

**DETERMINATION OF HENRY'S LAW CONSTANTS OF
ODOROUS CONTAMINANTS AND THEIR APPLICATION TO
HUMAN PERCEPTION**

by

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Chair: Andrea M. Dietrich

ABSTRACT

Although utilities attempt to avoid offensive smelling compounds in consumer's drinking water, their efforts are often hampered by a lack of data or knowledge of the physical, chemical, and sensory properties of odorants. Many factors affect the ability of a consumer to detect odors, including: concentration, presence of chlorine/other odorants, temperature, and the individual's sensitivity.

This research developed a simplified static-headspace technique to determine Henry's Law constants at multiple temperatures and then use these data to calculate the enthalpy of solution so that new Henry's Law constants can be calculated at any temperature using the van't Hoff Equation. The method was applied to three taste-and-odor compounds of moderate water solubility (about 100 mg/L). 2-Methylisoborneol (2-MIB) is a methylated monoterpene alcohol that is produced by actinomycetes and blue-green algae and has a musty odor that is detectable at 4-10 ng/L water. Geosmin, also produced by actinomycetes and blue-green algae, has a detectable earthy odor at 5-10 ng/L. *trans*-2, *cis*-6-Nonadienal is enzymatically synthesized from poly-unsaturated fatty acids by diatoms like *Synura* and has cucumber and fishy odors detectable at 10-40 ng/L levels.

The new static headspace method uses standard glassware used in odor-analyses. 500 mL wide-mouth Erlenmeyer flasks were modified with septum sampling ports to measure vapor phase concentrations by SPME/GC-MS. Unitless Henry's Law constants were determined at multiple temperatures using the vapor and aqueous phase concentrations. From the Henry's Law

constants, the enthalpies of reactions were calculated. For these compounds, the values for Henry's Law constants ranged from 0.002 to 0.02 for four temperatures between 20 to 45 °C with geosmin and 2-MIB having similar and higher values than for nonadienal. The constants increased with increasing temperature. The enthalpies of vaporization from the aqueous phase were determined to be in the range of 50-80 kJoule/mole.

The experiments were repeated with fulvic acid added to the aqueous media at different concentrations. The Henry's Law constants were decreased with the presence of fulvic acid; however no correlation between the concentration of fulvic acid and the decrease was observed. The decrease in constants for 2-MIB and geosmin were very small compared to nonadienal.

Finally the measured Henry's Law constants were used to predict gas phase concentrations of odorants for known aqueous concentrations of geosmin, 2-MIB, and nonadienal. The results were correlated to the human sensory data obtained from flavor profile analysis. The data demonstrated that as the gas phase concentration increased, the perceived odor intensity also increased, but only up to a certain point. The vapor phase concentration increased linearly as the aqueous phase concentration increased, but the FPA intensity increased at a lower rate and leveled-off. The increase in the FPA rating at 25°C was greater than at 45°C although the vapor phase concentration was greater at 45°C. For samples containing 400 and 600 ng/L geosmin, 400 and 600 ng/L, 2-MIB, 100 and 200 ng/L nonadienal, the increase in gas phase concentration did not increase the FPA ratings of the panelists.

It was concluded that, utilities will be challenged to assess and treat high concentrations of geosmin, 2-MIB, and nonadienal. Sensory analysis will not be predictive of aqueous or vapor concentration at high levels and may be misleading if used to determine a treatment strategy. Chemical analyses, especially solid phase microextraction technique is very effective in measuring these compounds even at low ng/L levels. The temperature-related Henry's Law constants can be used to assess remediation systems, human exposure and sensory perception by predicting gas phase concentration in a variety of situations, such as showering and washing dishes.

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INTRODUCTION

This thesis is presented in the Virginia Tech manuscript format. The first chapter is a review of the literature related to drinking water taste-and-odors, Henry's Law constant, solid phase microextraction. The second chapter is a manuscript formatted for journal submission which explains the experimental findings for major taste-and odor compounds, including Henry's Law constants, effect of presence of fulvic acid in the matrix on the constants, and correlation of headspace concentration calculated using the constants, to sensory data obtained in a previous study. In the appendices, the data and the calculations are presented.

CHAPTER I

LITERATURE REVIEW

PROBLEMS WITH ODOROUS COMPOUNDS IN DRINKING WATER

Customer Complaints

Once the waterborne diseases were eliminated from drinking water, the public started to pay attention to the way the water smelled or tasted. Although tastes and odors are not considered to be health hazards and hence are not regulated by primary drinking water standards, they result in consumer complaints. Undesirable odor in drinking water is a global problem, which has been identified in the Americas, Australia, Europe, Africa, and Asia (Whelton and Dietrich, 2004). Dissatisfied consumers may describe the taste of the tap water as chlorinous or its flavor as earthy, musty, medicinal, or grassy (Burlingame et al., 1987; Dietrich et al., 1991; Suffet et al., 1999; Mackey et al., 2001).

