in the TD. This subject is addressed in details in Section 5.3.

It is important to mention here the linearity of the isotopic measurements and the fact that the $\delta^{13}C$ value measured did not depend on the volume of the standard gas mixture injected as explained in Section 4.2.2.2. As seen in Figure 12, 13 and 14, normalized calculated values for $\delta^{13}C$ for each standard analyte were within the total acceptable uncertainty.

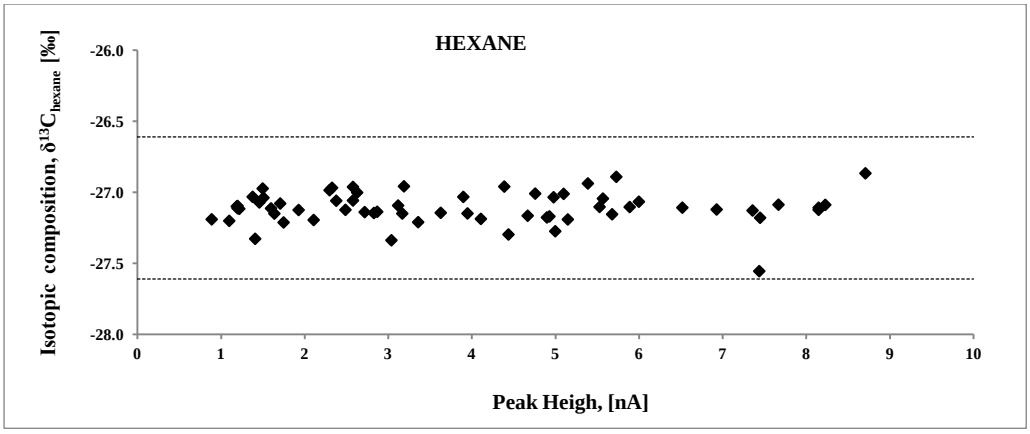

Figure 12. Standard hexane $\delta^{13}C$ values (-27.1 ± 0.5) [‰]

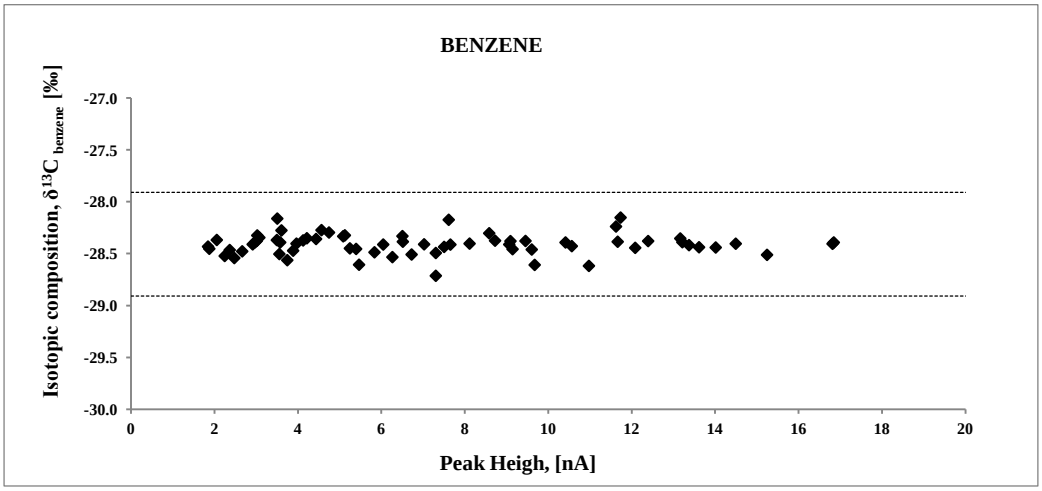

Figure 13. Standard benzene $\delta^{13}C$ values (-28.4 ± 0.5) [‰]

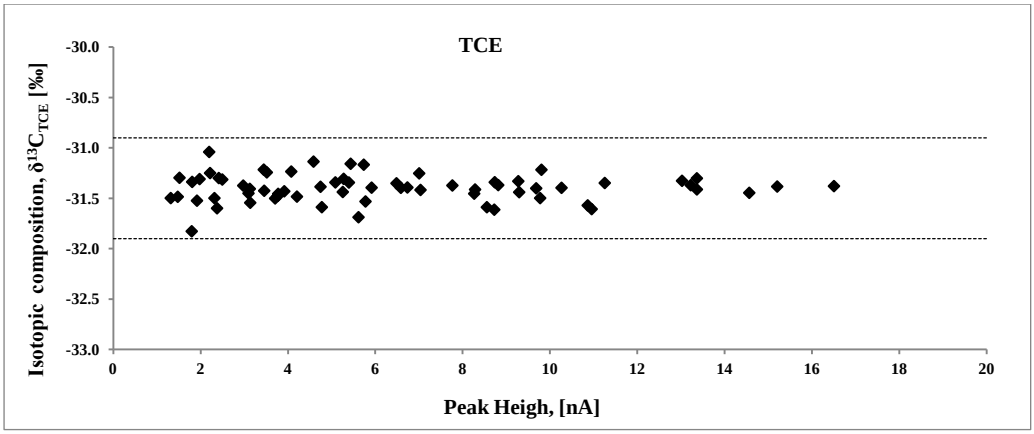

Figure 14. Standard TCE $\delta^{13}C$ values (-31.4 ± 0.5) [‰]

5.2 EFFCT OF THE WMS EXPOSURE TIME ON $\delta^{13}C$ VALUES

The effects of exposure time on $\delta^{13}C$ values measured by TD-GC-IRMS with WMS sampling and active sampling were evaluated and compared. Two sets of experiments were performed under the same conditions. The $\delta^{13}C$ results obtained from the first set of experiments for passive and active sampling are presented in Table 4, while results for the second set of experiments can be found in Table 5.

Table 4. $\delta^{13}C$ values obtained for each analyte in passive and active sampling in the time exposure study; first set of results [‰]; (the numbers in brackets represent the number of replicates for each experiment)

	Passive sampling	**Active sampling**	**Passive sampling**	**Active sampling**	**Passive sampling**	**Active sampling**
Time of exposure	**HEXANE**	**HEXANE**	**BENZENE**	**BENZENE**	**TCE**	**TCE**
(h)	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**
3	(2) -29.5	(3) -28.3	(2) -29.3	(3) -28.1	(3) -32.5	(3) -31.5
6	(3) -29.1	(3) -27.5	(3) -29.0	(3) -27.6	(3) -32.1	(3) -30.8
12	(4) -29.3	(3) -27.7	(4) -29.0	(3) -27.8	(4) -32.9	(3) 31.6
24	(3) -29.5	(3) -27.7	(3) -29.2	(3) -28.2	(3) -32.4	(3) -31.3
48	(2) -29.1	(3) -27.8	(2) -29.2	(3) -28.1	(2) -32.6	(3) -31.7
96	(3) -29.3	(3) -27.9	(3) -29.6	(3) -28.2	(3) -32.9	(3) -32.4
192	(4) -29.3	(3) -28.4	(4) -29.0	(3) 28.2	(4) -32.8	(3) -32.3
Average	**-29.3_0**	**-27.9_1**	**-29.1_9**	**-28.0_2**	**-32.6_0**	**-31.6_6**
Standard deviation	**0.2**	**0.3**	**0.2**	**0.2**	**0.3**	**0.5**
Difference between passive and active sampling	**-1.3_8**		**-1.1_7**		**-0.9_4**	

Table 5. $\delta^{13}C$ values obtained for each analyte for passive and active sampling in the time exposure study; second set of the results [‰]; (the numbers in brackets represent the number of replicates for each experiment)

	Passive sampling	**Active sampling**	**Passive sampling**	**Active sampling**	**Passive sampling**	**Active sampling**
Time of exposure	**HEXANE**	**HEXANE**	**BENZENE**	**BENZENE**	**TCE**	**TCE**
(h)	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$[‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**	**$\delta^{13}C$ [‰]**
3	(3) -29.1	(3) -27.8	(3) -29.0	(3) -27.8	(3) -32.5	(3) -31.6
6	(4) -29.5	(3) -27.3	(4) -28.9	(3) -27.7	(4) -32.5	(3) -31.2
12	(4) -29.3	(3) -27.9	(4) -29.4	(3) -27.7	(4) -32.8	(3) -31.9
24	(4) -29.5	(3) -28.0	(4) -29.2	(3) -28.0	(4) -32.7	(3) -31.6
48	(3) -29.2	(3) -28.3	(3) -29.4	(3) -28.3	(3) -32.6	(3) -31.6
96	(3) -29.7	(3) -27.8	(3) -29.1	(3) -28.0	(3) -32.4	(3) -31.9
192	(3) -29.4	(3) -28.8	(3) -29.1	(3) -27.9	(3) -32.9	(3) -32.6
Average	**-29.3_9**	**-27.9_9**	**-29.1_6**	**-27.9_1**	**-32.6_3**	**-31.7_7**
Standard deviation	**0.2**	**0.5**	**0.2**	**0.2**	**0.2**	**0.4**
Difference between passive and active sampling	**-1.4_0**		**-1.2_4**		**-0.8_5**	

By analyzing the data obtained in both studies, it can be concluded that the results were consistent and reproducible, with standard deviations within the accepted error of ±0.5‰ for all compounds. As mentioned earlier, $\delta^{13}C$ for passive samplers were used to measure the carbon isotopic composition of each chemical collected by the WMS, while $\delta^{13}C$ values for active samplers measured the carbon isotopic composition of each analyte inside the exposure chamber. The difference between these two measured $\delta^{13}C$ values represented isotopic fractionation. The magnitude of isotopic fractionation was found to be constant with time and independent of the time of exposure as seen in Figure 15, 16 and 17, where the slope of the line of best fit was close

to zero and R^2 was very small. In order to determine if this difference was significant, one tailed Student's t test was applied at 95% confidence level. From the t test analysis it was determined that for all compounds $t_{stat} > t_{critical\ one\text{-}tail}$ meaning that the differences between $\delta^{13}C$ values were significant. The probabilities that these differences were due to random factors were $1.6x10^{-7}$ and $4.9x10^{-6}$ for hexane for the first and the second study, respectively, $2.6x10^{-7}$ and $5.2x10^{-8}$ for benzene, and $2x10^{-4}$ for both studies for TCE.

