EXTRACTION OF ALCOHOLS FROM GASOLINE

USING SOLID PHASE MICROEXTRACTION (SPME)

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By

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(Abstract)

It is common practice to add oxygenates, such as ethers or alcohols, to gasoline in areas suffering from ozone or smog problems in order to reduce pollution. The most commonly used oxygenates are ethanol (EtOH) and methyl tert-butyl ether (MTBE). However, MTBE is now forbidden by the environmental protection agency (EPA) because of the possibility of ground water contamination. The current trend is to use EtOH, therefore this work focuses on the analysis and quantification of EtOH in gasoline by solid phase microextraction (SPME). The major problem in quantifying EtOH in gasoline is the coelution of hydrocarbons with EtOH. There have been several approaches to solve this problem; among the chromatographic ones, three major types have been proposed: (1) the first one uses a detector selective for oxygen containing compounds; (2) the second one uses two or more columns; (3) and the third one uses an extraction step prior to GC analysis. In this work an extraction step with water is used prior to a solid phase microextraction (SPME) sample preparation coupled to a gas chromatographic (GC) analysis.

Solid phase microextraction is a recent technique, invented by Pawliszyn in 1989, and available commercially since 1994. A fiber is used to extract small amounts (ppm, ppb, ppt) of analytes from a solution, usually water. The fiber is beneficial in concentrating analytes. Most work using SPME has been done with hydrophobic (non polar) analytes, extracted using a polydimethylsiloxane (PDMS; non polar) coating on a fused silica fiber. Since very little work has been done with polar analytes, the novel approach of this work is the extraction of EtOH.

Since EtOH is the analyte of interest, a polar fiber, carboxen/polydimethyl siloxane (Car/PDMS) is used. Two methods are used for quantification of EtOH in

gasoline: the method of a standard calibration curve, and the method of standard addition. They are both successful in quantifying the amount of EtOH in gasoline. The relative errors, with the method of standard addition, vary from 5.3% to 14%, while the ones with the method of calibration curve vary from 1.6% to 7.2%. Moreover, some extraction time studies for both direct and headspace sampling are performed. Direct sampling shows the presence of an equilibrium condition for the carboxen/PDMS fiber, for which no extraction theory is available. Conversely, headspace sampling shows no equilibrium state; after a sampling time of one hour, the amount of EtOH extracted decreases with sampling time. This is probably due to displacement of EtOH by other compounds in the fiber.

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CHAPTER 1 - INTRODUCTION

1.1 Background

1.1.1 History

For different reasons, it is very common to put additives in gasoline. Among those additives, oxygenates are commonly used in order to increase the amount of oxygen contained in gasoline. The oxygenates that are added can be either ethers (e.g., methyl tert butyl ether (MTBE), ethyl tert butyl ether (ETBE), and tert amyl methyl ether (TAME)) or alcohols (e.g., methanol (MeOH) and ethanol (EtOH)) [51]. Additives are chosen based on their cost and octane enhancing capabilities [50,58]. In the 1920s, MeOH and EtOH were already known to be octane enhancers, reducing knocking and allowing smoother burning [29,33,63]. They started being widely used since octane numbers in those days were quite low, therefore an improvement in engine performance by adding alcohols could easily be noticed. Lead additives started being substituted for alcohols since they were better octane enhancers, however they were banned in 1996 because they were major sources of lead contamination [33]. Therefore, the use of alcohols resurfaced.

Crude oil prices also influence the amount of oxygenates added to gasoline. Indeed, if crude oil prices are high, then it is more economical for the fuel blender to add oxygenates. For example, in the 1970s, during a period of oil crisis, gasoline supplies were restricted, and therefore more oxygenates were used as gasoline supplements. Up to 10 % alcohol was added to gasoline, yielding what became known as gasohol [54].

Methanol has been used in high concentration, in Canada, in specially designed cars, employing a specifically designed engine (“M85 fuel flexible vehicles”) [55]. Those cars can run with a gasoline mixture containing up to 85% MeOH. A minimum of 15% gasoline is required, in order to not only facilitate engine start during cold

weather, but also to add more safety to the whole blend. Indeed, MeOH burns with a flame that is almost invisible in the daylight; thus, an ignited fuel spill would barely get noticed. On the contrary, gasoline burns with a yellow flame, thus making the whole blend flame more visible [55].

Currently, the Clean Air Act Amendments of 1990 require the addition of oxygen to gasoline in areas suffering from ozone or smog problems in order to reduce pollution [58]. Such a reformulated gasoline (RFG) has to contain at least 2% oxygen by weight during the year and at least 2.7% oxygen by weight during the wintertime [62]. The most commonly used oxygenates are EtOH and MTBE. However, MTBE is now almost forbidden by the environmental protection agency (EPA) because of the possibility of ground water contamination [14,57,61,62]. Indeed, MTBE has been known to leak into drinking water sources from underground gasoline storage tanks, causing a complex problem because it is very difficult to remove it from water [57]. Even though this theory has been challenged by an MTBE producer [60], the current trend is to use EtOH, which is highly biodegradable and therefore will unlikely travel far from spills or leaks [38,57].

1.1.2 Advantages and disadvantages

The addition of oxygenates to gasoline offers many advantages, among which:

- more complete combustion and reduction of carbon monoxide emissions;
- being a renewable energy source;
- increased octane number;
- increased volatility.

Most importantly, the use of RFG reduces air toxic emissions and CO emissions, therefore reducing pollution emissions that cause ground level ozone problems [3,15,21,39,47,58]. Indeed, the addition of oxygenates allows a more complete combustion in the transient operation of the car. Furthermore, in the steady operation of the car, it shifts the reaction equilibrium to CO_2 rather than CO [21,51]. During engine

start or during vehicle acceleration (i.e., transient operation), an excess of gasoline is present in the burning chamber. This causes a lower oxygen-to-gasoline ratio, resulting in an incomplete combustion causing higher hydrocarbon emissions since there is not enough oxygen to burn all the gasoline hydrocarbons. Adding oxygenates increases the oxygen-to-gasoline ratio (i.e., "richer" gasoline-air mixture, richer in oxygen), which results in a more complete combustion [2,22]. During steady engine operation, the oxygen-to-gasoline ratio is the stoichiometric one ("normal" gasoline-air mixture). Adding oxygenates to the mixture produces an excess of oxygen and the reaction equilibrium is shifted towards CO_2 rather than CO. The addition of oxygenates also allow faster and more stable combustion.

The addition of oxygenates to gasoline is beneficial in reducing the dependency from non-renewable energy sources. Indeed, oxygenates can be produced from available sources (e.g., biomass, sewage, municipal and agricultural waste) [9,17,27,28,44,45,46,56], whereas oil, a natural (non-renewable) energy source, cannot.

Methanol, also known as "wood alcohol", can be either obtained by distillation of wood (oldest process), or produced synthetically using natural gas, coal gas, water gas or sewage gas at high temperature and pressure and in the presence of metallic catalysts, as follows [29]:

$$CO + 2H_2 \xrightarrow{ZnO-Cr_2O_3,\,400^\circ C} CH_3OH \quad (1)$$

Ethanol, also known as "grain alcohol", can be produced naturally from the fermentation of fruit juices, vegetable matter, and carbohydrates [29]. The ethanol hence produced, called "bio-ethanol", is wet, and therefore needs to be further distilled to remove excess water and to be purified. The fermentation reaction is as follows:

$$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 2CO_2 \quad (2)$$

Ethanol can also be produced synthetically, by a hydration reaction of ethylene, as follows [29]:

$$CH_2{=}{=}CH_2 \xrightarrow{H_2SO_4} CH_3CH_2OSO_2OH \xrightarrow{H_2O,heat} CH_3CH_2OH \quad (3)$$

Methyl tert butyl ether, can be produced in different ways, each having a common final step which is a reaction of methanol with isobutylene [29]:

$$(CH_3)_2C == CH_2 + CH_3OH \rightarrow (CH_3)_3COCH_3 \quad (4)$$

Oxygenates have a high octane number, therefore their addition to gasoline enhances the octane number of the gasoline mix, therefore reducing "knocking" in the engine [9,53]. If the octane number is already at the desired level, then it is possible to reduce the amount of other high octane compounds, like aromatics, which are sometimes toxic (e.g. benzene, toluene, xylene), and add more oxygenates to keep the same overall octane number.

Since they increase volatility, and thus allow for an easier engine start, oxygenates are added to gasoline in higher quantity during the wintertime. Indeed, gasoline needs to be mixed with air (vaporized) in order to burn in the engine, and thus it needs to be volatile. At low temperatures, gasoline vaporizes less easily, which can result in car stumbling or hesitating and slower engine warm-up [29]. Increased volatility of RFG is mostly true when alcohols are used. Indeed, MTBE only slightly increases the blend's volatility, and ETBE and TAME do not increase the blend's volatility [49].

There are also disadvantages in adding oxygenates to gasoline, among which:

- corrosion;
- lower energy content;
- increased cost;
- phase separation;
- increased volatility.

Especially in older engines, oxygenates can soften hoses and gaskets [54], and dissolve plastic parts [51]. Moreover, they can also corrode metal with different intensities, as follows: MeOH > EtOH > MTBE [29].

Oxygenates have a lower energy content than gasoline, thus reducing the fuel efficiency of RFG. For example, the addition of 10 volume % EtOH reduces the fuel efficiency by only a few percents. Indeed, the combustion of EtOH releases 76,000 British thermal units (Btu) per gallon, while the combustion of conventional gasoline releases 115,000 Btu per gallon. The combustion of RFG with 10 volume % EtOH releases only 111,100 Btu per gallon.

When the oil prices are not peaking, the cost of RFG increases because of the addition of oxygenates. So, unless there is a tax exemption for using oxygenates (and/or they are required by law), they will not likely be added [49].

When water is present in the gasoline, phase separation can occur if alcohols are the oxygenates used, since alcohols are very water soluble and would move to the bottom water phase. The top (alcohol deficient) gasoline phase would then have a lower octane number and may cause an engine to knock. Because of this problem, gasoline oxygenated with alcohols is not transported in pipelines, which sometimes contain water [49]. This problem is not seen with MTBE [51].

Finally, the increased volatility can lead to vapor lock in hot weather or high altitude [54]. Gasoline can vaporize in the fuel system and prevent the fuel pump from delivering sufficient gasoline to the engine. This would result in loss of power or engine shutdown [51].

1.1.3 Gasoline components

Gasoline is a very complex mixture, containing hundreds of different compounds. Those compounds can be divided into three classes:

- aliphatic compounds (poorly water soluble);
- aromatic compounds (moderately water soluble);
- oxygenated compounds (optional; alcohols highly water soluble).

A list of some of these common gasoline components, along with some of their physical properties, is shown in Table 1.1. An example of standard gasoline composition is shown in Table 1.2.

Table 1.1: Common components of gasoline, and some of their physical properties

	Compound	MW	b.p. (°C)	v.p. (mmHg) (@ 20oC)	water solubility (mg/L)
AROMATIC COMPOUNDS	benzene	78	80.1	76	1780
	toluene	92	110	22	515
	o-xylene	106	144.4	5	175
	m-xylene	106	139.1	6	_
	p-xylene	106	138.4	6.5	198
	ethylbenzene	106	136.2	7	152
ALIPHATIC COMPOUNDS	methane	16	-161	gas	24
	ethane	30	-88.6	_	60.4
	n-propane	44	-42.1	_	_
	n-butane	58	-6.2	1823	61
	n-pentane	72	30	430	_
	n-hexane	86	68.7	120	9.5
	n-heptane	100	98.4	35	3
	n-octane	114	125.5	11	0.66
	trimethyl-pentanes	114	99	_	0.56
OXYGENATED ADDITIVES	methanol	32	64.7	92	miscible
	ethanol	46	78.5	43.9	miscible
	methyl-t-butylether	88	252	252	miscible

Table 1.2: Twenty major components of API PS-6 unleaded gasoline (American Petroleum Institute, Washington D.C., 1988)

COMPONENT	Percent Weight (API, 1985)	Aqueous Solubility (mg/L)
2-methylbutane	8.72	49.6
m-xylene	5.66	185
2,2,4-trimethylpentane	5.22	2.4
toluene	4.73	554
2-methylpentane	3.93	15.7
n-butane	3.83	61.4
1,2,4-trimethylbenzene	3.26	57
n-pentane	3.11	47.6
2,3,4-trimethylpentane	2.99	2.3
2,3,3-trimethylpentane	2.85	2.6
3-methylpentane	2.36	17.9
o-xylene	2.27	175
ethylbenzene	2	161
benzene	1.94	1780
p-xylene	1.72	156
2,3-dimethylbutane	1.66	22.5
n-hexane	1.58	12.4
1-methyl,3-ethylbenzene	1.54	40
1-methyl,4-ethylbenzene	1.54	40
3-methylhexane	1.3	5

1.2: State of the Art

The discussion in the previous section (Section 1.1) shows the need to quantify oxygenates in gasoline. First of all, there is a need to quantify them during the blending of gasoline for quality assurance and process control purposes. Second, there is a need to quantify them during the delivery of gasoline, for example at gasoline stations, to check the accuracy of blenders' claims (e.g., consumers' associations, regulatory agencies), and also to check for possible contaminations [52].

The main problem encountered in performing a gas chromatographic analysis of oxygenates in gasoline is the coelution of aliphatic compounds with oxygenates, which leads to difficult quantification.

There have been several approaches taken to quantify oxygenates in gasoline, either using chromatographic techniques, or using other types of techniques, like spectroscopy. The chromatographic approaches can be subdivided into three main categories, based on the way they try to solve the coelution problem. Namely there are:

- approaches using two or more columns [16,52,59];
- approaches using a selective detector for oxygen containing compounds [10,11,12,18,43];
- approaches using an extraction step prior to chromatographic analysis [1,26,34].

The first two classes of approaches present the main problem of requiring specific instrumentation.

The standard test method for quantification of low molecular weight alcohols (such as methanol and ethanol) and MTBE in gasoline is the ASTM-D4815. This method uses two columns and a column switching valve [59]. The sample first goes through a polar column in order to eliminate the light non polar compounds (these go to vent). Then the valve is switched in order to have the remainder of the sample go through the second column and be measured. This column is non polar, so that alcohols and MTBE elute before the heavier hydrocarbons. Finally, the valve is switched back to its original position to backflush the heavy hydrocarbons. This is a complicated method and it requires specific hardware.

The ASTM method is one of the two methods currently used by the EPA for quantification of alcohols in gasoline [52]. The other method uses a water extraction step in order to eliminate hydrocarbon interferences, followed by chromatographic analysis of the water sample. Calibration standards are used, along with an internal standard (isopropanol) added to the gasoline before the extraction step, in order to quantify the amount of alcohols in gasoline [52].

Frysinger and Gaines [16] have quantified oxygenates using two-dimensional gas chromatography. Two columns are used in order to get better resolution. The first column separates compounds based on their volatility, while the second one separates compounds based on their polarity. The chromatogram obtained is a 2-D retention time plane with analytes organized by volatility and polarity properties.