The odor thresholds differ from one person to another and from one country to another. It depends on the sensitivity of the individual or the exposure of the population to a specific concentration of taste-and-odor causing compounds in the drinking water (Mackey et al., 2001). Consumers can detect taste, odor, hardness, temperature, color, chlorine concentration, hardness, or salinity changes in their tap water (Mallevalle and Suffet, 1987; Whelton, 2001).

Consumer acceptance of drinking water is crucial to the success of the drinking water industry, which spends millions of dollars to deal with the taste-and-odor problem. Water utilities work hard to provide better quality water to their consumers. Consumers judge the safety of the drinking water flowing through their taps by its aesthetic quality. Taste and odor, rather than the turbidity and color, are their primary tools to judge. Off-flavors are the signals of toxicity for the consumers (McGuire, 1995). The main reason for rejecting tap water as a beverage is the taste or flavor (Levallois et al., 1999). Dissatisfied water utility customers start purchasing bottled water or start using in home treatment or filter tap water (Mackey et al., 2001).

The complaints are very valuable because the first alarm of a problem comes from customers by a phone call or a letter stating the disturbing condition of the tap water (Whelton, 2003). Usually a very small percentage of the population is sensitive enough to detect small changes in the tap water quality and the complaints can be used to prevent and correct the problems before widespread public exposure (Mallevalle and Suffet, 1987).

Contributions of Water Supply

The origin and type of water source can influence taste and odor, especially when the water is drawn from different sources including surface-water and groundwater supplies. During the stratification periods, the hypolimnion of a lake or reservoir may become anoxic due to the eutrophic state of the water supply which results in nutrient release from the sediments. This condition also favors algal blooms and formation of taste and odor compounds (Cooke and

Carlson, 1989). Groundwater may contain the chemicals leaching from the geological formations that may contribute to taste-and-odor.

The first record of an off-flavor in drinking water was in 1850's (Wood et al., 1983). After debates and studies on the taste on odor of the water, it was concluded that the causes of taste and odor were the living organisms' metabolites and decaying vegetation in water (Sigworth, 1957). The organisms related to taste-and-odor in source water are actinomycetes, cyanobacteria, and fungi. The most common type of algae is diatoms and flagellated algae found as suspended in water or attached to the sediment. Algae produce numerous organic substances that cause taste-and-odor in drinking water supplies. Another potential contribution to taste and odor by algae is by the decomposition of algal metabolites and the decay of dead cells. It is necessary to identify the compounds and organisms to pinpoint the taste and odors (Mallevalle and Suffet, 1987).

A typical surface water problem is a cyanobacteria algal bloom during warmer months. Cyanobacteria such as anabaena, oscillatoria, symploca, and aphanizomenon, being the main group of microorganisms that are responsible for the earthy-musty odor in drinking water are mostly found as surface scum and benthic mat in eutrophic waters. The compounds produced by cyanobacteria include geosmin and 2-methylisoborneol and are difficult to remove with the conventional water treatment operations (Gerber and Lechevalier, 1965; 1969; Safferman et al., 1967).

Actinomycetes are filamentous bacteria that are found in the water and sediments of lakes and rivers (Mallevalle and Suffet, 1987). They are an important group of microorganisms for the aquatic ecosystems because of their ability to degrade complex plant residues (Goodfellow and Williams, 1983). Actinomycetes produce many compounds including 2-MIB and geosmin that contribute to the taste-and-odor problem in drinking water (Collins, 1971; Zaitlin et al., 2003).

Although earthy-musty tastes and odors are the most problematic, fishy and swampy tastes and odors are also difficult to remove. All persist in water unless intense measures are taken to remove them.

The tastes and odors in groundwater are usually caused either by biological activity or by the chemicals leaching from the geological formations. An example of sweetish taste and color can be given from the groundwater of Florida containing humic substances (Gaufin, 1964). Minerals also make the water taste salty or astringent. Another disturbing odor caused by hydrogen sulfide is mainly produced by sulfate-reducing bacteria found in some groundwaters. Because these compounds are not removed by the conventional treatment plants, consumers will receive the unpalatable water through their taps (Mallevalle and Suffet, 1987).