There are many factors that might lead to isotopic fractionation; however, in this study the only process that could cause this phenomenon was permeation of the analytes through the PDMS membrane. By examining the data in Tables 4 and 5 we can see that this difference was practically constant for all the analytes and independent of the exposure time. In isotopic fractionation caused by permeation two important factors must be considered: diffusion through and partitioning into and out of the PDMS membrane. These two PDMS characteristics were influencing the fractionation process differently. Isotopic fractionation due to diffusion and partitioning could be explained by the behaviour of the lighter isotopes versus the heavier isotopes.[5] In diffusion, lighter isotopes migrate faster when compared to heavier isotopes, making the two isotopes separate from one another.[5] This could explain the more negative $\delta^{13}C$ values obtained through passive sampling, which were depleted in ^{13}C relative to ^{12}C isotopes when compared with the more positive $\delta^{13}C$ values obtained in active sampling which were enriched in ^{13}C relative to ^{12}C isotopes. As well, in gas chromatography, compounds containing heavier isotopes elute earlier in comparison with lighter isotopes, which means that they have smaller partition coefficients.[15] As observed in this study, the retention times for $\delta^{13}C$ values obtained from active sampling were slightly shorter versus the retention times for $\delta^{13}C$ values obtained from passive sampling. This difference in elution times could be due to analytes being more enriched in the heavier isotope ^{13}C in active sampling than the passive sampling analytes which

were depleted of ^{13}C isotopes. The results obtained from these studies are presented graphically in Figures 15, 16 and 17.

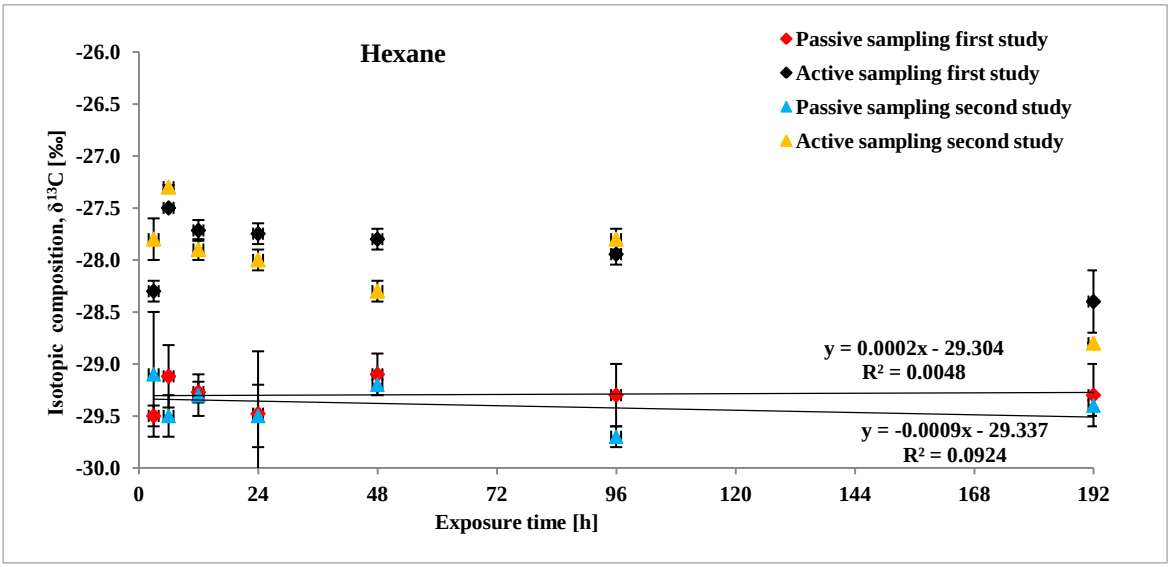

Figure 15. Hexane $\delta^{13}C$ values obtained in the time exposure studies vs. time.

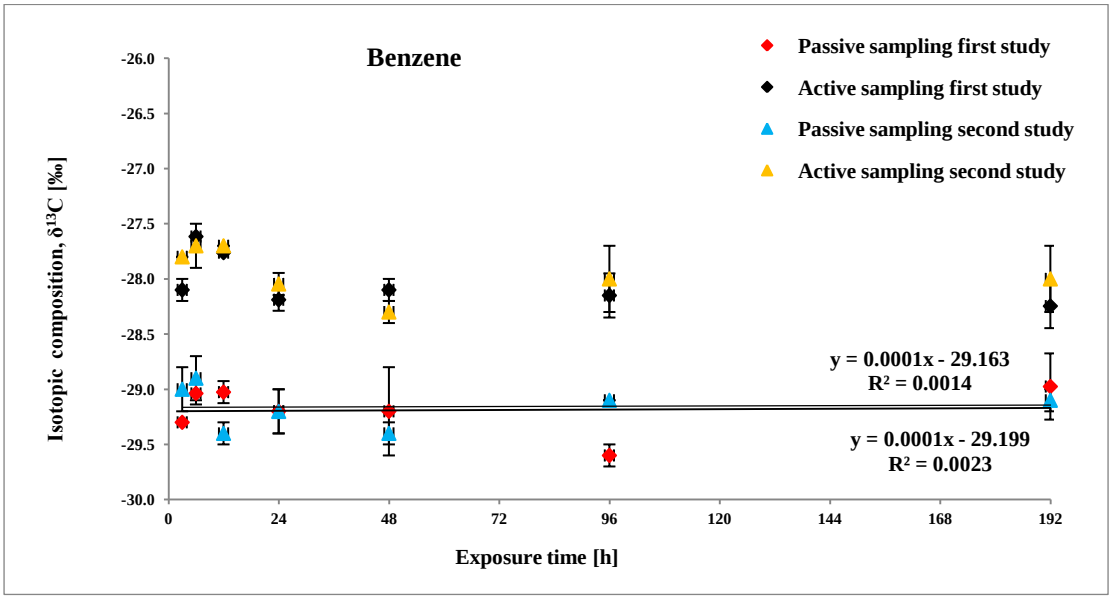

Figure 16. Benzene $\delta^{13}C$ values obtained in the time exposure studies vs. time.

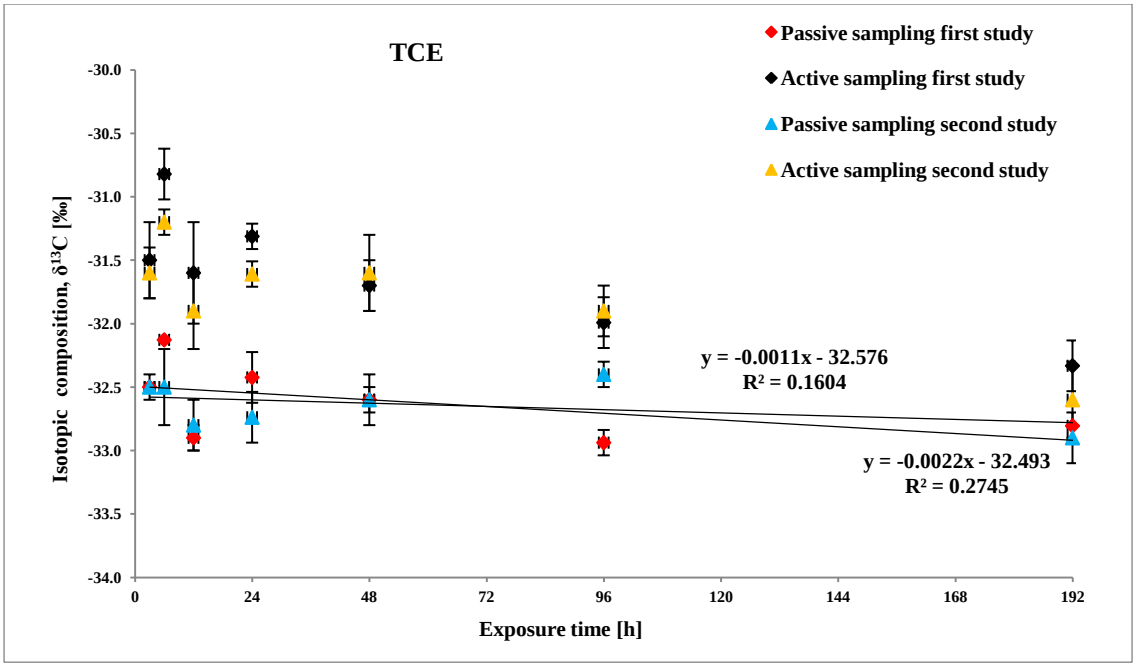

Figure 17. TCE $\delta^{13}C$ values obtained in the time exposure studies vs. time.