Kanai *et al.* [26] have analyzed MTBE, ETBE, and TAME in gasolines by GC/MS. They used an acetonitrile (ACN) extraction step to remove hydrocarbon interferences. They mixed ACN with gasoline in a separatory funnel, and shook the mixture for 5 minutes. Three layers formed after the addition of saturated sodium chloride: a top hydrocarbon layer, a middle ACN layer (containing most of the ethers), and a bottom aqueous layer. The top and bottom layers were discarded. The middle layer was passed through a disposable pipette fitted with glass wool to remove any residual water. Then the sample was heated for 25 minutes to eliminate the small amounts of hydrocarbons present. The volume of the final sample was measured and the sample analyzed by GC-MS. They used an internal standard to quantify the ethers; their interference removal technique was successful in removing the hydrocarbon interferences, however it led to a very poor recovery (12% recovery).

Agarwal [1] used diethylene glycol to extract low molecular weight alcohols from gasoline in order to quantify them by GC, by eliminating hydrocarbon interferences. He used propanol as an internal standard. His method had the disadvantage of using an organic solvent.

Pauls and McCoy [34] used a water extraction step before a GC analysis using a packed column and isopropanol as an internal standard. The disadvantage of their method is the introduction of water inside the GC column, which results in a shorter column lifetime.

Among the approaches using oxygen selective detectors, Verga *et al.* [43] and Di sanzo [12] used an oxygenates FID (O-FID) analyzer. Diehl *et al.* [11] used an atomic emission detector (AED) on a GC instrument. Diehl *et al.* [10] used a Fourier transform infrared (FTIR) spectroscope as a GC detector. Goode and Thomas [18] used a microwave-induced plasma (MIP) GC detector. These approaches all require chromatographic instrument modification.

Finally, some non-chromatographic methods have also been used to quantify oxygenates in gasoline. Choquette *et al*. [8] used Fourier transform near-infrared and Fourier transform raman spectroscopy. They showed that their technique was capable of quantifying four common oxygenate additives (MTBE, ETBE, TAME, and EtOH) in single-oxygenate gasoline mixtures, however they could achieve accurate quantification

only in well known and fixed neat-fuel composition. Sarpal *et al.* [40] have analyzed oxygenates in gasoline using ^{13}C NMR spectroscopy. Skloss *et al.* [42], Kalsi *et al.* [25], and Meusinger [32], have used ^{1}H NMR to analyze oxygenates in gasoline. Fodor *et al.* [13] and Iob *et al.* [23] have used FTIR spectroscopy.

A different approach to eliminating hydrocarbon interferences consists in using solid phase microextraction (SPME). The details of SPME will be discussed in the following chapter (Chapter 2). However, SPME uses a fiber for extracting analytes and this could be helpful in filtering some of the hydrocarbons. Gorecki *et al.* [20] have analyzed methanol, ethanol, and 2-propanol in unleaded gasoline and water using SPME. They used a custom made polar fiber, coated with Nafion perfluorinated resin. This fiber extracts analytes by adsorption and allowed good quantification of MeOH, but did not allow good quantification of ethanol and 2-propanol in water. Their work does not explain the details of the technique and only proves detection but no quantification of either MeOH or EtOH. They observed a non-linear response of analyte amounts extracted with this fiber at long sampling times. Indeed, since the coating surface has a limited number of adsorption sites, analytes with a lower affinity for the fiber are eventually displaced by the other analytes. They achieved better linearity by using two different experimental settings. The first one consisted in using a short extraction time with vigorous stirring; the second one consisted in using an extraction time for which some analytes did not reach equilibrium, with no stirring.

In this work we will quantify the amount of EtOH in gasoline using a combination of a water extraction step along with SPME-GC analysis. Our proposed method does not require specific instrumentation like in the multiple columns [16,52,59] and selective detector [10,11,12,18,43] cases. It also eliminates the use of organic solvent like in [1] and [26], and avoids the insertion of water inside the GC (detrimental to the column) like in [34].

In the following chapter we will provide some background information about SPME, and in Chapter 3 we will describe the experimental setup and methods. In Chapter 4 we will discuss our results, and finally we will conclude our work in Chapter 5.

CHAPTER 2 - SOLID PHASE MICROEXTRACTION

2.1 Introduction

Sample preparation is often a long and tedious process, and a time limiting factor in the analysis of compounds. Indeed, on average, two-thirds of the analysis time in chromatography is spent on sampling and sample preparation steps and only one-third on the analysis itself! Moreover, 90% of high performance liquid chromatography (HPLC) and gas chromatography (GC) users use two or more preparation techniques per sample. Therefore, it is important to minimize sample preparation time and optimize the efficiency of those steps. Solid Phase MicroExtraction is a quick sample preparation technique, where usually no other sample preparation step is required, hence minimizing the sample preparation time and the chance for error.

In the remainder of this chapter, we describe in detail the SPME technique (Section 2), the theory (Section 3) and the fibers (Section 4).

2.2 Technique

SPME is a recent technique, invented by Pawliszyn in 1989 [6] and available commercially since 1994. A fiber is used to extract small amounts (ppm, ppb levels) of analytes from a solution, usually water. This technique is composed of two steps [31]. First, an extraction step (illustrated in Fig. 2.1), where analytes get sorbed onto the fiber and extracted from the solution or the headspace. Then, a desorption step (shown in Fig. 2.2), during which analytes are thermally desorbed into a heated GC injection port.

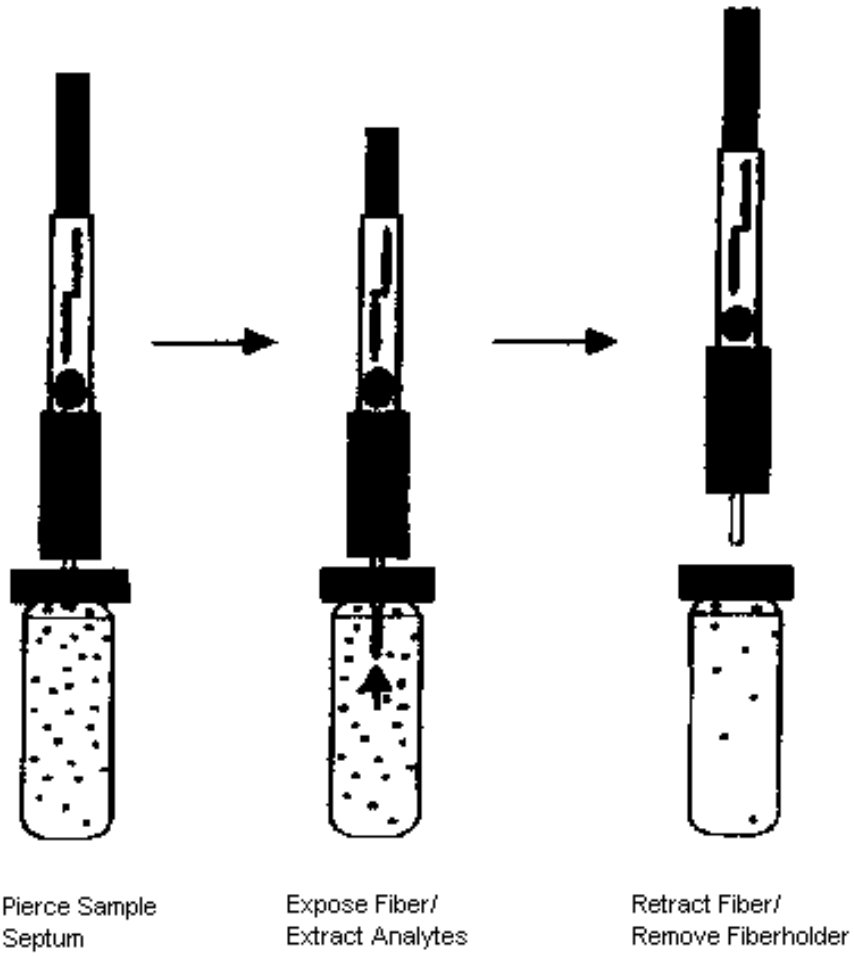

Fig. 2.1: Extraction step

The extraction step can be subdivided into three substeps. First, the sample vial septum is pierced by a septum piercing needle. Since the fiber is very fragile, the purpose of the septum piercing needle is to protect the fiber. After the septum is pierced, the fiber is exposed to the solution, either directly (i.e. direct sampling) or in its gas phase (i.e. headspace sampling). This allows the analytes from the solution to diffuse into the fiber. After a fixed amount of time the fiber is retracted inside the septum piercing needle, and the fiber holder (Fig. 2.3) is removed from the solution.

Click here to see an animation of the extraction step (28.6KB)

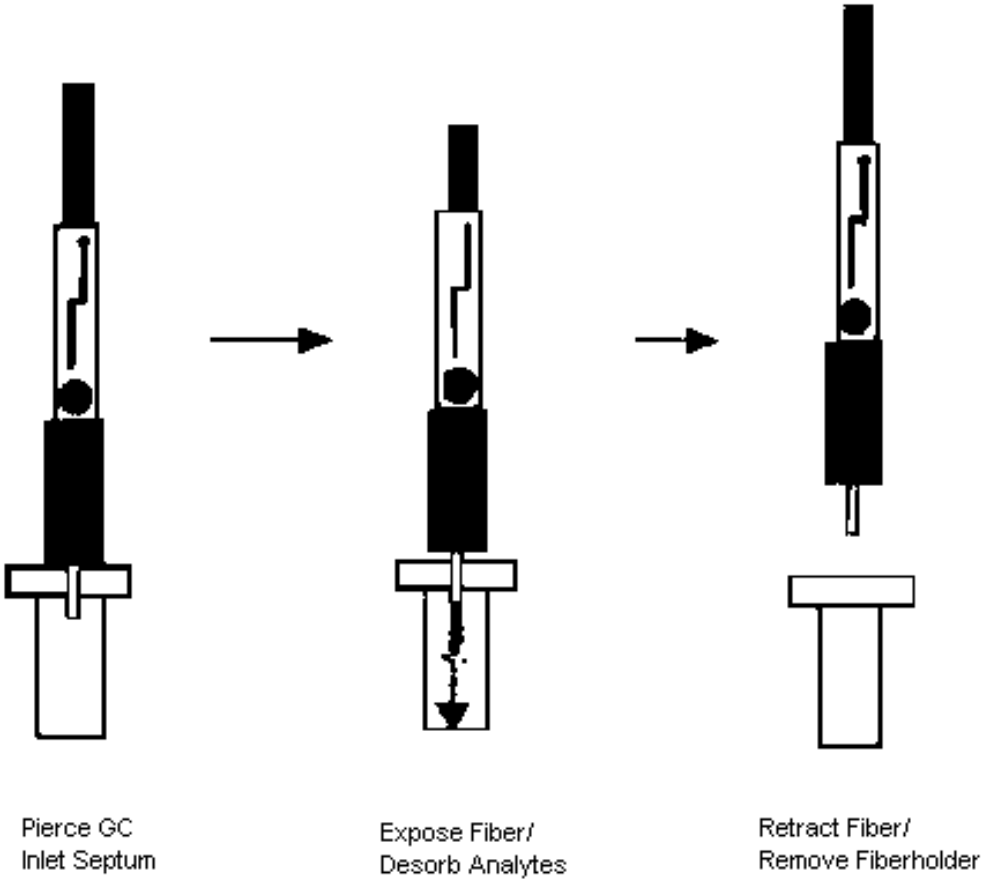

Fig. 2.2: Desorption step

The desorption step is also composed of three substeps. First, the GC inlet septum is pierced with the septum piercing needle. Then the fiber is exposed to the hot GC injection port, where the analytes are thermally desorbed. The fiber is left in the GC for a few minutes in order to allow complete desorption and cleaning. The fiber is finally retracted inside the septum piercing needle and the fiber holder is removed from the GC injection port.

Click here to see an animation of the desorption step (43.6KB)

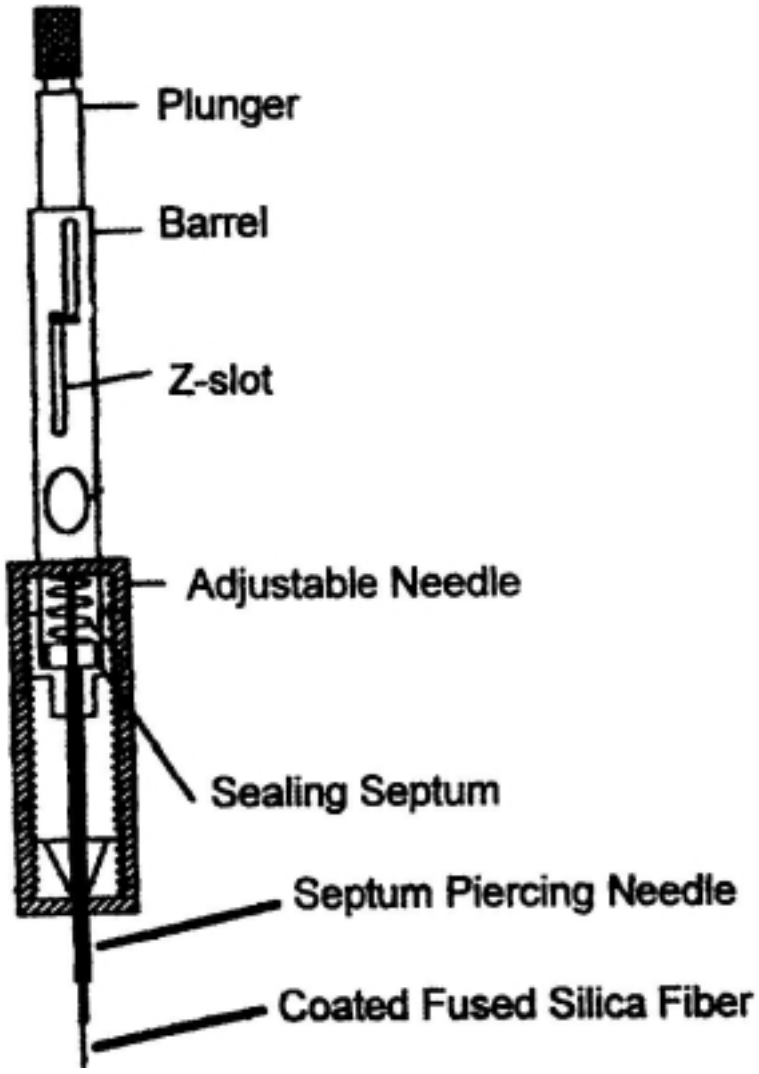

Fig. 2.3: Scheme of SPME assembly

SPME offers many advantages over other sample preparation techniques [36,48,64]:

- it is organic solvent free;
- it is low cost (in the order of hundreds of dollars);
- it is highly sensitive (analytes down to the ppm, ppb, and sometimes ppt levels can be detected [37]);
- it uses short extraction time (in the order of minutes);
- it is easy to use;

- it often does not require any other sample preparation step;
- it can easily be automated;
- it allows field sampling: sample the analytes on-site with a portable field sampler, then bring the capped fiber back to the lab for the actual analysis.