Contributions of Water Treatment Plant

Although many of the tastes and odors in drinking water come from the water supply, some other taste-and-odor causing compounds are produced during the water treatment processes. Especially the oxidants and disinfectants used for the treatment of water, reacting with

the organic compounds present, are the main reason for the formation of these by-products (Hrudey et al., 1988). Maintaining a disinfectant residual is a common application to ensure the inactivation of pathogens until the tap water reaches to the consumers (van der Kooij et al., 1999a;b). Before the finished water is pumped to the distribution system, ammonia is added to form chloramines, which are very stable. This process guarantees the safety of the water while it is distributed to consumers. However, chloramines may introduce a chlorinous, medicinal, or even fishy taste or odor to the drinking water (Mallevalle and Suffet, 1987).

Consumer complaints about taste-and-odor due to presence of disinfection by-products are one of the concerns related to the use of a disinfectant residual. Most of the complaints are related to the presence of chlorinous odors (Burlingame et al., 1987; Burlingame and Dahme, 1989; Suffet et al., 1996).

In 1989, AWWA conducted a nationwide survey of water utilities to evaluate taste and odor problems (Suffet et al., 1995). The results showed that 60 % of the utilities had the second main problem with disinfection and 49 % of the utilities pointed out that chlorine residual caused taste and odor problems (Khiari et al., 1999).

Chlorine dioxide which is a more powerful oxidant for disinfection, odor control, minimizing THM formation, and oxidation of soluble metals used as an alternative to chlorine, and the water utilities started to receive complaints about the tap water having a chlorinous, kerosenlike and cat-urine-like odors (Dietrich et al., 1992). These odors are produced by the reaction of chlorine dioxide with the organic substances present in the air (Hoehn et al., 1990).

Although ozone is a very efficient agent in removing tastes and odors and disinfection, the intermediate reactions produce aliphatic and aromatic aldehydes, which introduce a fruity and fragrant odor to the treated water (Anselme et al., 1985; Suffet et al., 1986; Hrudey et al., 1988).

Contributions of Water Distribution System

The water distribution system can be considered as a great biological and chemical reactor and hence many biological reactions may take place (Montiel et al., 1999). In 1989, AWWA conducted a nationwide survey of water utilities to evaluate taste-and-odor problems (Suffet et al., 1995). The results showed that 65 % of the utilities cited their main problem as the distribution system (Khiari et al., 1999). The compounds responsible for the taste-and-odor problems in the distribution system are mainly chlorinous solvents used for pipe coatings, emissions from the pipes, corrosion products, and the metabolites of the microorganisms (Dietrich et al., 2004a; Rigal and Danjou, 1999).

Water-use patterns can influence the residence times of water in the distribution system. Hence, water may stagnate and deteriorate in distribution mains, service lines, and storage reservoirs. In the distribution system, high organic carbon concentration, high temperature, low water velocity and long residence time favors microorganisms' growth that leads to the formation of musty, earthy, swampy, and fishy tastes and odors (Mallevalle and Suffet, 1987).

Another cause for the taste and odor problems within the distribution system is generally caused by pressure fluctuations in the main water system. The pressure disturbances include the water main breaks, street constructions, or the use of fire fighting connections. Due to the pressure changes, the settled matter at the bottom of the pipes may go back into the water flowing water (Mallevalle and Suffet, 1987).

Another source of tastes and odors may be the organic compounds released from the inner coating materials of the pipes. When the disinfectants react with these organic materials, chlorophenols are formed which have a pharmaceutical and medicinal taste and odor. This type of situation occurs mostly when the system is newly coated and operated. Chlorinated solvents' releases are reported leading to the detection of medicinal tastes and odors (Stinson and Carns, 1983). Plastic or burnt plastic taste and odor is associated with the organic compounds released from the synthetic pipes (Burman and Colbourne, 1979; Khiari et al 2002).

Corrosion of pipes, fittings, or mains containing iron, copper, or zinc may introduce considerable concentration of these metals and hence can impart an unpalatable taste to the drinking water (Cohen et al., 1960). If the pipes are permeable, migration of external contaminants can also be a source for the taste-and-odor problems (Reich et al., 1985). Hydrocarbons such as toluene, phenols, or chlorinated solvents such as trichloroethane may penetrate through low density polyethylene pipes (LDPE) (Marshall et al., 1982; Meheus et al., 1985). Polyvinylchloride (PVC) pipes are more permeable to contaminants than LDPE and high density polyethylene (HDPE) pipes (Kreft et al., 1981).

Contributions of Residential Plumbing

The dead ends and the hot water lines at home plumbing may enhance the growth of the bacteria. The biological reactions and reduction of certain materials lead to the formation of taste and odor compounds such as hydrogen sulfate in hot water pipes and heaters (Hack, 1981).

In addition, when water is left standing for a long time in the pipes, musty, earthy, muddy, phenol, chlorine, metallic, sour, bitter, and foul tastes and odors are formed. The compounds and materials responsible for these tastes and odors are 2-MIB, geosmin, disinfection by-products, chlorine dioxide residuals, and metal ions resulted from corrosion.