The graphs above show lack of dependence of the $\delta^{13}C$ values for all the analytes preconcentrated with WMS on time.

5.3 EFFECT OF THE ANALYTE AMOUNT COLLECTED BY WMS ON $\delta^{13}C$ VALUES

In this study the effect of the quantity of each analyte collected by WMS on $\delta^{13}C$ measured was analyzed and compared with $\delta^{13}C$ obtained through active sampling where the concentration of analytes in the exposure chamber was maintained constant during the entire experiment. The results obtained in this study are listed in Table 6.

Table 6. $\delta^{13}C$ values obtained for each analyte for passive and active sampling when the amount collected by WMS was increased with each exposure time [‰]; (the numbers in brackets represent the number of replicates for each experiment)

	Passive sampling	**Active sampling**	**Passive sampling**	**Active sampling**	**Passive sampling**	**Active sampling**
Time of exposure	**HEXANE**	**HEXANE**	**BENZENE**	**BENZENE**	**TCE**	**TCE**
(h)	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**
3	$^{(3)}$ -30.2	$^{(2)}$ -27.9	$^{(3)}$ -29.5	$^{(2)}$ -28.0	$^{(3)}$ -33.2	$^{(2)}$ -32.0
6	$^{(3)}$ -29.4	$^{(3)}$ -27.9	$^{(3)}$ -29.3	$^{(3)}$ -28.0	$^{(3)}$ -31.9	$^{(3)}$ -32.1
12	$^{(4)}$ -29.7	$^{(3)}$ -27.1	$^{(4)}$ -29.4	$^{(3)}$ -28.2	$^{(4)}$ -32.8	$^{(3)}$ -31.8
24	$^{(4)}$ -29.5	$^{(3)}$ -27.7	$^{(4)}$ -29.1	$^{(3)}$ -28.0	$^{(4)}$ -32.9	$^{(3)}$ -31.8
48	$^{(4)}$ -29.9	$^{(3)}$ -27.8	$^{(4)}$ -29.0	$^{(3)}$ -28.3	$^{(4)}$ -32.9	$^{(3)}$ -32.2
96	$^{(4)}$ -29.5	$^{(3)}$ -28.2	$^{(4)}$ -28.5	$^{(3)}$ -28.0	$^{(4)}$ -32.8	$^{(3)}$ -31.5
Average	**-29.7_0**	**-27.7_6**	**-29.1_3**	**-28.0_8**	**-32.7_5**	**-31.9_0**
Standard deviation	**0.3**	**0.4**	**0.4**	**0.1**	**0.4**	**0.3**
Difference between passive and active sampling	**-1.9_3**		**-1.0_5**		**-0.8_5**	

Because the concentration was maintained constant during the study, the amount of analytes collected by WMS increased considerably with exposure time. TD-GC-IRMS settings used for the first two exposures were the same as mentioned in Sections 4.21.2 and 4.2.2. On the other hand, for 12, 24, 48 and 96 hours exposure times, the amount of analytes sorbed by the WMS sorbent exceeded the upper limit of the analytical instrument (peak height greater than 19 nA). In order to obtain acceptable analytical response from the TD-GC-IRMS, two approaches were considered: one was to adjust the TD flows and obtain a suitable split ratio, and the other was to analyze an aliquot of the WMS sorbent to reduce the amount of the analyte reaching the GC column. Because manipulating the flows in the TD system is a meticulous task which is not reproducible, the latter approach was used in $\delta^{13}C$ measurements for WMS.

5.3.1 Method developed for WMS-TD-GC-IRMS when the amount of analyte collected by WMS exceeds the analytical instrument upper dynamic range limit

The purpose of this method was to determine whether the sorbent from the WMS can be split before the TD-GC-IRMS analysis to reduce the amount of analyte delivered to the system and to obtain an acceptable analytical response. From the experimental data, as the time of exposure doubled, the analytical response (peak height) doubled as well. Consequently, the analytical response for the 12, 24, 48 and 96 hours exposures could be predicted. Table 7 represents the experimental values obtained for the analytical response for 3 and 6 hours and the predicted values for the remaining times.

Table 7. TD-GC-IRMS analytical response obtained for 3 and 6 hours exposure time and the predicted values for 12, 24, 48 and 96 hours.

	Peak Height [nA]		
	Hexane	**Benzene**	**TCE**
3 h	2.1	6.5	8.8
6 h	4.3	13.1	17.1
12 h	8	28	36
24 h	16	56	72
48 h	24	112	144
96 h	48	224	288

As can be seen in Table 8, analytical responses predicted for the last 4 experiments with benzene and TCE exceeded the upper limit of the TD-GC-IRMS. For statistical reasons, randomization order of the experiments was followed. In this case, method development started with the 24 hours experiment and with the weighing of 1 mg of WMS sorbent exposed and

transferred directly into the TD tube for thermal desorption. The TD tube was already filled with conditioned sorbent prior to addition of the WMS sorbent aliquot. A Mettler Toledo UMT2 balance was used for WMS sorbent weighing. After analysis, it was determined that for 1 mg of sorbent weighted, the analytical response obtained was below the detection limit (peak height value lower than 1 nA). In order to increase this result, the sorbent amount weighted was increased to 10 mg. The result obtained in this case was above the detection limit (peak height values between 1-2 nA). To assure that the reproducibility and the accuracy of the results obtained were maintained, the amount of WMS sorbent aliquot was increased to 20 mg and the results obtained for the analytical response were in a higher range (peak height values between 2 and 8 nA). The same method was applied for 12, 48 and 96 hours exposure times. In the 12 hours experiment, however, the 20 mg sorbent aliquot was analyzed with splitless TD setup, and the entire amount from the TD tube was transferred into the GC column. This adjustment was necessary in order to obtain analytical response values in the 2 - 8 nA range. The reproducibility (n=3) of the weighing method developed was tested and was found to be good, with standard deviations below 0.4 ‰ for all the compounds.

Analyzing the data obtained from this study, it can be observed from Table 6 that the consistency and reproducibility of the results were maintained, and standard deviations were within the accepted error for all compounds. Statistical analysis of the difference between the $\delta^{13}C$ values obtained with passive and active sampling was performed using one tailed, paired Student's t test at 95% confidence level. The results determined that $t_{stat} > t_{critical\ one\text{-}tail}$ for all the analytes meaning that differences between the $\delta^{13}C$ values during both exposures were significant. The probabilities that the differences were due to random factors were $8.3x10^{-7}$ for hexane, $2.7x10^{-5}$ for benzene and $1x10^{-3}$ for TCE. The magnitude of isotopic fractionation was

found to be constant with time (as the slope of the line of best fit was close to zero and R^2 very small) and independent of the amount collected by the WMS sorbent. In addition, another statistical analysis was performed for the isotopic fractionation obtained in this study and the isotopic fractionation observed at room temperature in the time exposure study for each analyte and for both sampling methods using two tailed, paired Student's t test at 95% confidence level. The statistical tests found for all the analytes and for both sampling methods, with one exception, that $t_{stat} < t_{critical\ two\text{-}tail}$ meaning that no significant difference was observed between the isotopic fractionation obtained through both methods. The exception was found for hexane that had a different statistical result. In this case, for passive sampling $t_{stat} > t_{critical\ two\text{-}tail}$ meaning that the difference between the isotopic fractionation resulted in this case was significantly different, and the probability that this difference was due to random factors was 0.004. However, it should be pointed out that instrumental problems were encountered when determining $\delta^{13}C$ for hexane, therefore this result should be treated as tentative and further studies will need to be carried out. Figure 18 presents the analytical response (peak height) obtained in this study versus the time of exposures. It is only represented for 12, 24, 48 and 96 hours; this is because the measurements for $\delta^{13}C$ in these experiments followed the weighing method developed, thus making it easy to observe if there was any correlation between the amount adsorbed by the WMS sorbent and the exposure duration. In Figure 18, the 12 hours exposure time analytical response obtained through splitless TD analyses was recalculated to account for the fraction of sample used in the other experiments, so the data was comparable. The graph shows a steady increase in the amount for hexane and benzene. However, for TCE with the same exposure time, the amount increased and reached a maximum in 48 hours but declined slightly afterwards.

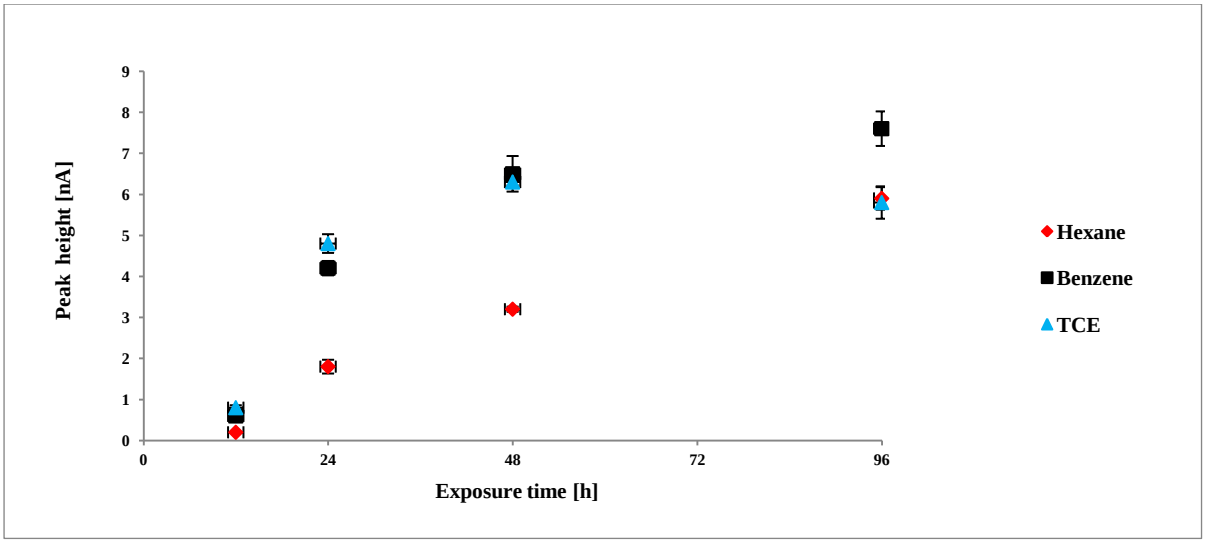

Figure 18. The analytical response versus time of exposure.