However there are two main disadvantages to this technique:

- it is limited to aqueous samples;
- it cannot be used for highly concentrated analytes.

SPME was originally used for trace analysis of impurities in water [4,5,7,24,30,31,36,37,]. Lately it has also been used in pharmaceutical, environmental, foods and flavors, forensic, and toxicology applications [36,48,64]. Most work has been done with hydrophobic (non polar) analytes, extracted using a polydimethyl siloxane fiber (PDMS; non polar fiber, most widely used). Since very little work has been done with polar analytes [20], the novel approach of this work consists in extracting polar analytes (MeOH, EtOH).

2.3 Theory

Two mechanisms are possible, according to the nature of the fiber. If the fiber is a liquid phase, the analytes are extracted by absorption; if the fiber is a porous particle blend, the analytes are extracted by adsorption. Absorption is a non-competitive process where analytes dissolve into the bulk of the liquid, whereas adsorption is a competitive process where analytes bind to the surface of the solid [19]. In the adsorption case, there is a limited number of sites where analytes can bind to. When all the sites are occupied, the fiber is saturated. Therefore the linear range of adsorption-type fibers is smaller than the one for absorption-type fibers. In a competitive process, analytes of higher affinity for the coating can displace analytes of lower affinity for the fiber.

In this section we will explain some of the theory behind the use of SPME. We will first start by analyzing the equilibrium process (thermodynamics) [35], and then consider the dynamics that lead to equilibrium (kinetics) [2]. The thermodynamic and kinetic expressions are derived for the absorption mechanism only. The thermodynamic

expression for most of the adsorption-type fibers is similar to the one for absorption-type fibers, and the same conclusion is valid, if a sufficiently dilute solution is used. The carboxen/PDMS fiber is an exception, and no extraction model has been developed for it so far [19]. Indeed, this fiber has pores small enough to cause capillary condensation, which can result in a higher extraction capacity of the fiber for some analytes [19]. However if the analytes concentrations are low enough, capillary condensation is negligible [19].

2.3.1 Determination of amount of analyte extracted at equilibrium (thermodynamics)

Let's consider the following three phases, shown in Fig. 2.4 (direct sampling mode), and Fig. 2.5 (headspace sampling mode):

- fiber coating (*f*), with volume V_f;
- gas phase, or headspace (*h*), with volume V_h;
- homogeneous matrix (e.g. pure water) (*s*), with volume V_s.

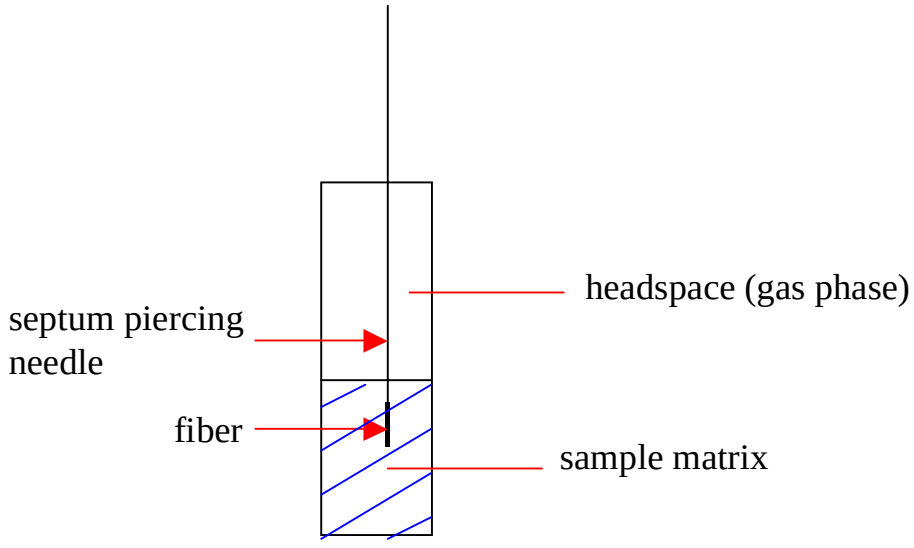

Fig. 2.4: Direct sampling

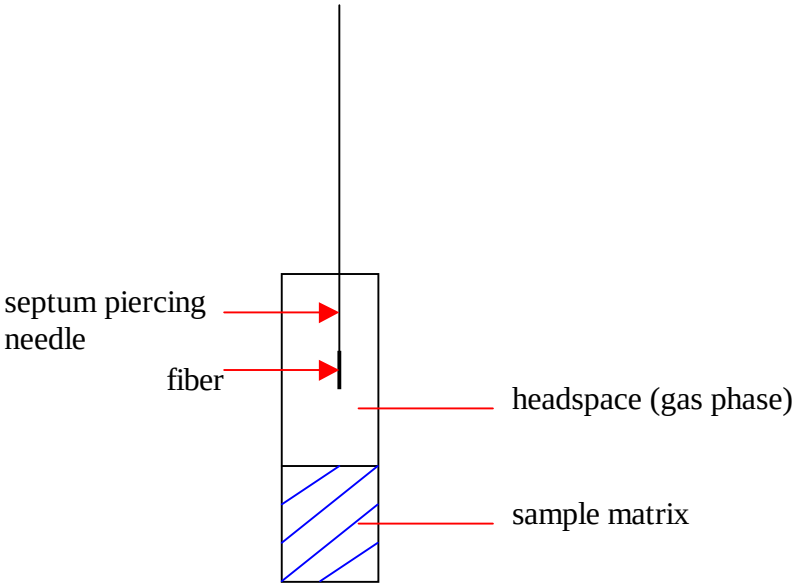

Fig. 2.5: Headspace sampling

Determination of coating volume:

A fused silica solid fiber is coated with a thin film of sorbent. The coating having a cylindrical shape, its volume can be calculated using the formula for a cylindrical section. Therefore, the volume of the fiber is: $V_f = \pi\left(R^2 - r^2\right)h$

where: R = radius of coated fiber

r = radius of uncoated fiber

h = length of the fiber

coating thickness = $R - r$

Example: A carboxen/PDMS fiber, which has an 85 μm thick and 1 cm long coating, on a fused silica rod of 110 μm internal diameter, would lead to a 0.5 μL volume for the sorbent phase.

As long as the three volumes (fiber coating, headspace, and homogeneous matrix volumes) are constant, the amount of analyte extracted is independent of the location of the fiber in the system (headspace or directly in the sample) at equilibrium [35,36].

If we assume there are no losses (i.e., biodegradation or adsorption on walls of sampling vessel), then mass is conserved, therefore the number of moles is conserved, and the following equation can be written [35]:

$$C_0 V_s = C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s \quad (1)$$

where:

- C_0 is the initial concentration of the analyte in the matrix;
- C_f^{∞}, C_h^{∞}, and C_s^{∞} are the equilibrium concentrations of analyte in the fiber, headspace, and solution (matrix) respectively.

The mass of analyte sorbed by the coating at equilibrium is:

$$n^{\infty} = C_f^{\infty} V_f \quad (2)$$

Multiplying and dividing the right side of Eq. (2) by $C_0 Vs$, we obtain:

$$n^{\infty} = \frac{C_f^{\infty} V_f C_0 V_s}{C_0 V_s} \quad (3)$$

Replacing the denominator with the right term of Eq. (1), we get:

$$n^{\infty} = \frac{C_f^{\infty} V_f C_0 V_s}{C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s} \quad (4)$$

Dividing both the numerator and denominator by C_s^{∞}, we obtain:

$$n^{\infty} = \frac{\frac{C_f^{\infty} V_f C_0 V_s}{C_s^{\infty}}}{\frac{C_f^{\infty} V_f}{C_s^{\infty}} + \frac{C_h^{\infty} V_h}{C_s^{\infty}} + V_s} \quad (5)$$

Let's now define two partition coefficients that express the proportion of analyte at equilibrium between two of the three phases:

1- Sample-coating partition coefficient: $K_{spme} = C_f^{\infty} / C_s^{\infty}$

2- Sample-headspace partition coefficient: $K_{hs} = C_h^{\infty} / C_s^{\infty}$

Note that a third partition coefficient (coating-headspace) could be defined, but it would be dependent on the two previously defined partition coefficients.

Substituting these partition coefficients into Eq. (5), we get:

$$n^{\infty} = \frac{K_{spme} V_f C_0 V_s}{K_{spme} V_f + K_{hs} V_h + V_s} \quad (6)$$

Let's consider two cases: first the case where there is some headspace; second the case where there is no headspace.

Case 1: There is headspace

Since V_f is very small (μL), generally $K_{spme}V_f << V_s$, Eq. (6) can be written as:

$$n^{\infty} \cong \frac{K_{spme} V_f C_0 V_s}{K_{hs} V_h + V_s} \quad (7)$$

Dividing the numerator and denominator by V_s, we get:

$$n^{\infty} \cong K_{spme} V_f \frac{1}{1 + K_{hs} \frac{V_h}{V_s}} C_0 \quad (8)$$

Note that the amount of analyte extracted at equilibrium by absorption is proportional to C_0 and is dependent on the sample, headspace, and coating volumes.

Case 2: Assuming no headspace:

In the case there is no headspace (V_h = 0), Eq. (8) becomes:

$$n^{\infty} = K_{spme} V_f C_0 \quad (9)$$

This equation shows that the amount of analyte extracted (n) at equilibrium by absorption, by direct sampling and in the absence of headspace, is independent of the volume of the sample matrix (V_s), and depends only on the initial analyte concentration (C_0) and coating volume (V_f). This is very important, as it implies that it is not necessary to sample a well defined volume of the matrix, which therefore allows easy field sampling.

The same conclusions are valid for the adsorption process if the solution is dilute enough.

2.3.2 Dynamic process (kinetics) of direct SPME

The amount of analyte extracted by the fiber, by direct sampling, is an increasing function of time, as follows [2]:

$$n = n^{\infty}[1 - e^{-t/\tau_s}] \tag{10}$$

where: n^{∞} is the amount of analyte extracted at equilibrium, given by Eq. (9); and τ_s is the time constant for direct sampling. This latter variable is a characteristic time of the equilibrium process: the smaller the time constant the faster the equilibrium is achieved. The time constant is dependent on mass transfer coefficients of the analyte in the sample matrix and the polymer film, on sample and fiber volumes, on fiber-coating coefficient, and on the surface area of the fiber coating. This time constant is directly related to the sampling time needed to get the desired recovery percent. As we can see in Table 2.1, extraction times higher than three time constants yield recovery percents of at least 95%.

Table 2.1: Recovery percents for different sampling times

t	Recovery %
τ_s	63.2
$2\tau_s$	86.5
$3\tau_s$	95.0
$4\tau_s$	98.2
$5\tau_s$	99.3
$6\tau_s$	99.8

When the extraction time t reaches infinity (equilibrium conditions), the exponential term reaches zero, and the amount extracted is equal to the amount extracted at equilibrium. When t is held constant, the amount extracted is proportional to the amount extracted at equilibrium, and hence is proportional to the initial concentration of the analyte in the sample matrix. Thus, in theory, it does not matter what sampling time is used, as long as the same sampling time is used for a determined set of

experiments. In practice, however, if the sampling time is too short, then a small error in time measurement would lead to a large error in analyte amount extracted (high curve slope). Therefore, in practice, it is better to choose a sampling time close to the equilibrium condition, where the slope of the extraction time curve would start approaching zero.

2.3.3 Dynamic process (kinetics) of headspace SPME

Headspace sampling involves two mass transfers which determine the speed of extraction of the analytes by the fiber:

- the mass transfer at the condensed/ headspace interface
- the mass transfer at the headspace/ polymer interface

Case 1: Mass transfers are equal (steady state mass transfer)

The amount of analyte extracted as a function of time can be expressed as [2]:

$$n = n^{\infty}[1 - e^{-t/\tau_h}] \tag{11}$$

Like previously, n^{∞} is the amount of analyte extracted at equilibrium as given by Eq. (8), and τ_h is the time constant for the headspace sampling mode. The time constant now also depends on the evaporation constant of the solution. The same conclusions can be reached as for the direct sampling mode.

Case 2: Mass transfers are not equal (non-steady-state mass transfer)

The amount of analyte extracted as a function of time can be expressed as the sum of two exponential terms [2]:

$$n = \alpha[1 - e^{-t/\tau_1}] + \beta[1 - e^{-t/\tau_2}] \tag{12}$$

The time constant τ_2 depends only on the analyte diffusion rate in the polymer film. The time constant τ_1 depends on both the analyte evaporation into the headspace and the analyte diffusion into the polymer phase. The coefficients α and β are both

proportional to C_0, thus the analyte amount extracted is proportional to the initial concentration of analyte in the solution, as long as the extraction time is held constant. Hence, the same conclusion about the selection of a sampling time is achieved here.

2.4 Fibers

Since the fiber (coating) is the "heart" of the extraction, it is very important to select the right fiber for the desired application. The fiber coating should be selected based on film thickness and polarity [64].

The film thickness affects both speed and capacity. As film thickness increases, film capacity is increased and speed is decreased. A film that is too thick may induce carry-over of analytes from one sample to another. In today's world, most of the time, the fastest extraction would be wanted, meaning that the preferred choice for a fiber would be one with a thin film. However, using a fiber with a thin film would not be good if the fiber is not selective enough for the analytes of interest, and/or if the fiber has a higher selectivity for other analytes (of non-interest). Therefore, in order to determine what film capacity is wanted, we need to also take into account the amount of analytes of non-interest that may have a high affinity for the fiber. Hence, a thin film is best for analytes which have a significant affinity for the fiber (high fiber-coating partition coefficient), whereas a thicker film would be preferred for other analytes.

The polarity of the fiber influences its selectivity according to the principle of "like prefers like": polar analytes are better extracted with a polar fiber, whereas non polar analytes are better extracted with a non polar fiber.

Different coatings are available commercially in different thicknesses and polarities, and the best combination of these latter needs to be determined according to the coatings available on the market. The presently available coatings are either liquid phases or porous particle blends. Supelco (State College, PA) has exclusive patent rights for the sale of SPME fibers.

Liquid phases extract analytes by absorption, which is a non-competitive process. Therefore the matrix composition does not affect the amount of analytes extracted, and the linear range is broad [19]. These phases include Polydimethylsiloxane (PDMS), Polyacrylate (PA), and Carbowax (CW). The PDMS phase is the first and most widely used fiber. The PDMS phases are non polar and are the most commonly used due to their versatility and durability. They are available in three film thicknesses: 100, 30, and 7 μm. The PA phase is polar. At room temperature, it is not a liquid but a solid or "glass" phase. The diffusion of the analytes in and out of the coating is slower, hence the equilibration times are longer and the desorption temperature needs to be higher. The CW phase is polar and water soluble. In order to reduce its water solubility it must be crosslinked.