Differences in the analytes behaviour can be attributed to the adsorption process of the chemicals in contact with the sorbent.[48] In this process, the chemicals are adhering to the sorbent's surface and this process depends on the sorbent type and on the chemical nature of the analytes.[48] At constant temperatures, there is a correlation between the sorbate concentration and its affinity towards the sorbent.[48] As seen in Figure 18, hexane had a linear sorption isotherm, and hexane affinity toward the sorbent remained the same over time.[48] Conversely, with TCE in this study, it was observed that at higher sorbent saturation competitive sorption started playing a significant role at longer exposure times, causing the amount sorbed to peak and then decrease.[48] Similar behaviour was observed for benzene, except that the sorption maximum has not been reached at 96 hrs.

In the next graphs, Figure 19, 20 and 21, the $\delta^{13}C$ values obtained for each analyte in this study are shown as a function of time. It can be observed that there was no dependence between the two variables.

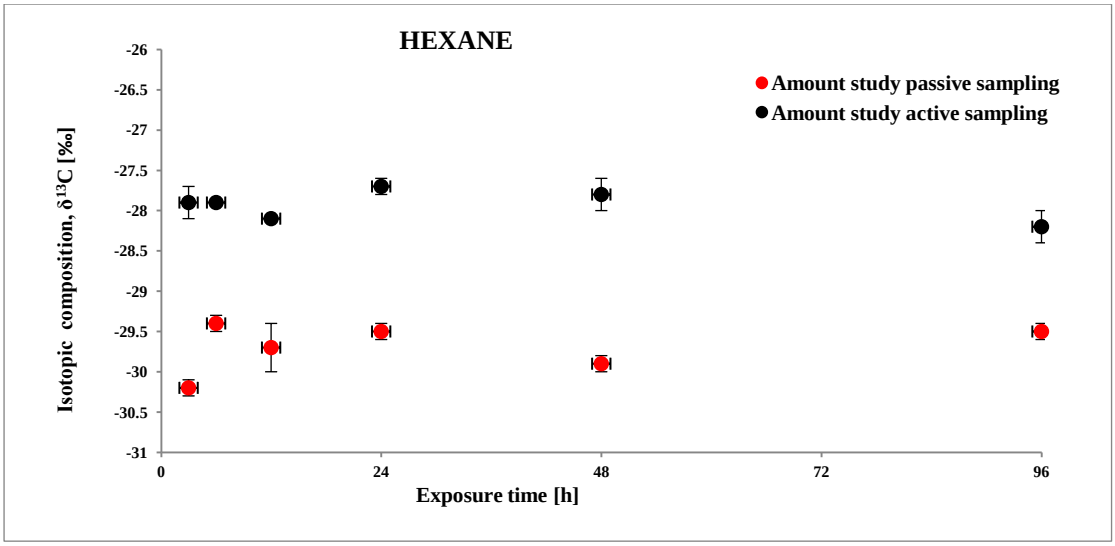

Figure 19. $\delta^{13}C$ values for hexane obtained when the analyte amount collected by WMS was increased with each exposure time.

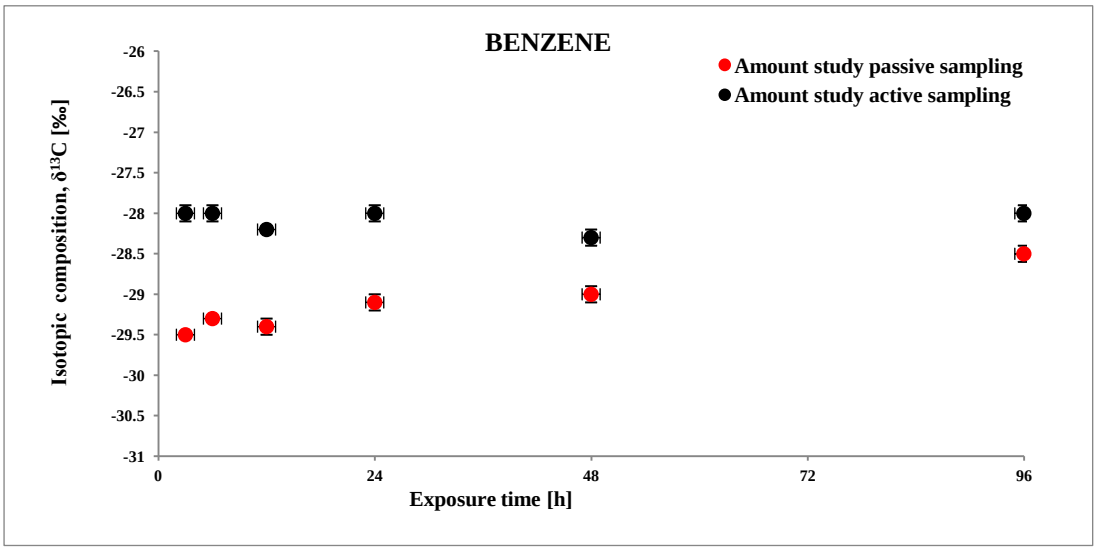

Figure 20. $\delta^{13}C$ values for benzene obtained when the analyte amount collected by WMS was increased with each exposure time.

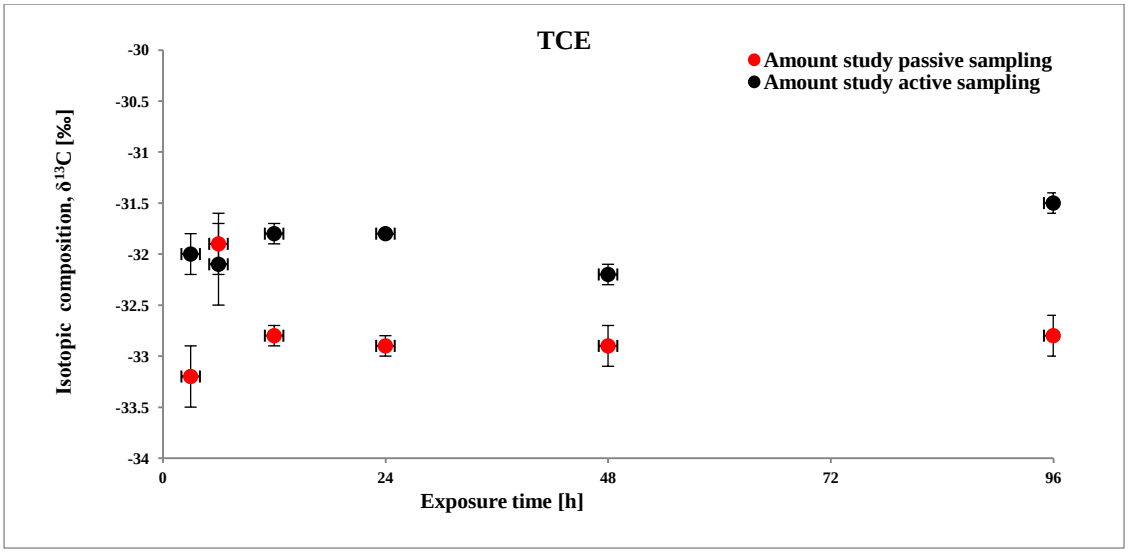

Figure 21. $\delta^{13}C$ values for TCE obtained when the analyte amount collected by WMS was increased with each exposure time.

5.4 EFFECT OF THE WMS EXPOSURE TEMPERATURE ON $\delta^{13}C$ VALUES

In his thesis, Seethapathy determined that at lower temperatures, WMS uptake rates increased.[41] Thus, due to the importance of this relationship between temperature and uptake rate, an analysis on the effect of temperature on $\delta^{13}C$ values measured by passive sampling was conducted. The results obtained from this experiment are presented in Table 8.

Table 8. $\delta^{13}C$ values obtained for each analyte for passive and active sampling when the temperature in the exposure chamber was 12 °C [‰]; (the numbers in brackets represent the number of replicates for each experiment)

	Passive sampling	**Active sampling**	**Passive sampling**	**Active sampling**	**Passive sampling**	**Active sampling**
Time of exposure	**HEXANE**	**HEXANE**	**BENZENE**	**BENZENE**	**TCE**	**TCE**
(h)	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**	**$\delta^{13}C$**
6	(3) -29.2	(3) -28.1	(3) -29.0	(3) -27.4	(3) -32.8	(3) -32.3
12	(4) -29.2	(3) -28.1	(4) -29.3	(3) -28.1	(4) -32.7	(3) -31.6
24	(4) -29.0	(3) -28.1	(4) -28.6	(3) -27.4	(4) -31.9	(3) -31.4
48	(4) -29.5	(3) -27.5	(4) -29.1	(3) -28.2	(4) -32.4	(3) -32.0
96	(2) -29.1	(2) -28.0	(2) -28.6	(2) -28.5	(2) -32.1	(2) -32.4
Average	**-29.2_0**	**-27.9_6**	**-28.9_2**	**-27.9_2**	**-32.3_8**	**-31.9_4**
Standard deviation	**0.2**	**0.3**	**0.3**	**0.5**	**0.4**	**0.4**
Difference between passive and active sampling	**-1.2_4**		**-1.0_1**		**-0.4_4**	

As can be observed in Table 8, the $\delta^{13}C$ values obtained at 12 °C were consistent, reproducible and with standard deviation within the accepted error for all the chemicals. In order to determine if the exposure temperature influenced the isotopic fractionation obtained in this study, the results were statistically compared with the isotopic fractionation results determined in the time of exposure study (refer to Section 5.2) when the experiments were performed under the same conditions but at room temperature. The isotopic fractionation obtained for different temperature experiments for each analyte and for both sampling methods were analyzed using a two tailed, paired Student's t test at 95% confidence level. The statistical tests found for all the analytes that $t_{stat} < t_{critical\ two\text{-}tail}$, meaning that no significant difference was observed between isotopic fractionation obtained through both studies. In other words, the probability that the differences between $\delta^{13}C$ values for the two sampling methods obtained at different temperatures

would occur due to random factors was in all the cases higher than 0.05. The magnitude of isotopic fractionation was found to be constant with time (as the slope of the line of best fit was close to zero and R^2 very small) and independent of the exposure temperature. Although temperature did not affect the isotopic fractionation, it did affect the analytical instrument response obtained. This can be explained by the temperature dependability of the PDMS permeability towards each chemical.[41] Permeation is a temperature-dependent process and for each analyte permeating through the PDMS polymer the diffusion coefficient decreases with decreasing temperature, while the partitioning coefficient increases.[41] In Section 3.1 the relationships between the WMS uptake rates and these two parameters was discussed. The analyte with the highest uptake rate was TCE (3.3 mL/min), followed by benzene (2.4 mL/min) and hexane (1.3 mL/min).[41] As seen in Tables 9, 10 and 11, for each chemical and each exposure time, the TD-GC-IRMS peak height measured increased for the same experiments at lower temperature.

Table 9. Hexane analytical response measured at different temperatures.

Exposure times [h]	**Analytical response [nA] 22 °C**	**Analytical response [nA] 12 °C**
6	2.8	5.7
3	2.2	3.2
24	2.3	4.0
48	2.0	2.8
96	1.9	3.5

Table 10. Benzene analytical response measured at different temperatures.

Exposure times [h]	Analytical response [nA] 22 °C	Analytical response [nA] 12 °C
6	8.3	10.6
3	6.7	9.5
24	6.7	10.9
48	5.7	7.7
96	4.6	7.7

Table 11. TCE analytical response measured at different temperatures.

Exposure times [h]	Analytical response [nA] 22 °C	Analytical response [nA] 12 °C
6	**11.1**	**14.0**
3	**8.1**	**12.4**
24	**8.2**	**12.9**
48	**6.9**	**9.8**
96	**5.2**	**8.0**

Lowering the exposure temperature to 12 °C did not affect the carbon isotopic composition for the analytes collected by WMS. Figures 22, 23 and 24 show that $\delta^{13}C$ values measured at lower temperature had no significant variations in relation to exposure time.

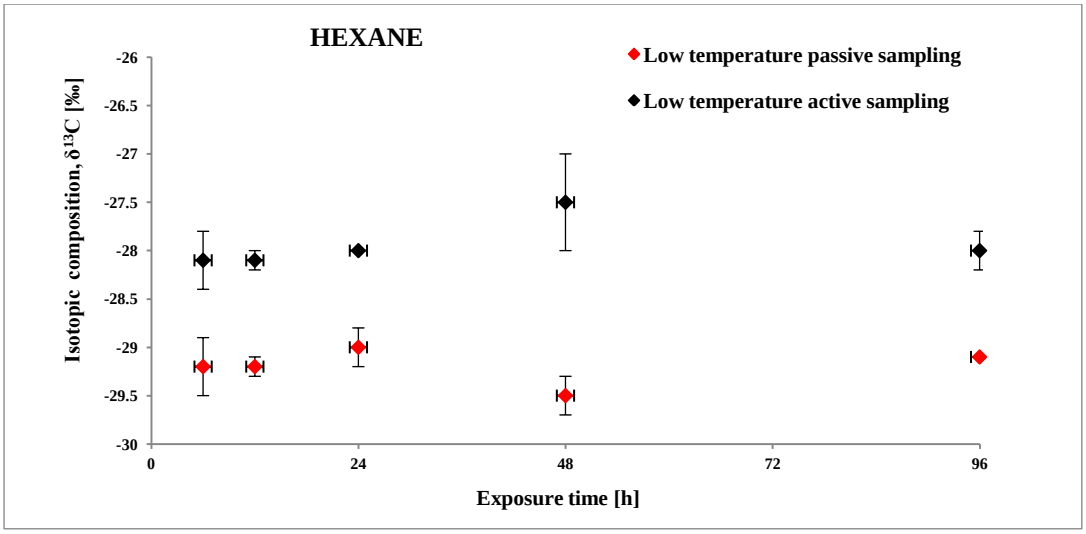

Figure 22. Hexane $\delta^{13}C$ values obtained at 12 °C vs. exposure time.

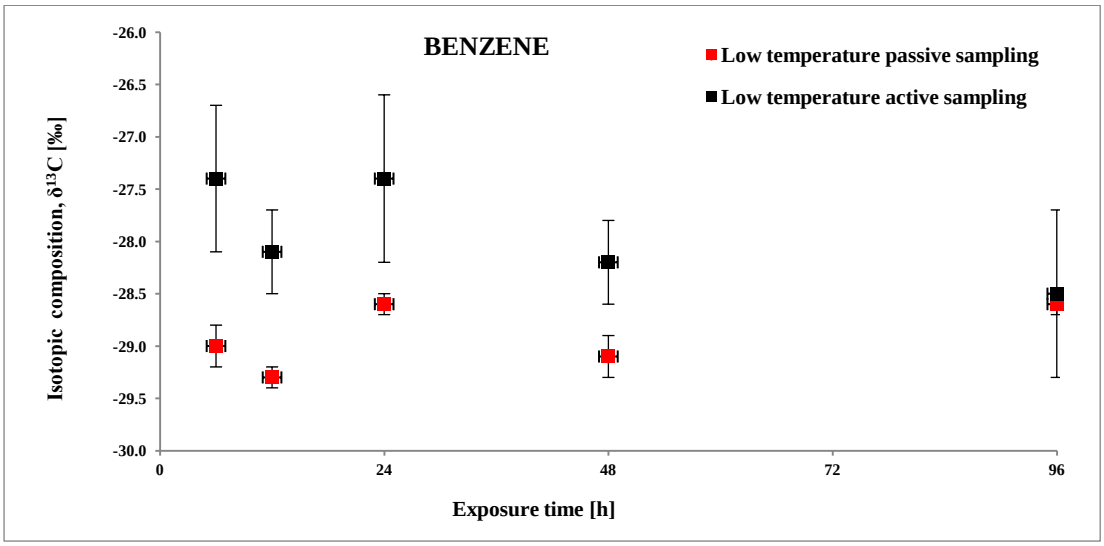

Figure 23. Benzene $\delta^{13}C$ values obtained at 12 °C vs. exposure time.

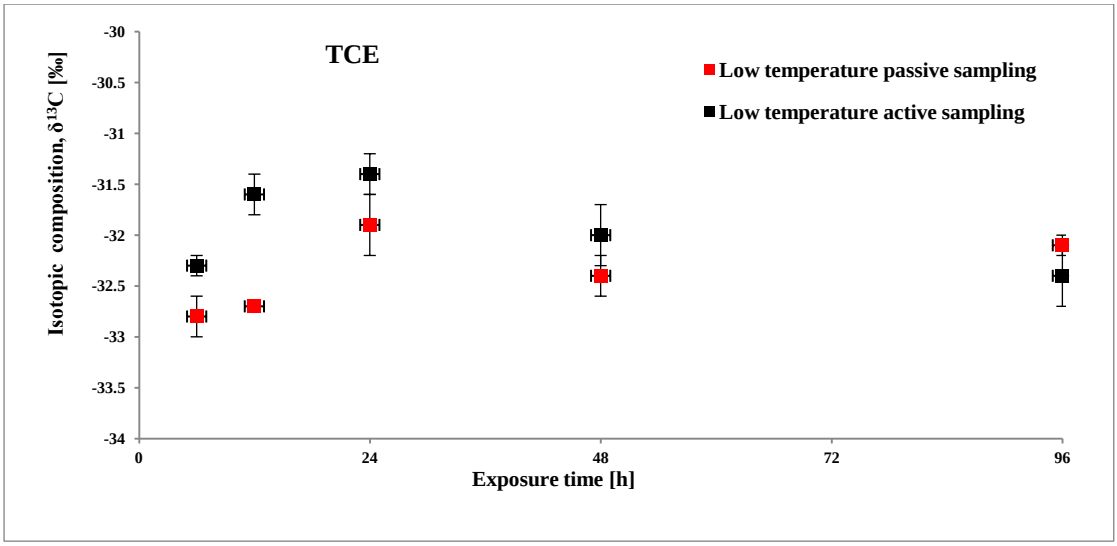

Figure 24. $\delta^{13}C$ values for TCE at 12 °C vs. exposure time.