Porous particle blends extract analytes by adsorption, which is a competitive process. Since there are a limited number of sites where analytes can bind to, analytes of lower affinity for the coating can be displaced by analytes of higher affinity for the coating. Therefore it is important to work at low analyte concentrations. The porous particle blends have different pore sizes, and extract analytes based on their size. These particle blends can be placed into three categories: micro-pores (< 20 A), meso-pores (20-500 A), and macro-pores (>500 A). The carboxen coating consists of mostly micro-pores, the divinylbenzene one consists mostly of meso-pores, and the templated resin one consists mostly of macro-pores.

Stability of fiber coating:

If a fiber is improperly used, its coating may get stripped off, resulting in an inefficient fiber with no more ability to extract analytes. The stability of the fiber coating is determined by its physical attachment to the fused silica core [64]. Less stable coatings can swell and dissolve in the presence of polar solvents or high temperatures. Nonbonded coatings have no crosslinking agents and are therefore the least stable. Crosslinked coatings have crosslinking agents (such as vinyl groups) which interact with each other to form a more stable film, however they are not bonded to the fused silica core. Finally, bonded coatings are the most stable because they not only

have crosslinking agents which interact with each other but they also are bonded to the fused silica core (silanol bonds).

CHAPTER 3 - EXPERIMENTAL SETUP AND METHODS

3.1 Instrumentation

For the analysis and quantification of alcohols, we used a Hewlett Packard Model 5890 gas chromatograph, equipped with a flame ionization detector (FID) (shown in Fig. 3.1). In order to confirm peak identities, we used a HP Model 6890 gas chromatograph, equipped with a mass selective detector HP Model 5973 (illustrated in Fig. 3.2). Finally, for the sample preparation by SPME, we used a Supelco fiberholder (shown in Fig. 3.3).

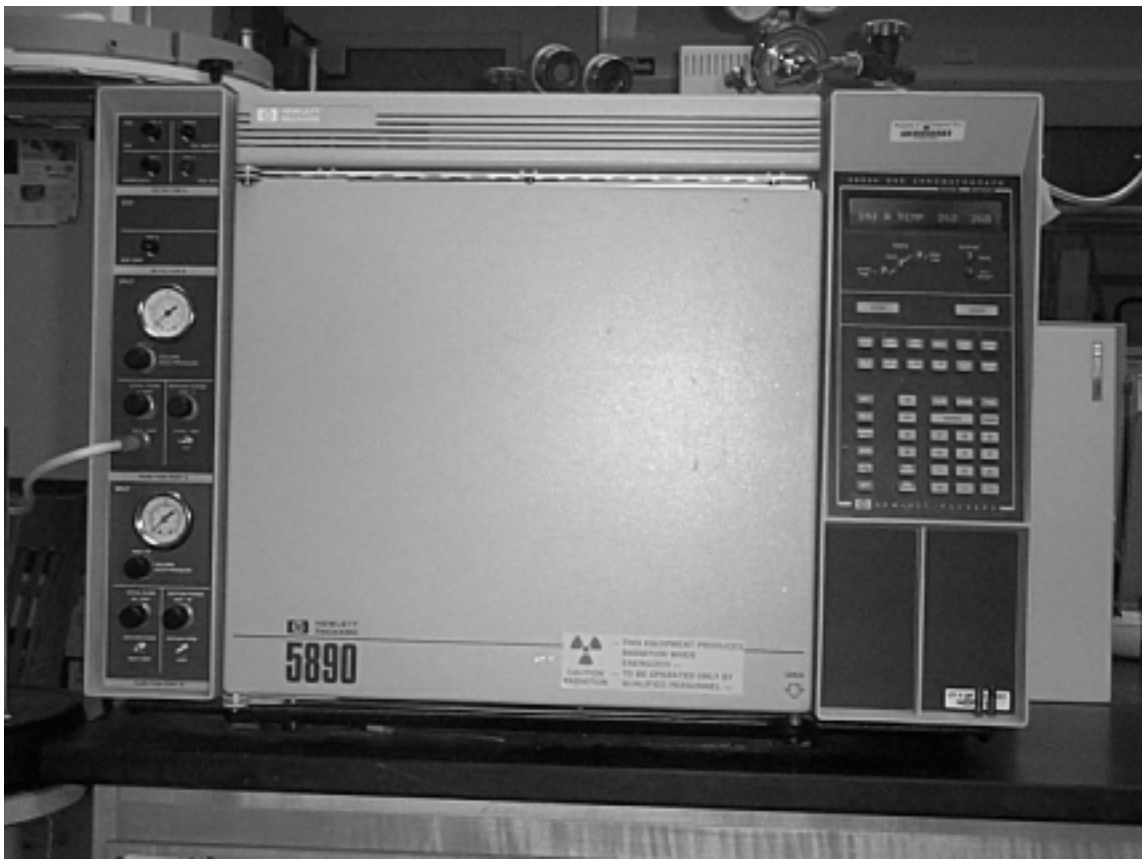

Fig. 3.1: HP-5890 GC

Fig. 3.2: GC-MS 5973, HP-6890

In the remainder of this chapter, we describe in detail the sample preparation steps (Section 2), the GC analysis conditions (Section 3), and the data analysis techniques that were employed (Section 4). Finally, Section 5 concludes the chapter with some remarks on salt addition.

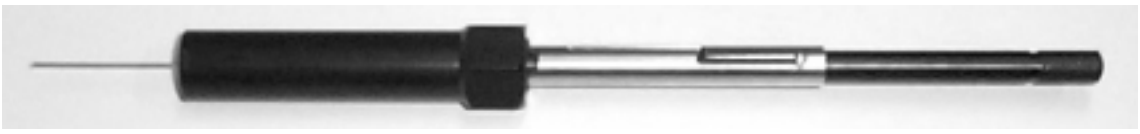

Fig. 3.3: Fiberholder

3.2 Sample preparation

3.2.1 Gasoline samples

Gasoline samples were obtained from a local gas station. In this area, oxygenates are not required to be added since this is not a high pollution area. Indeed, due to current gasoline and oxygenates prices, adding these to the gasoline would increase the cost of making gasoline. Premium fuels may contain MTBE to increase the octane number. Only regular unleaded gasoline samples will be used for this quantification study, focused on the quantification of ethanol. Since the gasoline samples do not contain any ethanol, we will make our own sample, containing 6.6 weight % EtOH (5.8 volume % EtOH), which corresponds to the 2 weight % oxygen required by the Clean Air Act Amendments. The volume % of EtOH and MTBE required to obtain 2 weight % and 2.7 weight % oxygen containing gasolines are given in Table 3.1. Densities of ethanol and gasoline are given in Table 3.2, where the density of gasoline has been determined by weighing a specific volume of gasoline. All the calculations used to convert volume % oxygenates to weight % oxygenates are shown in detail in Appendix A. We used anhydrous EtOH to prepare our "oxygenated" gasoline sample. We assumed that the molecular interactions between any two mixing compounds are negligible, which means that we consider the volumes additive (i.e., the total volume is equal to the sum of the individual volumes). We also assumed that the temperature change across experiments is negligible.

Table 3.1: Relation between oxygenate amounts and volumes

Oxygenate	Wt. % Oxygen	Vol. % Oxygenate
EtOH	2.0	5.8
	2.7	7.8
MTBE	2.0	11
	2.7	14.8

Table 3.2: Densities at 25 °C

Compound	Density (g/mL)
EtOH	0.7760
gasoline	0.6752

3.2.2 Mixing procedure

As mentioned in Chapter 1, it can be difficult to quantify oxygenates in gasoline by simple gas chromatography, due to hydrocarbon interferences with the oxygenated additives. As can be seen in Table 3.3, gasoline is composed of about 48.9 % aliphatics and 48.6 % aromatics, with about 94.5 % of the aromatics and only 1.3 % of the aliphatics being water soluble. Therefore, most of the aliphatic compounds (and also some aromatic compounds) can be left behind by extracting them with water. This is the approach that will be used here. It is similar to the one used by Pauls and McCoy [34], who used a water extraction step before a GC analysis. Their method has the problem of introducing water into the GC, which is detrimental for the selected column.

In this section we will describe the procedure of extraction and how to obtain the diluted solution that will be analyzed by SPME-GC.

Table 3.3: Regular unleaded gasoline water solubility

	% wt. Alkanes(enes)	**% wt. Aromatics**
Neat Gasoline	48.9%	48.6%
Water Soluble Fraction	1.3%	94.5%

The mixing procedure consists of five steps:

1- Mix 2 mL of gasoline with 2 mL of HPLC grade water

2- Shake well for 1 minute

3- Wait 4 minutes, until phase separation occurs

4- Discard the (top) gasoline layer

5- Take 10 μL of aqueous layer and dilute to 100 mL with HPLC grade water

An original 6.6% EtOH solution would be diluted to 6.6 ppm using that procedure.

3.2.3 SPME conditions

The following conditions have been used:

- Fiber: Carboxen-PDMS
- Sampling type: Direct sampling in water
- Extraction time: 10 minutes with stirring
- Desorption time: 10 minutes at 260 °C

Several fibers have been evaluated, however this was the fiber of choice since this was the one showing the least amount of interfering peaks. This also is the most polar fiber commercially available. Carboxen is a carbon molecular sieve, consisting of solid particles (2 to 10 μm thick) embedded in a PDMS phase. Its small pores allow separation of small analytes by retention in the pores. This is another interesting feature of this fiber since the alcohols of interest are relatively small (MeOH and EtOH molecular weights are 32 and 46 Daltons respectively).

Both direct and headspace sampling were considered. However, direct sampling is preferred due to better sensitivity.

The extraction time, *t*, has to satisfy the following equation, derived in Appendix B:

$$t \geq \tau \ln\left(\frac{\Delta t}{\varepsilon\tau} + 1\right)$$

where: Δt is the error in extraction time measurement; τ is the time constant of the extraction process; and ε is the maximum relative error in analyte amount extracted.

An extraction time of 10 minutes for direct sampling satisfies this equation and therefore was chosen for direct sampling. The next Chapter details an extraction time study in both direct and headspace sampling.

A desorption time of 10 minutes was experimentally chosen since it is long enough to avoid carry-over from one sample to another.

3.3 GC conditions

The following GC conditions were used:

- Column: HP-INNOWAX (crosslinked polyethylene glycol), 30 m long, with 1.0 μm film thickness and 0.53 mm i.d. This is a polar column.
- Oven temperature program: 65 °C for 4 min; program to 200 °C at 60 °C/min
- Injector temperature: 260 °C
- Detector (FID) temperature: 290 °C
- Operating mode: splitless, with purge valve open after 1 min
- Column headpressure: 2 psi, linear gas velocity: 41 cm/sec

Both MeOH and EtOH are polar and have relatively low boiling points (64.6 °C and 78.3 ^{o}C respectively). Therefore, a non polar column (such as DB-5) allows a fast analysis; however, it does not allow good resolution because of the alcohols' close boiling points. A polar column (such as HP-INNOWAX) will solve this problem, by allowing a higher retention of the alcohols in the column stationary phase. We used a HP-INNOWAX column, with a 30 meter length, a 1.0 μm film thickness, and a 0.53 mm internal diameter. A "fat" film, as well as a big internal diameter has been chosen, in order to obtain an even greater retention of the alcohols and therefore yield a better separation.

We initially used the following oven temperature program (later changed to the current temperature program). We started the oven temperature at 40 °C, held it for 3 minutes, then ramped the temperature up to 60 °C at 10 °C/min in order to separate the

two alcohols. Finally, we ramped the temperature up to 200 °C at 40 °C/min and held it at 200 °C for 10 minutes, in order to eliminate all the remaining gasoline components. This oven temperature program allowed good separation of methanol and ethanol. However, an unknown compound (which was later identified as benzene by GC-MS) was found to be interfering with the ethanol. In order to solve this interference problem and be able to quantify EtOH, we changed the temperature program to the following one. The temperature is first held constant at 65 °C for 4 minutes in order to allow a good separation of methanol and benzene. Then it is rapidly increased to 200 °C at a rate of 60 °C/min and held at 200 °C for 10 min, in order to eliminate the remaining gasoline compounds. Note that a rate of 60 °C/min will probably not be achieved, however this programming ensures that the remaining compounds will be eliminated as fast as possible. Moreover, our experimental results will not be affected by the actual rate. We now focus solely on the EtOH and ignore the MeOH. This is feasible since our original gasoline sample does not contain MeOH.

The injector temperature is set at 260 °C, which is also the fiber desorption temperature. The detector used is a flame ionization detector (FID), set at 290 °C.

The operating mode is splitless, with the purge valve open after 1 minute. A SPME liner (0.75 mm internal diameter) is used instead of the conventional splitless liner (2 mm internal diameter), in order to allow a faster flow rate through the liner. This allows the analytes to be more focused at the beginning of the column, therefore resulting in narrower chromatographic peaks.

Finally, the column headpressure is set at 2 psi, in order to have a flow rate through the column of 5.4 mL/min, corresponding to an average linear velocity of 41 cm/sec.

3.4 Data analysis

Two data analysis approaches are considered: the method of calibration curve (using calibration standards), and the method of standard addition.

3.4.1 Method of calibration curve

In the method of calibration curve, standard solutions with different alcohol concentrations are prepared in water. A calibration curve is then constructed, by plotting the detector responses (peak areas) versus the alcohol concentration. The linear portion of that curve will be used to find the alcohol concentration in an unknown sample. This method works well if the standard solutions are prepared in the same matrix as the actual samples. However, it may not be accurate in our case. Since the SPME of alcohols in gasoline from water is done in a slightly different matrix than the extraction of pure alcohols from water, the calibration curve may vary slightly. Moreover, there is the possibility of errors due to non-quantitative transfer in the mixing procedure. The method of calibration curve should be preferred whenever non-oxygenated gasoline of the same type of the one to be analyzed is available. Indeed, once the calibration curve is plotted, it can be used to analyze several gasoline samples. Only one measurement or one set of replicates is needed to quantify the ethanol amount in a desired gasoline sample. Therefore this method would be fast and very useful for quality control measurements.

3.4.2 Method of standard addition

The method of standard addition consists in spiking different amounts of alcohols in the oxygenated gasoline sample in order to obtain solutions with different alcohol concentrations. The detector response can then be plotted against the added concentration of alcohol. This is referred to as a standard addition curve (Fig. 3.4). The unknown EtOH concentration can be found by extrapolating the best fit line to the *x*-axis intercept. That intercept will be the unknown EtOH concentration. If the equation of the best fit line is written in the form $y = mx + q$, then the *x*-axis intercept is equal to the *y*-axis intercept (q) over the slope (m).