The results obtained were important with respect to the applicability of the WMS in field studies for soil gas contamination determinations. Here, the lower temperature was purposely selected at 12 °C to represent a value close to real temperature values in soil gas at the time of sampling.

6. CONCLUSIONS

A WMS-TD-GC-IRMS method for the determination of the carbon isotopic composition of the contaminants in soil gas and vapour intrusion pollution was successfully developed. WMS allows the determination of the carbon isotopic composition of the analytes at concentrations as low as 0.65 mg/m^3 for hexane, 0.88 mg/m^3 benzene and 4.38 mg/m^3 for TCE. The results obtained in all studies showed good data reproducibility and consistency, with standard deviations within the commonly accepted analytical error of ± 0.5 ‰. The sampling processes introduced small isotopic fractionation in all cases; however, the degree of fractionation remained practically constant and independent of sampling time, mass collected and temperature of exposure. Table 12 summarizes all results obtained throughout the studies.

Table 12. $\delta^{13}C$ values obtained for the analytes in all studies [‰].

	Hexane Passive Sampling	**Hexane Active Sampling**	**Benzene Passive Sampling**	**Benzene Active Sampling**	**TCE Passive Sampling**	**TCE Active Sampling**
Time effect study 1	-29.3	-27.9	-29.2	-28.0	-32.6	-31.7
Time effect study 2	-29.4	-28.0	-29.2	-27.9	-32.6	-31.8
Amount collected	-29.7	-27.8	-29.1	-28.1	-32.8	-31.9
Temperature effect	-29.2	-28.0	-28.9	-27.9	-32.4	-31.9
Average	**-29.4**	**-27.9**	**-29.1**	**-28.0**	**-32.6**	**-31.8**
Standard Deviation	**0.2**	**0.1**	**0.1**	**0.1**	**0.2**	**0.1**

The results were very consistent with standard deviations lower than 0.2 ‰. This research could serve as a basis for future studies in CSIA for fingerprinting application in the determination of pollution sources in vapour intrusion or soil gas contamination studies.

7. WMS-TD-GC-IRMS IN A FIELD STUDY

For the second part of this research, the WMS-TD-GC-IRMS method was tested in a field study. The objective was to provide a comparison between the results obtained from the WMS-TD-GC-IRMS method and the solvent based active sampling method for gas phase sample collection for CSIA. Here, analysis of data was conducted to establish if there was any significant difference between the results obtained by the two different methods. The WMS were used to sample gases collected during a gasoline biosparging treatment investigation. During this experiment (funded by Chevron, and under the supervision of Professor Ramon Aravena) where the isotopic composition of a mixture of contaminants in the gas phase was already being monitored by this technique (see below), WMS were exposed at the same time. A full comparison between the results obtained by both methods is presented.

For this experiment, an air sparging system was implemented to remediate a simulated gasoline spill performed under controlled conditions (compounds listed in Table 13). Evolution of the biodegradation process and physical removal by volatilization were assessed by monitoring concentration and isotopic composition of the extracted gases (so called off-gas). The different volumes of contaminants injected in this experiment are presented in Table 13. The pilot experiment was conducted at the Canadian Force Base Borden in Angus, which is located approximately 90 km northwest of Toronto, Ontario (see Figure 25 for site location). The experiment started on October 24th, 2011, and ended on November 7th, 2012. It was put on hold during the winter season, between December 21st, 2011, and March 27th, 2012 due to weather conditions. Only the off-gas system and the sampling technique will be described, since other details are not relevant for this part of the study (specific information about the cell and system used for this experiment can be found in L.C. Nelson Msc. Thesis).[49]

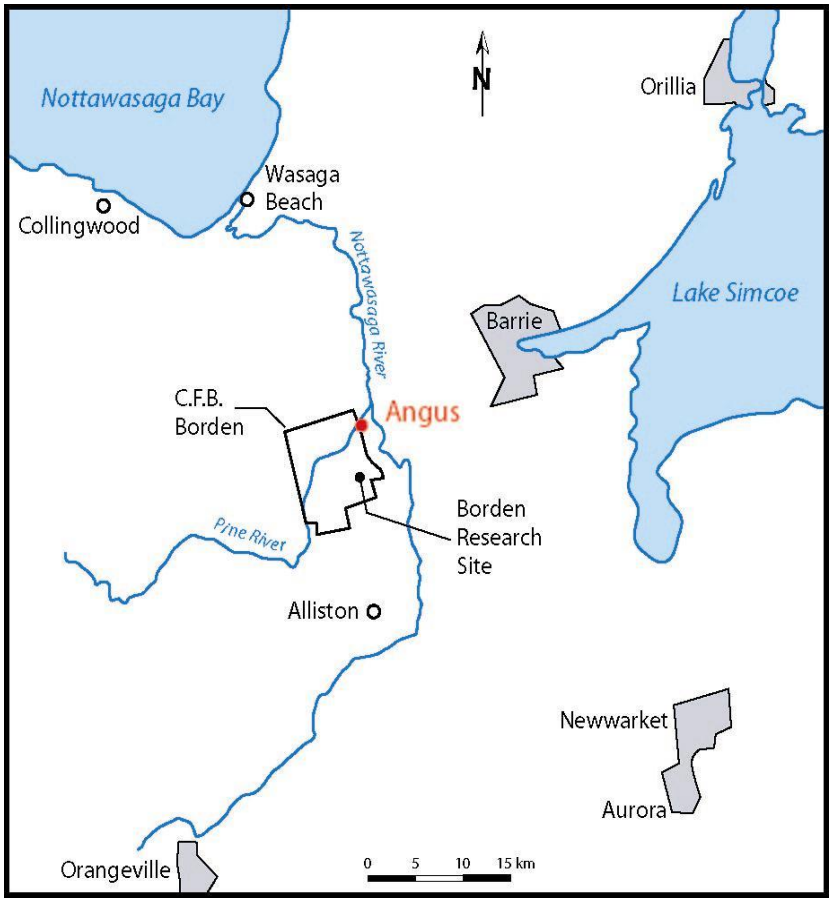

Figure 25. Site map.

Table 13. List of chemicals used in the Borden experiment.

Compound name	Volume [L]	Mass [g]
Isooctane	50	34600
Isopentane	50	30800
Cyclopentane	20	15020
Octane	20	14050
Benzene	5	4383
Toluene	2.5	2167
Naphtalene	2	2320
o-xylene	1	864
1-2-4 trimethylbenzene	1	876
MTBE	0.5	370
TOTAL	**152**	**105450**

7.1 METHODS

For the collection of the gas phase during the sparging process, a box cover was installed over the cell, and a vacuum pump was used to draw the air from the cell.[49] The vacuum flow rate was set higher (150 L/min) than the sparging flow (125 L/min) to ensure complete recovery of the released gas. Continuous total hydrocarbon concentration measurements were carried out using a portable PID detector connected to the collection gas system. Sampling for carbon isotopic composition determinations was performed during the sparging process approximately every week from October to December 2011, when the hydrocarbon concentrations were high (see Table 14), and every 2-4 weeks from March to November 2012, when hydrocarbon concentrations were much lower and a longer exposure time was required (see Table 14). Hydrocarbon concentration variations during the entire experiment are illustrated in Figure 26.

Table 14. Exposure times for WMS.

Periods for WMS samplings		WMS exposure time in days
Oct. 28/2011	Nov.12/2011	15
Nov.12/2011	Nov.18/2011	7
Nov.18/2011	Nov.21/2011	4
Nov.21/2011	Nov.29/2011	9
Nov.29/2011	Dec.11/2011	13
Dec.11/2011	Dec.21/2011	11
Mar.27/2012	Mar.30/2012	3
Mar.03/2012	Apr. 04/2012	33
Apr. 04/2012	May 05/2012	32

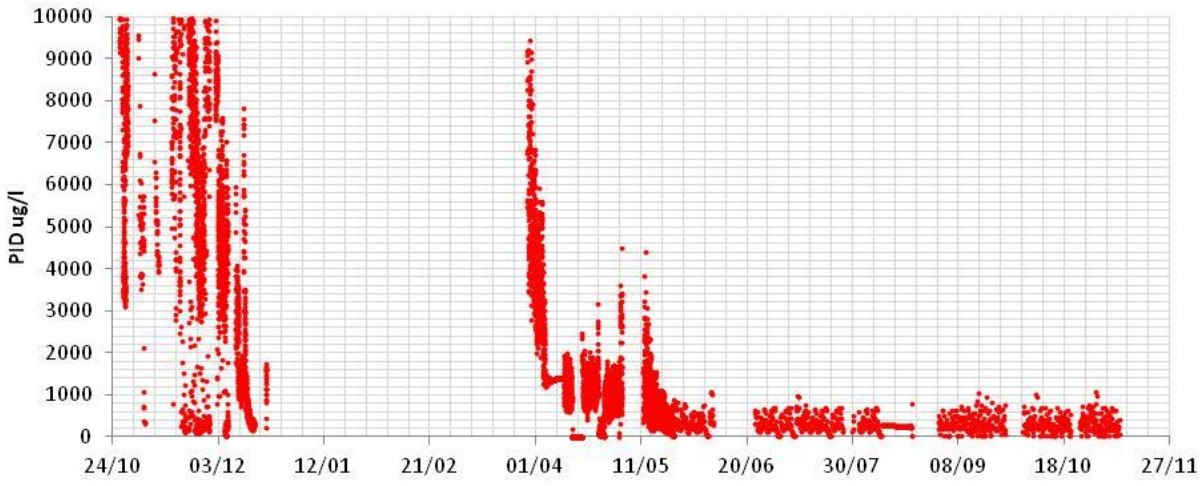

Figure 26. Hydrocarbon concentration variations during the experiment[50]

The two sample collection systems used for data comparison were solvent based active sampling (methanol in this experiment) and the WMS. In order to draw a constant amount of gas from the off-gas collector system, a peristaltic pump was employed. For the solvent based active sampling method, the gas was flushed into a 40 mL vial with 30 mL methanol for a period of time. Flushing time was dependent on the concentration measured with the PID (lower concentration leading to longer extraction times).