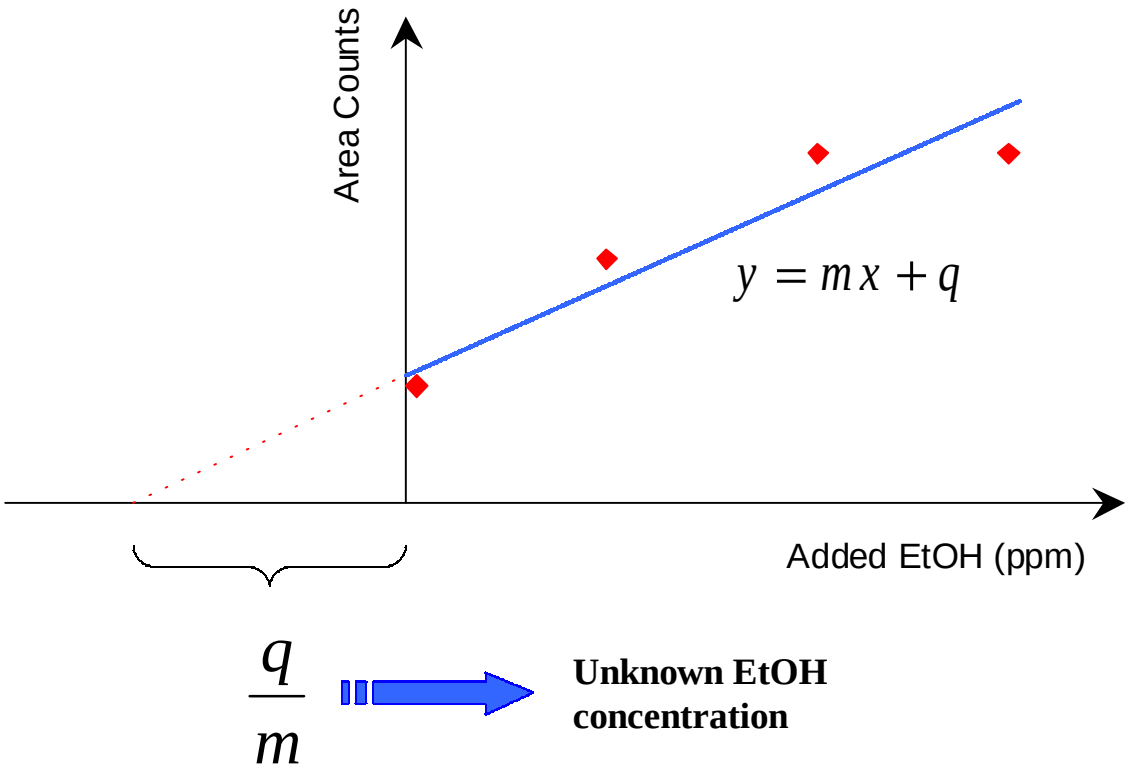

Fig. 3.4: Standard addition method

In this research, we spiked respectively 40, 80, 120, and 160 µL of EtOH in the 6.6 weight % EtOH gasoline solution, in order to get gasoline solutions of respectively 8.7, 10.7, 12.6, and 14.4 weight % EtOH. These solutions were then further extracted with water and diluted to the desired ppm amounts for analysis. The details of these computations are explained in Appendix A. This method is a little more time consuming than the previous one, since each gasoline sample analysis requires 4 to 6 measurements (original sample and spiked samples) or 4 to 6 sets of measurements. Therefore it would be good to use by the regulatory agencies, since these would be interested in analyzing gasoline samples of various composition. In the quality control case, however, where the gasoline samples contain the same amounts of different components, this method does not offer any major advantage over the first one, but is

more time consuming. Therefore, in this case, the first method would be the preferred one.

3.5 Salt addition

It is common, in some SPME applications, to add salt to an aqueous solution in order to reduce the solution's solvating power [36,48,64]. Hence, moderately water soluble compounds may be "salted out" and go into the headspace and/or the SPME fiber. In this case, adding salt to the solution has been tried and discarded. The salt, after a few samplings, can get onto the fiber and is difficult to be removed. Also there is an accumulation of salt in the liner, which implies that the liner needs to be taken out of the GC and cleaned often.

CHAPTER 4 - RESULTS AND DISCUSSION

4.1 Linearity curves

In order to verify the linear range of quantitative GC methods for methanol, ethanol, and methyl-tert-butyl-ether in water, linearity curves were experimentally determined and are shown in Figs. 4.1, 4.2 and 4.3 respectively. In these curves the blue points exhibit a close to linear behavior and therefore are used to fit the linear model, obtaining a very good R^2 value. On the contrary, the pink points indicate measurements significantly departing from linearity. The linearity ranges for the two alcohols and the ether were found to be much larger than what has been reported in the literature [41]. Indeed, using the carboxen/PDMS fiber for the analysis of C_1-C_8 alcohols and MTBE in water, linear ranges of respectively 10 ppb to 1 ppm and 1 ppb to 500 ppb were reported [41]. In this study we found the methanol curve to be linear between 14 and 229 ppm, the ethanol curve to be linear between 0.7 and 113 ppm, and the MTBE curve to be linear between 10 and 45 ppm. The two lowest MTBE concentrations we used were 40 ppb and 390 ppb; lower MTBE concentrations would need to be prepared and analyzed quantitatively in order to check for linearity at lower MTBE levels.

A simple GC injection of 2900 ppm MeOH, 2500 ppm EtOH and 1800 ppm MTBE in water, through a 4 mm i.d. splitless liner, was performed for peak area reference. The corresponding chromatogram (Fig. 4.4) showed very similar peak areas for the three analytes. A SPME-GC experiment was then performed using a solution of oxygenates in water that is 400 times more dilute than the one used for simple GC injection (in order not to saturate the fiber). The corresponding chromatogram (Fig. 4.5) showed significantly different peak areas for each of these oxygenates even though they were spiked into water at similar concentrations. The polar fiber is more selective for MTBE than for the alcohols. Indeed, MTBE is the least polar of these compounds, therefore it likes the water the least and has the highest sample-coating partition coefficient. Methanol, which is the most polar of these three oxygenates, likes to stay in

the water the most and therefore has the lowest sample-coating partition coefficient. Ethanol, which is more polar than MTBE, and slightly less polar than MeOH, has an intermediate partition coefficient, and therefore an intermediate peak area.

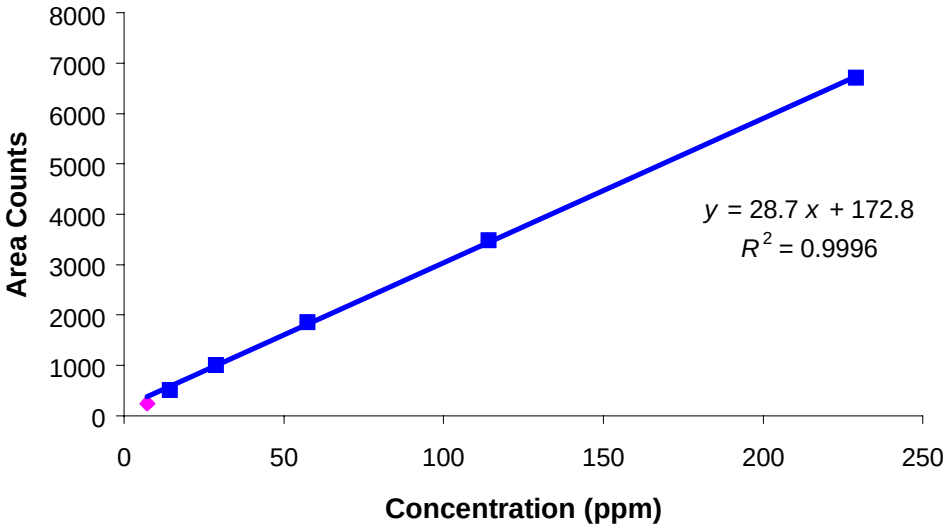

Fig. 4.1: Linearity curve for methanol (F.I.D)

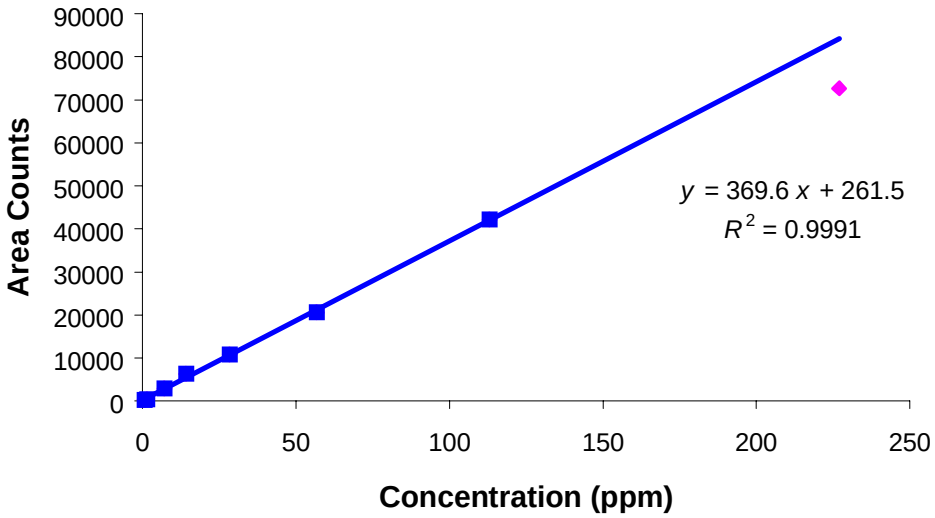

Fig. 4.2: Linearity curve for ethanol (F.I.D)

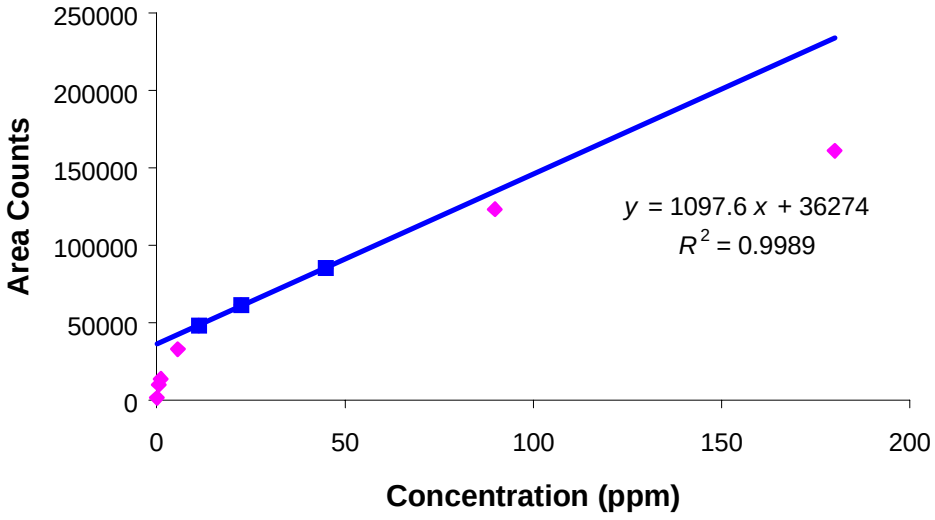

Fig. 4.3: Linearity curve for methyl-tert-butyl-ether (F.I.D)

Column: HP-INNOWAX, 30 m × 0.53 mm i.d. × 1.0 µm f.t.
Oven: 40 °C (3 min) to 62 °C (0 min) @ 10 °C/min
to 200 °C (10 min) @ 40 °C/min

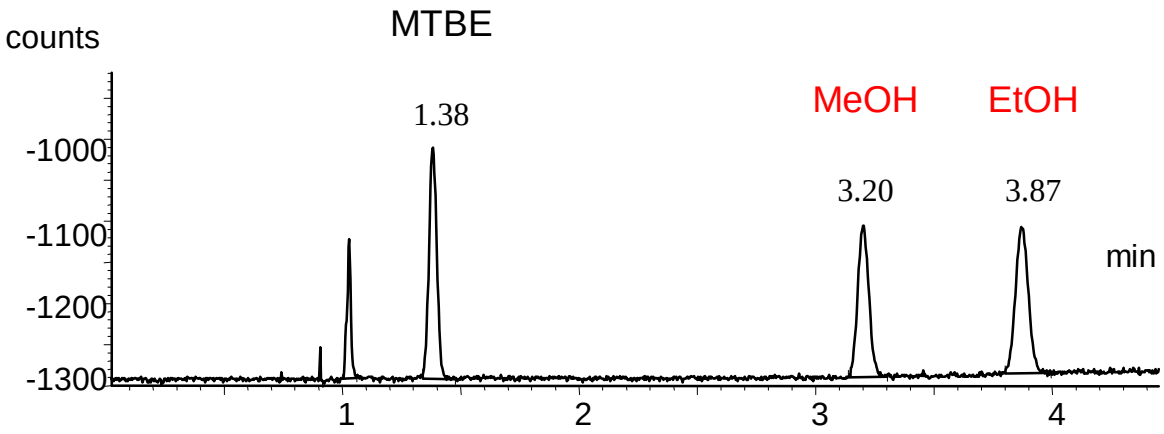

Fig. 4.4: GC of oxygenates spiked into water

Column: HP-INNOWAX, 30 m × 0.53 mm i.d. × 1.0 µm f.t.
Oven: 40 °C (3 min) to 62 °C (0 min) @ 10 °C/min
to 200 °C (10 min) @ 40 °C/min

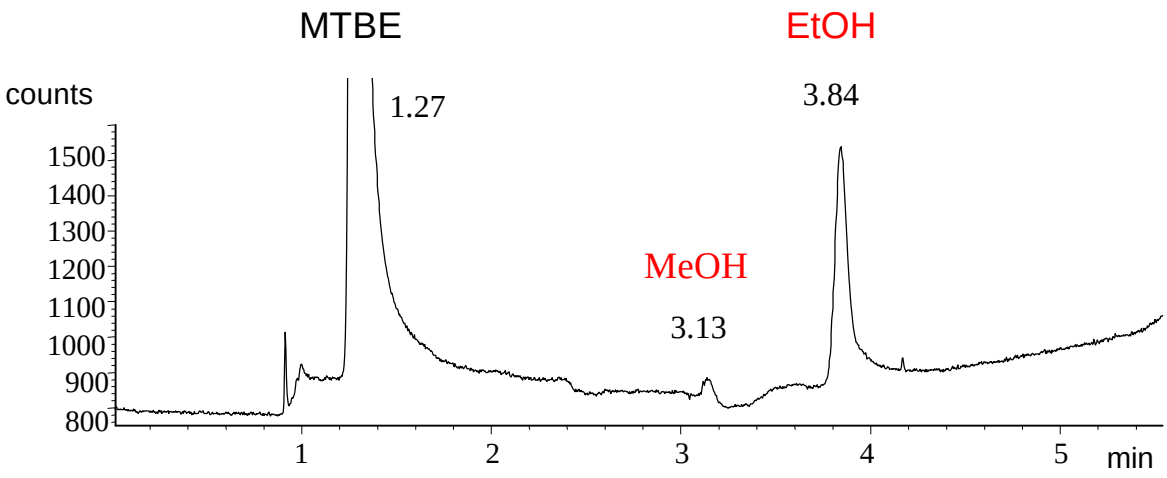

Fig. 4.5: SPME-GC of oxygenates spiked into water

4.2 Extraction time curves

The water extraction procedure was shown to be effective in eliminating interfering hydrocarbon peaks. Only the interfering benzene remains in the solution at our limits of detection. Selecting the right oven temperature program, as described in Chapter 3, allows us to obtain good separation of EtOH and benzene, as can be seen in Figs. 4.6 and 4.7. The chromatogram in Fig. 4.6 has been obtained using a 39 ppm EtOH in water solution, corresponding to a 5.7 weight % EtOH in the original gasoline stock solution. The EtOH and benzene peaks are well separated, and therefore easily quantifiable. In order to avoid fiber saturation, we decided to work with a more dilute sample. We chose a 4.3 ppm EtOH in water diluted sample, corresponding to a 6.2 weight % EtOH in the gasoline stock solution. As seen in Fig. 4.7, EtOH was detected, therefore our method is good for quantifying EtOH at these levels. Unfortunately, this EtOH concentration does not fall in the linear range of quantification, therefore there may be slight inaccuracies in the quantification of EtOH. However, a more dilute

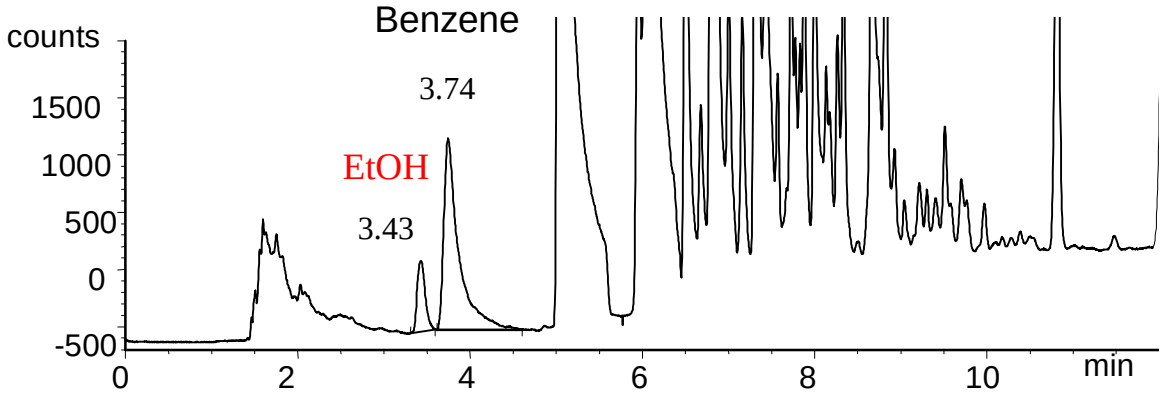

Fig. 4.6: SPME-GC of 39 ppm EtOH in the water extracted gasoline fraction

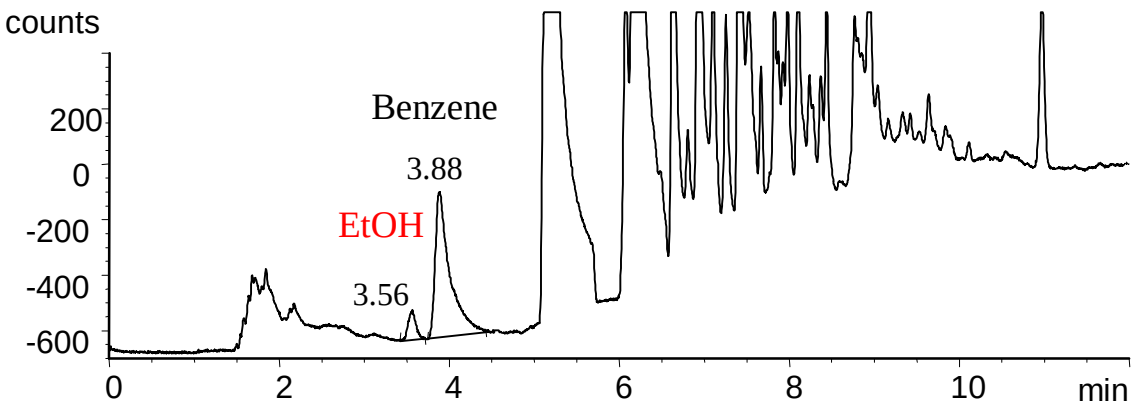

Fig. 4.7: SPME-GC of 4.3 ppm EtOH in the water extracted gasoline fraction

solution could not be used since the EtOH peak would have been smaller than the limit of quantification (LOQ).

As a first step in the analysis, we performed an extraction time study, that is we studied how the area counts for EtOH vary with different extraction times. Two extraction time curves were plotted, one by performing direct sampling experiments (Fig. 4.8), the other, by performing headspace sampling experiments (Fig. 4.9), both using a 4.5 ppm EtOH in water dilute solution. These two extraction time curves only show qualitative results, since the fiber used for the direct sampling study was stripped off before the headspace sampling study could be done. A different fiber had to be used, and therefore quantification was not possible.

As was shown in Chapter 2, it is not necessary to choose a sampling time close to equilibrium, since at any time the amount of analyte extracted by the fiber is directly proportional to the initial concentration of analyte in the solution. However, it is important to choose an extraction time where the slope is low in order to minimize the propagation of error, since a slight error in extraction time directly propagates into an error in area counts. The steeper the slope, the higher the error in area counts for a

given error in extraction time measurement. In the direct sampling case (Fig. 4.8), the amount of analyte extracted increases relatively quickly during the first five minutes. Then it levels out, until it is stable. In Appendix B, it is proven that, if the error in sampling time measurement is 5 seconds, the sampling time has to be at least 4.2 minutes. Using a conservative approach we chose a sampling time of 10 minutes.

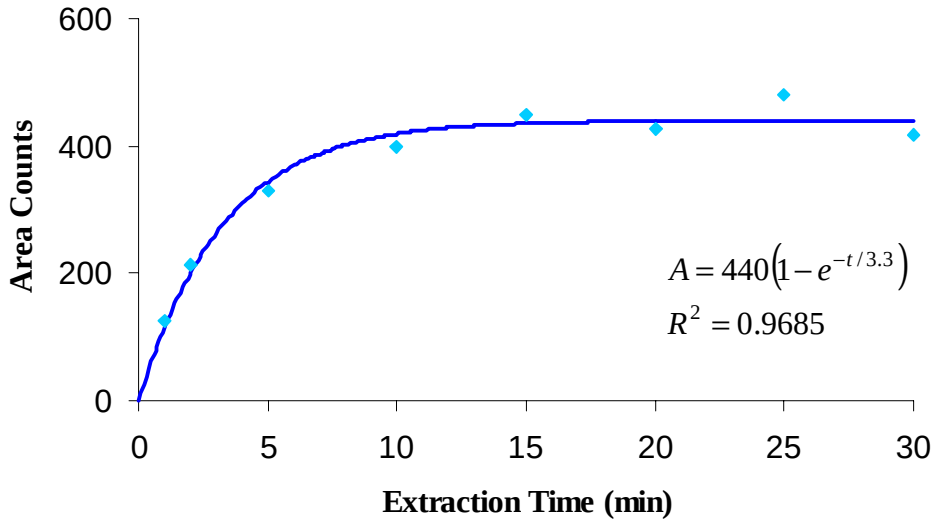

Fig. 4.8: Direct sampling extraction time curve

Using headspace sampling (Fig. 4.9), the amount of EtOH extracted increases rapidly during the first 60 minutes. After 60 minutes, instead of increasing more slowly and reaching a steady value, it starts decreasing. This phenomenon may be characteristic of this carboxen/PDMS fiber, as it saturates with gasoline components. Figure 4.9 also shows the amount of other compounds (divided by 200 in order to properly scale the plot) extracted by the fiber during the same analysis. It can be noticed that as the amount of EtOH extracted starts to decrease, the amount of other compounds still increases, which seems to confirm the presence of displacement effects. However, the last sampling point is an exception in that the amount of both EtOH and other compounds extracted decreased. This is probably due to evaporative losses in the sampling vial. The carboxen/PDMS fiber does not behave exactly like the other adsorption type fibers, and no extraction theory is available for it yet [19]. Since

the carboxen coating has such small pores, capillary condensation could occur, leading to a greater adsorption capacity for some analytes [19]. This capillary condensation can occur in addition to the possible replacement effects (where analytes with low affinity for the fiber are displaced by analytes with higher affinity for the fiber) common to adsorption type fibers. The capillary condensation effect is negligible if the analytes' concentrations are low enough [19]. Thus, as long as the EtOH level stays above the limit of quantification, it might be advisable to use a more dilute water extracted gasoline solution. Also, using a more polar fiber (not yet commercially available) may improve the method's % RSD's.

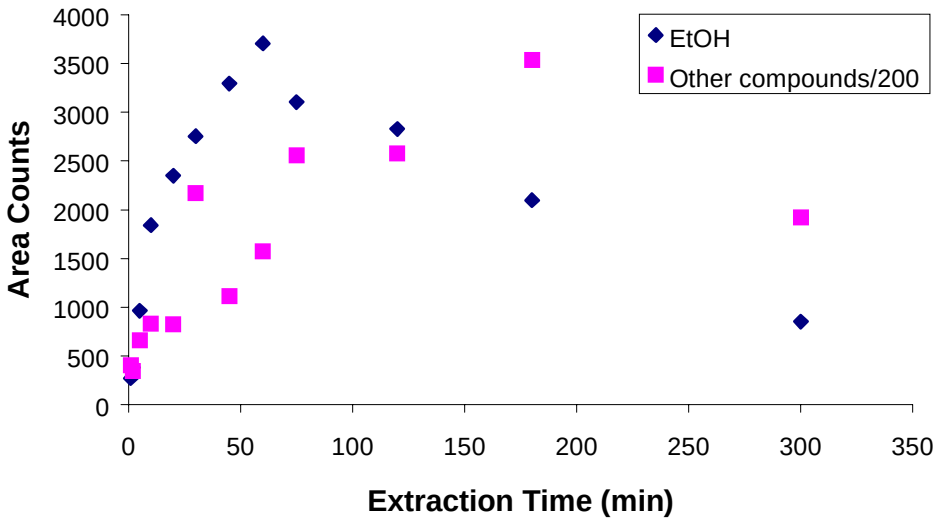

Fig. 4.9: Headspace sampling extraction time curve

4.3 Standard addition curves

In this section, the method of standard addition is used to quantify the amount of EtOH present in the stock solution. The stock solutions are first extracted with water and then diluted with water to the corresponding ppm amount. The standard addition curves are plotted using the added ppm amounts of the EtOH in the water fraction.

Once the ppm amount of the EtOH in the water fraction is determined using the standard addition curve, the weight % EtOH in the gasoline stock solution can be calculated.

Three experimental sets using direct sampling will be presented:

1 - using a 5.7 % EtOH stock solution
2 - using a 6.6 % EtOH stock solution, prepared right before using it for obtaining the diluted solutions
3 - using a 6.6 % EtOH stock solution, used to prepare the dilute solutions 24 hours after it was prepared

Each experiment comprises five solutions, the first being the original solution (diluted from the stock solution) and the other four being spiked ones (diluted from the spiked stock solution). For each solution, three replicate analyses were performed to average out errors. The average, standard deviation and percent relative standard deviation (% RSD) were calculated and plotted on a graph of area counts versus added concentration of EtOH in water (in ppm). Other researchers have reported an average value of 10 % RSD when using SPME in the same concentration levels as used in this research, therefore a 10 % RSD will be considered as reasonable. Note that a standard deviation is not very meaningful when only three samples are used, however it still gives some indication about the results' precision. It was more important for us to be able to perform the entire study during the same day in order to avoid day-to-day instrument and/or solutions variations; therefore more than three replicates for each solution was not possible.

In the first set of results (Table 4.1), the %RSD values are reasonable, even though two of them are slightly above 10%. The measurements, along with error bars representing their standard deviation, are shown in Fig. 4.10. The R^2 value obtained for the best fit line is slightly lower than 0.9, meaning that the line fits the results reasonably well. The EtOH concentration in water is found to be 4.1 ppm, which corresponds to a 6.0 weight % EtOH in gasoline. The actual weight % EtOH in gasoline being 5.7 %, our results reflect a 5.3 % error with respect to the "true" EtOH concentration in gasoline.

Table 4.1: Data set 1, using 5.7 wt.% EtOH stock solution (3.9 ppm EtOH in water)

Solution	EtOH Area	Average	Std. Dev.	%RSD
1 (original) X (3.9 ppm)	558.6 657.9 442.7	553.1	107.7	19.5
2 X + 0.4 ppm (4.3 ppm)	695.9 681.1 779.0	718.7	52.8	7.3
3 X + 1.1 ppm (5.0 ppm)	899.5 837.1 903.4	880.0	37.2	4.2
4 X + 1.9 ppm (5.8 ppm)	827.7 986.9 784.7	866.4	106.5	12.3
5 X + 2.7 ppm (6.6 ppm)	962.7 1081.9 outlier	1022.3	84.3	8.2

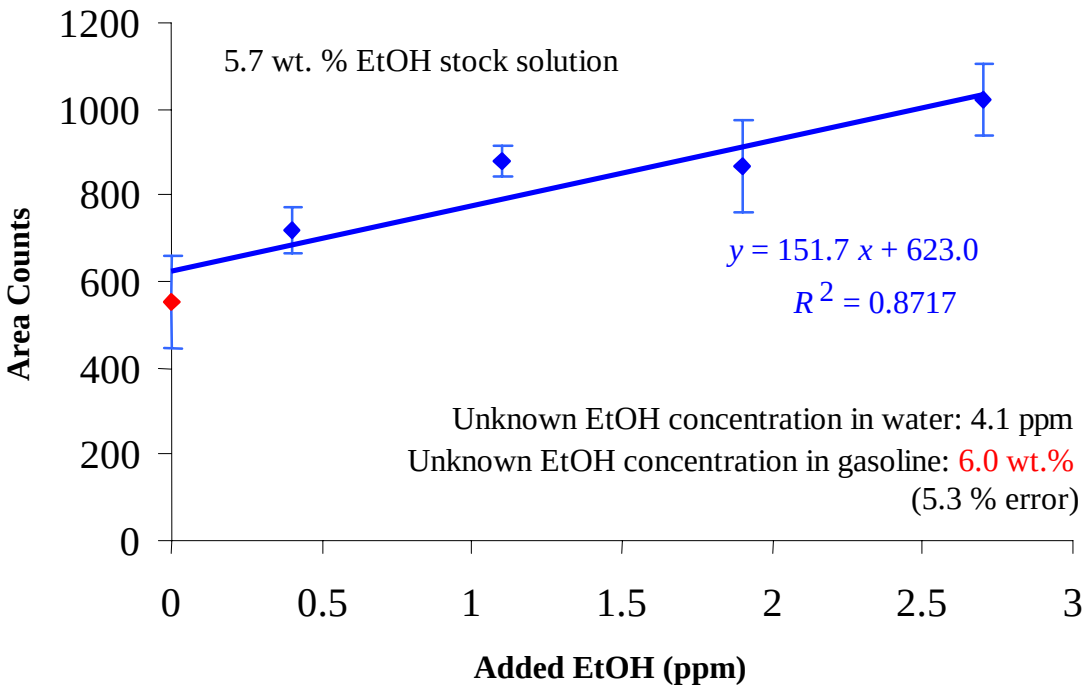

Fig. 4.10: Standard addition curve using result set #1

Table 4.2: Data set 2, using 6.6 wt.% EtOH stock solution (time 0) (4.5 ppm EtOH in water)

Solution	EtOH Area	Average	Std. Dev.	%RSD
A (original) X (4.5 ppm)	352.1 363.0 385.2	366.8	16.9	4.6
B X + 1.6 ppm (6.1 ppm)	489.4 441.3 478.1	469.6	25.2	5.4
C X + 3.1 ppm (7.6 ppm)	577.4 562.6 596.7	578.9	17.1	3.0
D X + 4.7 ppm (9.2 ppm)	706.4 749.6 772.1	742.7	33.4	4.5
E X + 6.2 ppm (10.7 ppm)	888.5 890.9 857.3	878.9	18.8	2.1

The second set of results is presented in Table 4.2. All five solutions show a percent RSD less than 5.5 %. The measurements are shown in Fig. 4.11. The line fits the results very well (R^2 = 0.9915). The EtOH concentration in water is found to be 4.1 ppm, which corresponds to a 6.0 weight % EtOH in gasoline stock solution. The actual weight % EtOH in gasoline being 6.6 %, our results reflect a 9.1 % error with respect to the "true" EtOH concentration in gasoline.