For WMS, the passive samplers were initially installed as represented in Figure 27, inside a Shop Vac. The exposures times were adjusted to collect sufficient amounts of compounds for CSIA.

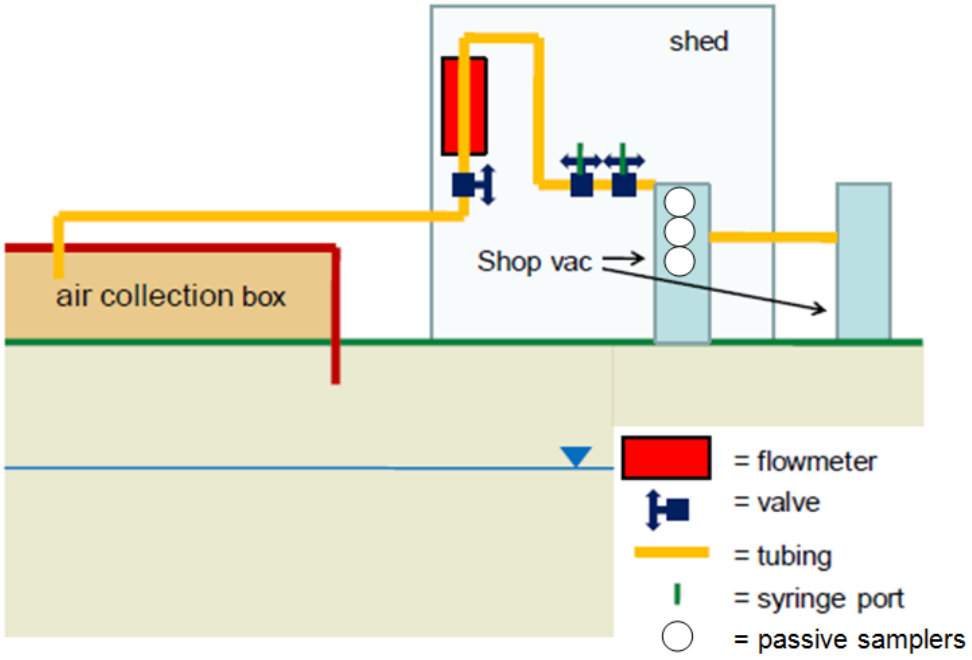

Figure 27. The exposure setup for WMS sampling at the beginning of the experiments (adapted from reference 49)

The initial sampler location (used in the first 3 sampling events) proved to be non-optimal, as the samplers were moving continuously because of the high flow rate of the extracted gas (inside the Shop Vac). Consequently, the deployment position was modified (Figure 28), and this new installation for WMS was used during the exposures until the end of the experiment.

Figure 28. The modified exposure system for WMS sampling.

The solvent based active sampling method for gas phase VOC collection for CSIA was developed and studied by Daniel Bouchard and Daniel Hunkeler, University of Neuchatel. It is currently under review. This sampling technique uses solvent-based active sampling and consists of purging air through a defined amount of an organic solvent which acts as a sink for VOCs. For gas phase collection, methanol was chosen as the organic solvent. The reproducibility of the $\delta^{13}C$ measurements for VOCs dissolved in the solvent has previously been demonstrated by Bouchard and Hunkeler, and the values reported here from this sampling technique can be considered representative of the isotopic composition of the compounds in the gas phase.[51]

The samples collected by the solvent based active sampling were analyzed by the Isotope Laboratory Facility at the University of Neuchatel in Switzerland. The analysis was performed using an Agilent TM 7890 GC coupled with IsoPrime TM 100 via combustion interface IsoPrime GC5. The extraction of the analytes was performed by purge and trap (P&T) analysis. In the P&T a volume of 1 mL of the methanol solution is added to 10 mL water, which is then introduced to the P&T system. The band of analytes released from the trap by thermal desorption is refocused by a cryogenic trap. The GC oven temperature was held isothermally at 50°C for 10 min, and then ramped to 180°C at 5°C/min. The helium carrier gas flow was 1.7 mL/min. Samples

collected using the above method were tested in duplicate for carbon isotopic composition determination. The passive samplers used in this project were fabricated in our laboratory and analyzed as described in Sections 4.3 and 5.3.1.

7.2 RESULTS AND DISCUSSION

The WMS samples collected as described in Section 7.1 were sent to the University of Waterloo, where they were kept in their original packages at room temperature and office environment for a period of approximately 12 months. Because of the long period of time elapsed between sampling and analysis, GC-MS analysis in full scan mode was carried out for the WMS exposed on October 28, 2011, using solvent desorption to verify the presence of analytes in the sorbent (see Figure 29). The GC-MS method used here was developed by Seethapathy in his thesis.[41]

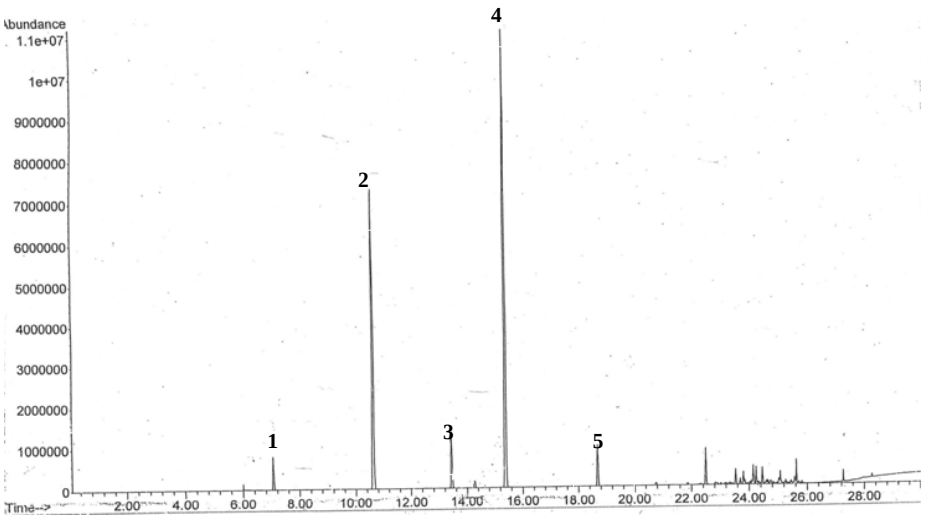

Figure 29. WMS GC-MS chromatogram (sampler exposed on October 28).

As can be seen in Figure 30, the highest analytical signals in the GC-MS chromatogram were attributed to isooctane and octane (peaks 2 and 4); other compounds identified were hexane (peak 1), toluene (peak 3) and o-xylene (peak 5). Due to the low analytical signals for hexane, toluene and o-xylene, they were not detected when analyzed with TD-GC-IRMS. A possible reason for this could be that the analytes amounts collected by the WMS were below the detection limit for TD-GC-IRMS analytical instrument. However, for the other two compounds, isooctane and octane, the mass collected by WMS exceeded the TD-GC-IRMS analytical response range (peak height over 19 nA). Considering these findings, the method described in Section 5.3.1 was used for the analysis of WMS field samplers for isooctane and octane. This method was modified for this application; however, the principle remained the same. For each sampler tested the weighing of WMS sorbent started with 1 mg. Depending on the analytical response obtained, the sorbent amount was adjusted to obtain optimum peak height. As mentioned in Section 5.3.1, this value fell between 2 and 10 nA because in this range the $\delta^{13}C$ values measured for each analyte maintained reproducibility and total uncertainty fell within

±0.5 ‰. Three passive samplers were exposed at the same time for each day of exposure. From each sampler, 3 replicates were analyzed, for a total of 9 WMS $\delta^{13}C$ values measured per exposure day. Results obtained with the methanol technique and WMS for isooctane and octane analysis are presented in Tables 15 and 16, respectively. The calibration method used for TD-GC-IRMS was the same as described in Section 4.3, and the internal laboratory standards used for the analytes were -28.4 ‰ for isooctane and -25.5 ‰ for octane. The absence of the other compounds in WMS (presented in Table 13) could be explained by volatilization of these chemicals due to incorrect WMS storage conditions after sampling, as well as the long period elapsed between exposure and analysis.