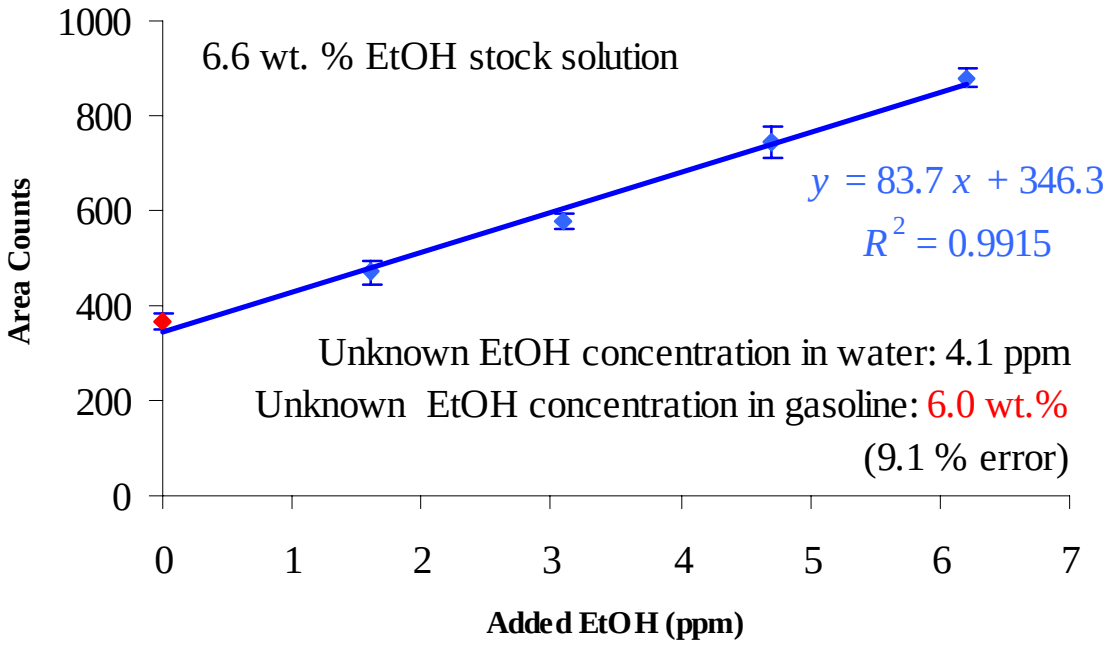

Fig. 4.11: Standard addition curve using result set #2

The third set of results is presented in Table 4.3. Most of the solutions show a percent RSD below 6.1 %, with only one of them having a % RSD above 10 %. The measurements are shown in Fig. 4.12. The graph shows a line that fits the results very well (R^2 = 0.9910). The EtOH concentration in water is found to be 5.1 ppm, which corresponds to a 7.5 weight % EtOH in gasoline stock solution, yielding a 14 % error in the measurement of EtOH content in gasoline.

Table 4.3: Data set 3, using 6.6 wt.% EtOH stock solution (time 48 hours) (4.5 ppm EtOH in water)

Solution	EtOH Area	Average	Std. Dev.	%RSD
A (original) X (4.5 ppm)	384.4 421.3 411.4	405.7	19.1	4.7
B X + 1.6 ppm (6.1 ppm)	502.2 487.8 547.8	512.6	31.4	6.1
C X + 3.1 ppm (7.6 ppm)	769.5 671.0 604.3	681.6	83.1	12.2
D X + 4.7 ppm (9.2 ppm)	742.1 812.0 803.5	785.9	38.2	4.9
E X + 6.2 ppm (10.7 ppm)	865.5 916.9 885.4	889.3	25.9	2.9

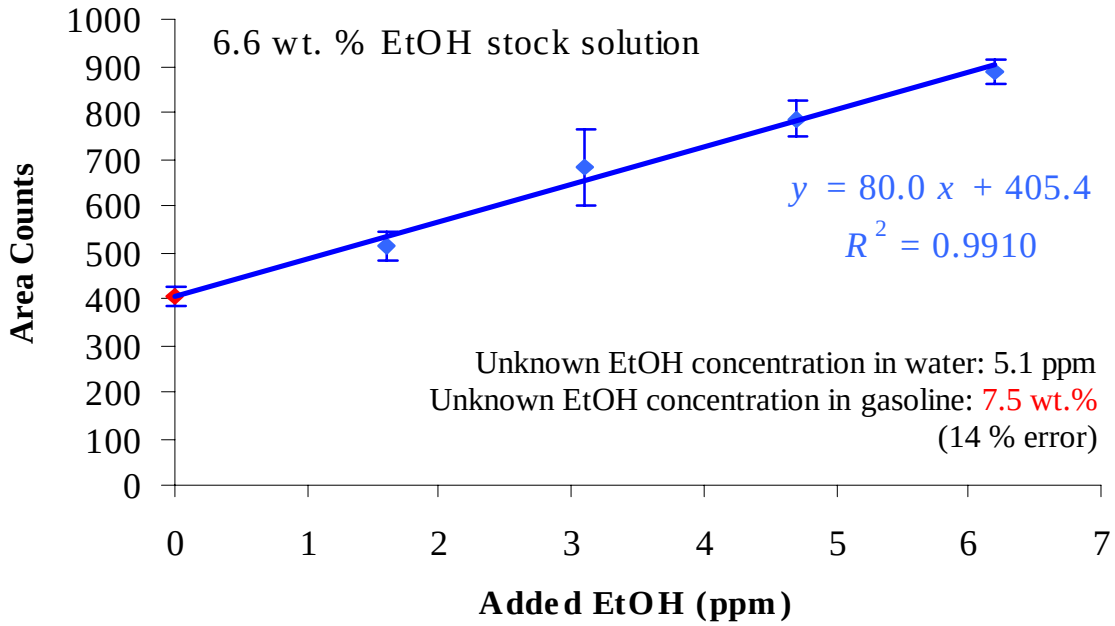

Fig. 4.12: Standard addition curve using result set #3

4.4 Calibration curves

In this section calibration curves are used to quantify the amount of EtOH present in the stock solution. Since the gasoline samples obtained from a local gas station do not contain alcohols, it is possible to use this method. Standard solutions with known amounts of EtOH were prepared. Stock solutions with known amounts of EtOH can then be anlyzed to test the accuracy of this method. In this work, for practical purposes, we used the solutions that were prepared for the standard addition method. We selected four solutions to be our calibration standards. The remaining solution was considered as our unknown sample. Three results are presented, one each taken from the three data sets previously described (Section 4.4).

From the first data set, we chose solution 4 (8.3 weight % EtOH in gasoline) to be our unknown sample, with solutions 1,2,3 and 5 acting as the calibration standards. The calibration curve hence obtained is shown in Fig. 4.13. The R^2 value of the best fit line

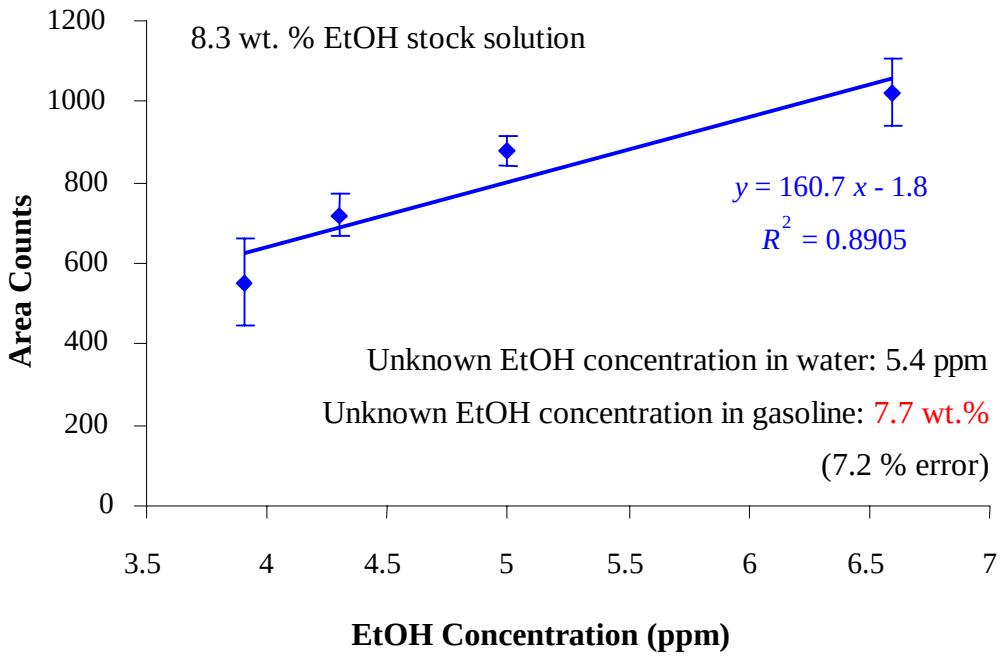

Fig. 4.13: Calibration curve using result set #1

is slightly lower than 0.9, which is acceptable. The unknown EtOH concentration in water is found to be 5.4 ppm, which corresponds to 9.5 weight % EtOH in gasoline. This results in a 7.2 error %.

From the second data set, we chose solution D (12.6 weight % EtOH in gasoline) to be our unknown sample, with solutions A,B,C, and E acting as the calibration standards. The calibration curve is illustrated in Fig. 4.14. The R^2 value is 0.9902, which means the best fit line fits the data very well. The unknown EtOH concentration in water is found to be 9.3 ppm, which corresponds to 12.8 weight % EtOH in gasoline. This results in a 1.6 error %.

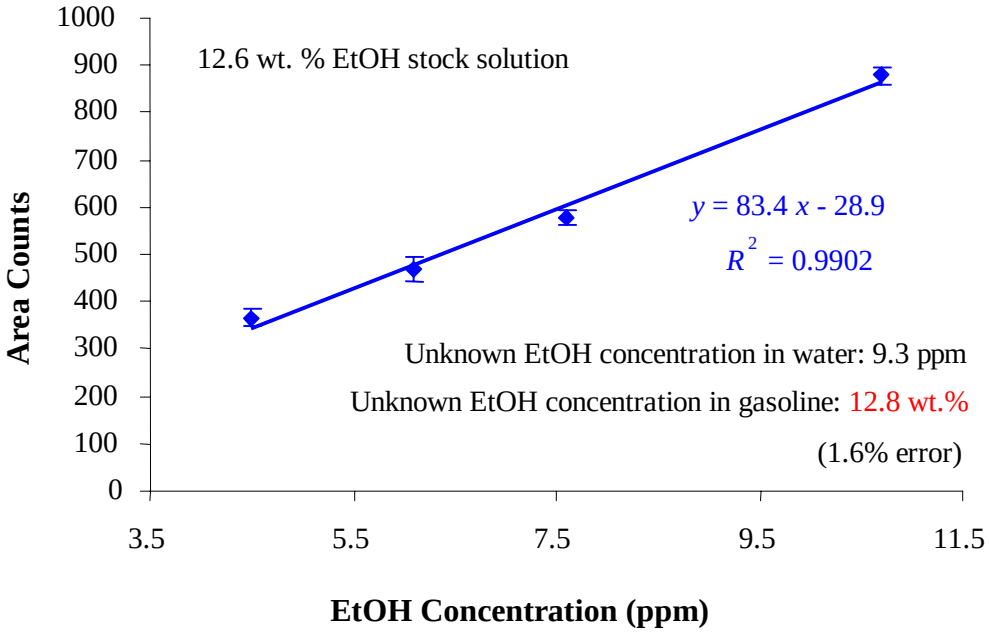

Fig. 4.14: Calibration curve using result set #2

From the third data set, we chose solution D (12.6 weight % EtOH in gasoline) to be our unknown sample, with solutions A,B,C, and E acting as the calibration standards. The calibration curve is illustrated in Fig. 4.15. The R^2 value is 0.9898, which means the line fits the data very well. The unknown EtOH concentration in water is found to be 9.3 ppm, which corresponds to 12.8 weight % EtOH in gasoline. This results in a 1.6 error %.

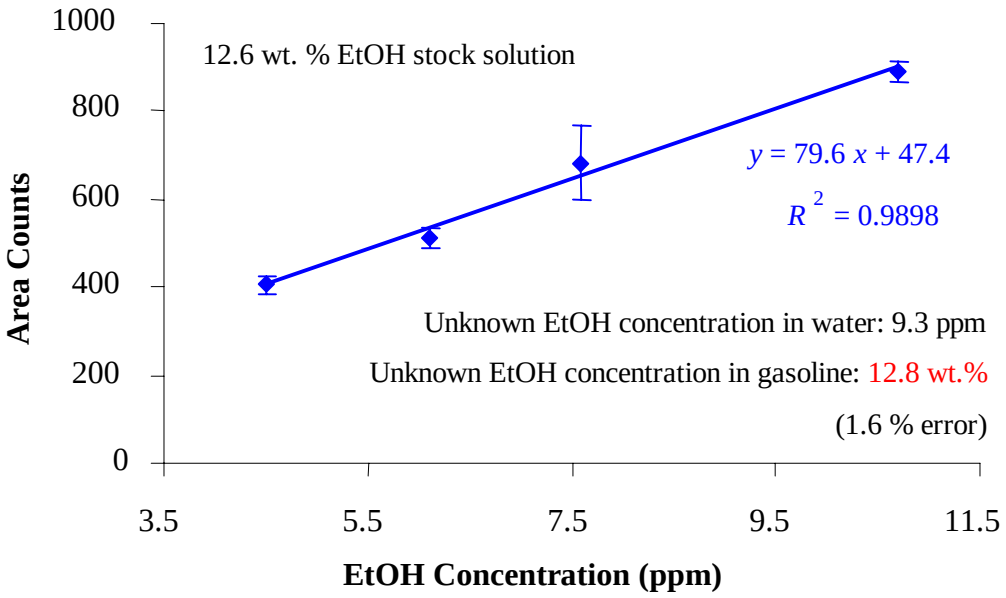

Fig. 4.15: Calibration curve using result set #3

CHAPTER 5 - CONCLUSIONS

The Clean Air Act Amendments of 1990 require the use of reformulated gasoline (RFG) in areas suffering from ozone or smog problems. RFG is oxygenated gasoline and has to contain at least 2 weight % oxygen year-round, and 2.7 weight % oxygen during the winter time. The two most common oxygenates added to gasoline to satisfy these conditions were ethanol (EtOH) and Methyl tert butyl ether (MTBE). Since MTBE is almost banned by the EPA because of the possibility of ground water contamination, the current trend is to use EtOH. Therefore, this work focused on the determination and quantification of EtOH in gasoline.

The main problem in performing a chromatographic analysis of EtOH in gasoline is the coelution of aliphatic compounds with EtOH. In order to solve this problem, several approaches have been used in the past, including three main chromatographic types. One type uses a detector selective for oxygen containing compounds. Another one uses two or more columns of different polarities. The last one uses an extraction step prior to GC analysis. Since the first two types of approaches require modifications of readily available instruments, we decided to use the latter approach. Indeed, we chose to perform an extraction step with water, prior to a SPME-GC analysis. Our approach did not require use of organic solvent as did Hiromitsu *et al.*'s [26] and Agarwal's [1], and avoided inserting water solvent in the GC, as did Pauls and McCoy [34]. When conceiving this water extraction step, we were not aware that Pauls and McCoy [34] had already used an extraction step with water prior to GC analysis for quantifying EtOH in gasoline. Our approach was quite similar to his, with a similar water extraction step time and GC analysis time. However, injecting water into the GC slightly damages the GC column and reduces its lifetime. SPME solves this problem since no solvent is introduced into the GC. Solid phase microextraction, recent technique invented by Dr. Pawliszyn in 1989 and commercially available since 1994, allows concentration of the analytes in the solution and allows interferences removal by means of a fiber. Gorecki *et al.* [20] attempted to use SPME-GC to quantify MeOH and EtOH in gasoline, using a custom-

made polar fiber. However, their work does not explain the details of the technique and only proves detection but no quantification of either MeOH or EtOH.

In this work, a polar fiber (carboxen/PDMS) was used to perform the extraction of EtOH from the diluted water extract. This fiber is the most polar fiber commercially available. Two methods have been used to quantify the amount of EtOH present in a gasoline sample: the method of standard addition; and the method of calibration curve. The method of calibration curve should be the method of choice if gasoline "base" samples (gasoline samples of same composition as the oxygenated gasoline sample, but not containing EtOH) are available. These gasoline "base" samples are needed to prepare the calibration standards. If a large number of samples have to be analyzed, this method is less time consuming than the method of standard addition. In the case of quality control measurements or process control in a plant, for example, where the oxygenates get blended into "base" gasoline, this method would be the preferred one. If gasoline "base" samples are not available, then the method of standard addition should be used, due to the impossibility to generate calibration curves using the same extraction matrix. A different extraction matrix may yield slightly inaccurate results. For example, for testing gasoline samples coming from a gas station, this method would be the method of choice, since the "base" gasoline may not be available to establish a calibration curve.

The experimental results of this work for both of these methods showed common SPME % RSD values lower than 10%, good linearity (R^2 values mostly greater than 0.99 and sometimes of about 0.88), and most error percents in the detected EtOH quantity in gasoline lower than 9.1%. Moreover, the study of extraction time by direct sampling very closely confirmed an exponential law theoretically predicted for other types of fibers. The same study conducted for headspace sampling yielded an initial increase of analyte amount extracted with increasing sampling times. After a specific sampling time, the amount of analyte extracted started to decrease. This might be explained by losses that accumulate and become observable after long extraction times. Or this may be may due to the carboxen/PDMS fiber's specific extraction characteristics. Since this fiber does not behave exactly like the other adsorption type fibers, no adsorption kinetic model is available for it yet [19]. Since the carboxen coating has such small pores, capillary condensation could occur, leading to a greater adsorption capacity for some analytes [19].

This capillary condensation can occur besides the possible replacement effects (where analytes with low affinity for the fiber are displaced by analytes with higher affinity for the fiber) common to adsorption type fibers. The capillary condensation effect is negligible if the analytes' concentrations are low enough [19]. Thus, using a more dilute water extract solution might be advisable. Also, using a more polar fiber (not yet commercially available), may improve the method's % RSDs. This is a topic for future research.

Appendix A – EtOH Content Calculations

A.1 Conversion from volume % EtOH to weight % EtOH in gasoline

This conversion is needed for concentration (in ppm) determination of the dilute water extract solution. Indeed, by knowing the EtOH weight % in gasoline, when performing the gasoline-water extraction, the EtOH weight transferred from the gasoline layer to the water layer can be determined. Then the concentration of the diluted water extract can be calculated.

We have a solution of gasoline and EtOH of total volume V, with Y volume % of EtOH. What is the weight percent X of EtOH corresponding to this volume percent Y?
Let V_e be the volume of EtOH added to the gasoline, and V_g be the volume of gasoline.
Let d_e and d_g be the densities of EtOH and non-oxygenated gasoline respectively.
Then the total volume is:

$$V = V_e + V_g \tag{1}$$

The volume % EtOH can be written as:

$$Y = \frac{V_e}{V_g} \times 100 \tag{2}$$

The weight % of EtOH, X, can be expressed as a function of densities and volumes, as follows:

$$X = \frac{d_e V_e}{d_e V_e + d_g V_g} \times 100 \tag{3}$$

Dividing the numerator and denominator by $d_e V_e$, Eq. (3) becomes:

$$X = \frac{100}{1 + \frac{d_g V_g}{d_e V_e}} \tag{4}$$

Solving for V_g using Eq. (1), and then substituting this expression in Eq. (3), we obtain:

$$X = \frac{100}{1 + \frac{d_g}{d_e}\left(\frac{V - V_e}{V_e}\right)} \tag{5}$$

Solving for V/V_e using Eq. (2), and then substituting this expression in Eq. (5), we get:

$$X = \frac{100}{1 + \frac{d_g}{d_e}\left(\frac{100}{Y} - 1\right)} \tag{6}$$

A 5.8 volume % EtOH in gasoline solution (with 0.776 g/mL EtOH and 0.6752 g/mL gasoline) would correspond to 6.6 weight % EtOH in gasoline.

A.2 Conversion from weight % EtOH to volume % EtOH in gasoline

We have a solution of gasoline and EtOH of total volume *V*, with *X* weight % of EtOH. What is the volume % *Y* of EtOH corresponding to this weight % *X*?

Let's use Eq. (6), and solve the equation for *Y*. First, we multiply both sides of Eq. (6) by the denominator and divide both sides by *X*, this leads to:

$$1 + \frac{d_g}{d_e}\left(\frac{100}{Y} - 1\right) = \frac{100}{X} \tag{7}$$

Rearranging Eq. (7), and solving for *100/Y*, we get:

$$\frac{100}{Y} = \frac{d_e}{d_g}\left(\frac{100}{X} - 1\right) + 1 \tag{8}$$

Rearranging Eq. (8), and solving for Y, we get:

$$Y = \frac{100}{1 + \frac{d_e}{d_g}\left(\frac{100}{X} - 1\right)} \tag{9}$$

Eq. (9) can also be written as:

$$Y = \frac{100}{1 + \frac{d_e}{d_g}\left(\frac{100 - X}{X}\right)} \tag{10}$$

A.3 Spiking calculations for added ppm amount determination

Let w_{te}, w_e, and w_s be the total EtOH weight, the EtOH weight, and the spiked EtOH weight, respectively, in the spiked oxygenated gasoline sample.

If we mix 1 mL oxygenated gasoline with 1 mL water, and if we assume total transfer of EtOH amount from the gasoline layer to the water layer, then, in 1 mL of water extract there are $(w_e + w_s)$ grams of EtOH.

Therefore, in 10 μL of water extract , there are $10^{-2}(w_e + w_s)$ grams of EtOH.

Hence, diluting 10 μL of this water extract to 100 mL, we get an EtOH concentration equal to:

$$C = \frac{10^{-2}(w_e + w_s)g}{100mL} = \frac{10^{-4}(w_e + w_s)g}{1mL} = \frac{10^{2}(w_e + w_s)\mu g}{mL} = 100(w_e + w_s)\ \text{ppm}$$

If no EtOH is spiked into the oxygenated gasoline, then this concentration becomes:

$$C_i = 100(w_e)\,\text{ppm} \tag{11}$$

This means that the added concentration of EtOH in the dilute water extract solution is equal to:

$$C_{added} = 100(w_s)\,\text{ppm} \tag{12}$$

By finding *Ci* from the standard addition curve, we can find w_e using Eq. (11). Knowing w_e and knowing the weight of the oxygenated gasoline (w_{og}), we can calculate the EtOH weight % in gasoline. Knowing w_e and knowing the EtOH density, we can also find the corresponding EtOH volume in the oxygenated gasoline sample, and thus also calculate the EtOH volume % in gasoline.

Appendix B – Sampling Time calculations

Determination of sampling time needed to obtain a relative error in analyte amount extracted lower than a specified value

The purpose is to determine the minimum sampling time required to achieve a certain degree of accuracy in analyte amount extracted.

Let n be the amount of analyte extracted, t be the sampling time, and ε be the maximum relative error in analyte amount extracted. We want:

$$\frac{\Delta n}{n} \leq \varepsilon \tag{1}$$

Let's derive an experssion for $\Delta n/n$. First, using derivatives, we have:

$$\frac{dn}{dt} \cong \frac{\Delta n}{\Delta t} \tag{2}$$

Dividing both sides of Eq. (2) by n, we get:

$$\frac{1}{n}\left(\frac{dn}{dt}\right) \cong \frac{\Delta n}{n}\left(\frac{1}{\Delta t}\right) \tag{3}$$

Solving for $\Delta n/n$ in Eq. (3), we obtain:

$$\frac{\Delta n}{n} \cong \frac{1}{n}\left(\frac{dn}{dt}\right)\Delta t \tag{4}$$

From Eq. (1) and Eq. (4), it follows that:

$$\frac{1}{n}\frac{dn}{dt}\Delta t \leq \varepsilon \tag{5}$$

Dividing both sides of Eq. (5) by Δt, we obtain:

$$\boxed{\frac{1}{n}\frac{dn}{dt} \leq \frac{\varepsilon}{\Delta t}} \tag{6}$$

The amount of analyte extracted by direct sampling, as was shown in Chapter 2, is related to sampling time, according to the following equation (Chapter 2, Eq. 10):

$$n = n^{\infty}(1 - e^{-t/\tau}) \tag{7}$$

Taking the derivative of n with respect to t in Eq. (7), we get:

$$\frac{dn}{dt} = \frac{n^{\infty} e^{-t/\tau}}{\tau} \tag{8}$$

Dividing both sides of Eq. (8) by n, we obtain:

$$\frac{1}{n}\frac{dn}{dt} = \frac{n^{\infty}}{n}\frac{e^{-t/\tau}}{\tau} \tag{9}$$

Substituting the left side of Eq. (6) by the right side of Eq. (9) we get:

$$\frac{n^{\infty}}{n}\frac{e^{-t/\tau}}{\tau} \leq \frac{\varepsilon}{\Delta t} \tag{10}$$

Substituting n in Eq. (10) with its expression in Eq. 7, and simplifying the obtained equation, we obtain:

$$\frac{1}{1-e^{-t/\tau}}\frac{e^{-t/\tau}}{\tau} \leq \frac{\varepsilon}{\Delta t} \tag{11}$$

Multiplying both sides of Eq. (11) by τ, ($\tau > 0$), we get:

$$\frac{e^{-t/\tau}}{1-e^{-t/\tau}} \leq \frac{\varepsilon\tau}{\Delta t} \tag{12}$$

Let's introduce a new variable, z, such as:

$$z = e^{-t/\tau} \tag{13}$$

When t varies from 0 to ∞, z varies from 0 to 1, and (1-z) varies from 0 to 1. Substituting this new variable into Eq. (12), we obtain:

$$\frac{z}{1-z} \leq \frac{\varepsilon\tau}{\Delta t} \tag{14}$$

Multiplying both sides of Eq. (14) by (1-z), (1-$z > 0$), we get:

$$z \leq \frac{\varepsilon\tau}{\Delta t}(1-z) \tag{15}$$

Developing the right side of Eq. (15), adding $\frac{\varepsilon\tau}{\Delta t}z$ to both sides, and factoring out z, we obtain:

$$z\left(1+\frac{\varepsilon\tau}{\Delta t}\right) \leq \frac{\varepsilon\tau}{\Delta t} \tag{16}$$

Dividing both sides of Eq. (16) by the term in parentheses (positif), we get:

$$z \leq \frac{\varepsilon\tau / \Delta t}{1 + \varepsilon\tau / \Delta t} \tag{17}$$

Simplifying Eq. (17), we obtain:

$$z \leq \frac{\varepsilon\tau}{\Delta t + \varepsilon\tau} \tag{18}$$

Substituting z in Eq. (18) by its expression in Eq.(13), we get:

$$e^{-t/\tau} \leq \frac{\varepsilon\tau}{\Delta t + \varepsilon\tau} \tag{19}$$

Taking the natural log of the expressions on both sides of Eq. (19), we obtain:

$$-\frac{t}{\tau} \leq \ln \frac{\varepsilon\tau}{\Delta t + \varepsilon\tau} \tag{20}$$

Multiplying both sides of Eq. (20) by $-\tau$ (negative), we get:

$$t \geq -\tau \ln \frac{\varepsilon\tau}{\Delta t + \varepsilon\tau} \tag{21}$$

Rearranging Eq. (21), we obtain:

$$\boxed{t \geq \tau \ln\left(\frac{\Delta t}{\varepsilon\tau} + 1\right)} \tag{22}$$

Example:

If:

τ = 3.3 minutes = 198 seconds

Δt = 5 seconds

ε = 1 % = 0.01

Then:

t ≥ 4.2 minutes

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