Table 15. Isooctane $\delta^{13}C$ values obtained in field exposure using the solvent based active sampling method (a) and WMS (b) [‰] (the numbers in brackets represent the number of replicates for each experiment).

a)

Solvent based method	$\delta^{13}C$	Std. Dev.
24/10/2011	(2) -25.7	0.0
25/10/2011	(2) -26.0	0.1
26/10/2011	(2) -26.3	0.2
16/11/2011	(2) -25.8	0.0
21/11/2011	(2) -25.9	0.1
28/11/2011	(2) -25.8	0.2
01/12/2011	(2) -26.0	0.1
21/12/2011	(2) -25.9	0.0
26/03/2012	(2) -25.7	0.0
04/04/2012	(2) -25.8	0.0
11/04/2012	(2) -25.8	0.0
26/04/2012	(2) -26.1	0.1
23/05/2012	(2) -26.1	0.1
Average	**-25.9**	**0.1**

Difference between the two two methods	**-1.2**	-

b)

WMS method	$\delta^{13}C$	Std. Dev.
28/10/2011	(3) -24.9	0.7
12/11/2011	(9) -26.0	0.3
18/11/2011	(9) -26.5	0.6
21/11/2011	(3) -27.2	0.0
29/11/2011	(9) -26.5	0.3
11/12/2011	(9) -27.1	0.7
21/12/2011	(6) -27.6	0.4
30/03/2012	(9) -27.3	0.4
18/04/2012	(9) -29.3	0.6
02/05/2012	(9) -28.2	0.4
Average	**-27.1**	**0.4**

Table 16. Octane δ13C values obtained in field exposure using the solvent based active sampling method (a) and WMS (b). [‰] (the numbers in brackets represent the number of replicates for each experiment)

a)

Solvent based method	$\delta^{13}C$	Std. Dev.
24/10/2011	(2) -30.3	0.1
25/10/2011	(2) -30.7	0.0
26/10/2011	(2) -30.5	0.3
16/11/2011	(2) -30.2	0.1
21/11/2011	(2) -30.3	0.1
28/11/2011	(2) -30.5	0.2
01/12/2011	(1) -30.6	--
21/12/2011	(2) -30.3	0.2
26/03/2012	(2) -30.6	0.3
04/04/2012	(2) -30.7	0.0
11/04/2012	(2) -30.6	0.3
26/04/2012	(2) -30.6	0.2
23/05/2012	(2) -30.6	0.1
Average	**-30.5**	**0.2**

Difference between the two two methods	**-1.2**	-

b)

WMS method	$\delta^{13}C$	Std. Dev.
28/10/2011	(3) -30.6	0.9
12/11/2011	(9) -31.5	0.1
18/11/2011	(9) -31.5	0.1
21/11/2011	(6) -31.8	0.0
29/11/2011	(9) -31.6	0.1
11/12/2011	(9) -32.3	0.2
21/12/2011	(6) -32.0	0.2
30/03/2012	(9) -32.1	0.3
18/04/2012	(9) -32.1	0.1
02/05/2012	(9) -31.9	0.1
Average	**-31.7**	**0.2**

The data obtained in the Tables above are presented graphically in Figure 30 for isooctane and Figure 31 for octane.

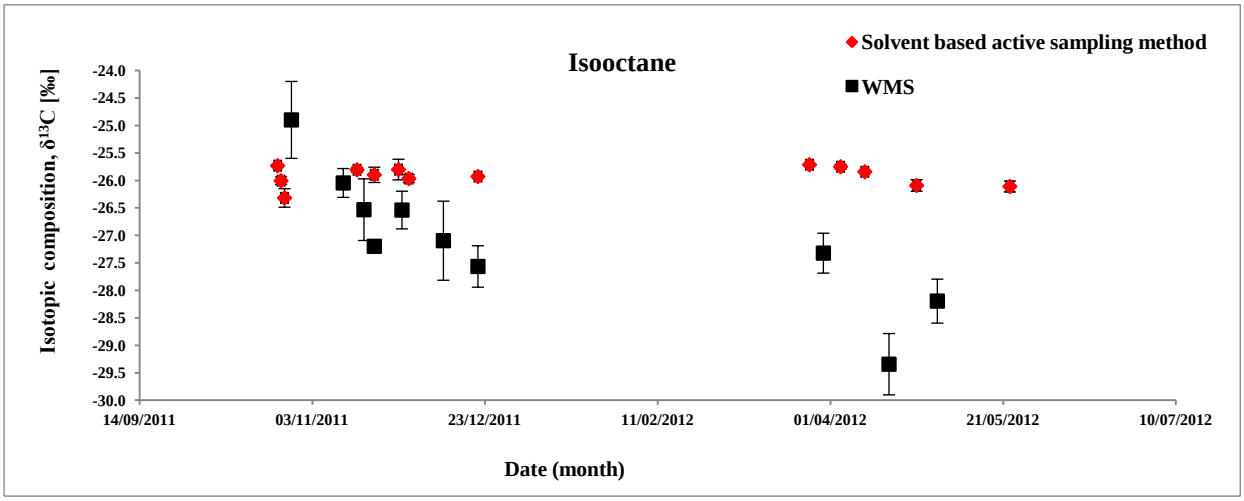

Figure 30. Isooctane $\delta^{13}C$ values obtained with solvent based active sampling and with WMS.

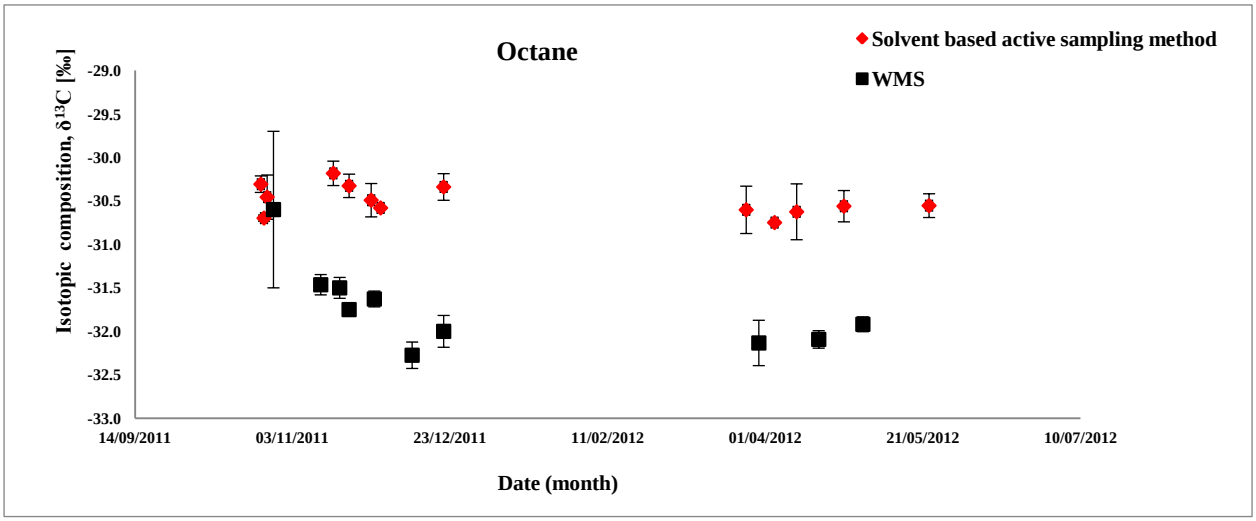

Figure 31. Octane δ^{13} values obtained with solvent based active sampling and with WMS.

As can be seen in Figures 30 and 31, the correlation between the results obtained using the two methods was good for both cases. For solvent based active sampling method, the results were consistent during the entire period of sampling with a standard deviation below 0.3 ‰ for both analytes. On the other hand, in WMS sampling the reproducibility of the results within one sampler (n=9) was below 0.5‰ for isooctane and below 0.3 ‰ for octane. As observed on October 28, 2011, WMS reproducibility was 0.7 ‰ for isooctane and 0.9 ‰ for octane; this could be attributed to the improper sampler deployment during the sampling time at the beginning (the samplers were under constant movement inside the Shop Vac). The difference between the $\delta^{13}C$ values measured with both collection methods was 1.2 ‰ (see Table 15 and Table 16). This could be representative for the isotopic fractionation observed in the experimental part for the three studies analyzed. Values obtained for carbon isotopic measurements for WMS were slightly more negative when compared to the solvent base active sampling technique, meaning that they were depleted in ^{13}C relative to ^{12}C isotopes.

Thus, it can be concluded that the WMS collection method has a good potential in vapour intrusion studies as long as the slight isotopic fractionation during sampling is taken into consideration. The advantage of the weighing method developed in this study is that replicate analyses could be carried out from one sampler. This is not the case when a lower analyte mass is collected by the sampler, but to overcome this problem a higher mass could be collected by using longer exposure times. On the other hand, GC-MS analysis prior to TD-GC-IRMS is not necessarily required in this case to determine the analytical response for the entire sample. The analyte mass adsorbed by the sampler could be anticipated from the IRMS analytical response obtained. An important aspect to be considered should be WMS deployment, as improper

deployment could result in inconsistent $\delta^{13}C$ measurements within the sampler when the sorbent weighing method is used.

7.3 Conclusions

The Waterloo Membrane Sampler was employed in this research to determine its potential applicability in fingerprinting applications through compound specific isotope analysis. The new method developed was then applied in a field study and the WMS yielded similar results when compared with the solvent-based active sampling technique. The results obtained were consistent with the results of laboratory experiments in spite of non-optimal storage and handling of samplers. However, more research is needed for a full method evaluation. Coupling WMS with CSIA could represent a powerful tool in vapour intrusion studies.

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