Since 1960's, many type of pipes are in the market for transport and storage of water. These pipes made of organic materials are selected because of their durability and ease of use; however they alter the quality of the water they contain. The materials in the pipes leach and introduce bad taste to the water (Rigal, 1992).

Inorganic compounds, such as salts at a concentration higher than the taste threshold concentration result in impaired water taste. For a neutral water taste, the salt concentration should be approximately same with the adapted concentration of saliva (Mallevalle and Suffet, 1987). Metal ions that can be present in drinking water include iron, copper, manganese, and zinc. Iron having the lowest detection threshold is suspected of affecting the taste of the water the most (Cohen et al., 1960). In many cases, the tastes and odors caused by the inorganic compounds are mainly the compounds found in the untreated waters.

Corrosion is the main reason for the high concentrations of copper, iron, and lead. Although the trigger of corrosion is a complex issue, it depends on the pH, pE, sulfate, chloride, hardness, organic and inorganic ions, alkalinity, natural organic matters, and microorganisms in the water (Dietrich et al., 2004a).

Taste and Odor Episodes throughout the World

Taste-and-odor problems became an issue after the surface waters were used as drinking water sources in Europe, Americas, Japan, and Australia (AWWARF, 1993; Magara and Kunikane, 1986; Yagi et al., 1988).

Hu and Chiang (1996), focused on the odorous compounds produced by cyanobacterium in a drinking water treatment plant in central Taiwan. The authors found brown granules attached to the walls of water inlet tank, and the microorganisms were isolated and identified to be cyanobacterium. By closed-loop stripping analysis, geosmin and 2-MIB were detected at nanogram-per-liter levels.

Izaguirre and his colleagues in 1982 isolated *oscillatoria* strains and *anabaena* species from three different water supplies in California. Closed-loop stripping followed by gas chromatograph/mass spectrometer proved the presence of geosmin and 2-MIB, which are responsible for earthy-musty tastes and odors in water.

SELECTED ODOROUS COMPOUNDS IN DRINKING WATER

2-Methylisoborneol

2-Methylisoborneol is produced by both cyanobacteria and actinomycetes (Rosen et al., 1970; Izaguirre et al., 1982, 1983; Scholler et al., 2002). It has a musty odor that can be defined as damp basement (Gerber, 1969). Odor threshold for 2-MIB is 1 to 20 ng/L at 45°C (McGuire et al., 1981; Rashash et al., 1997). Customer complaints start at 12 ng/L but the intensity of the odor can be mitigated by the presence of chlorine (Simpson and MacLeod, 1991; Worley et al., 2003). It has a molecular weight of 154.3 g/mol, density of 0.93 g/mL at 20°C, water solubility of 7.3×10^{-5} mg/L and Henry's Law constant of 0.0027 at 25°C (Lalezary et al., 1984; Pirbazari et al., 1992). 2-MIB is produced intracellularly and its release to the water occurs mainly when the algae producing it die and decompose. 2-MIB can not be removed by conventional water treatment operations. It can be partially removed by adsorption onto powdered or granular activated carbon (GAC) (Sontheimer et al., 1988; Lalezary et al., 1988; Kirk et al., 2004) which will not be an adequate treatment if the problem is severe. Oxidation with chlorine, potassium permanganate, or chlorine dioxide is a common water treatment process which cannot eliminate odorous algal metabolites such as 2-MIB and geosmin (Dietrich et al., 1995; Peterson et al., 1995). Their tertiary alcoholic structures make the compounds resistant to oxidation (Wnorowski, 1992; Hu et al., 2003). Ozone and hydrogen peroxide are advanced oxidants that can eliminate 2-MIB, but the efficiency depends on the water quality (Nerenberg et al., 2000). A study by Kim et al. (1997) showed that by using a GAC filter and post-ozonation, taste-and-odor compounds were removed below threshold odor number (TON). Anselme et al. (1988) found

ozonation as an effective method to remove earthy, musty, fishy, and muddy tastes-and-odors from drinking water. Another long-term control measure that is used in United States is application of copper sulphate to surface waters to prevent the algal blooms (Sklenar and Horne, 1999). The chemical formula of 2-MIB is $C_{11}H_{20}O$.

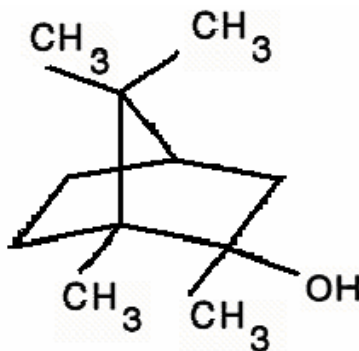


Figure-1.1: Molecular Structure of 2-MIB

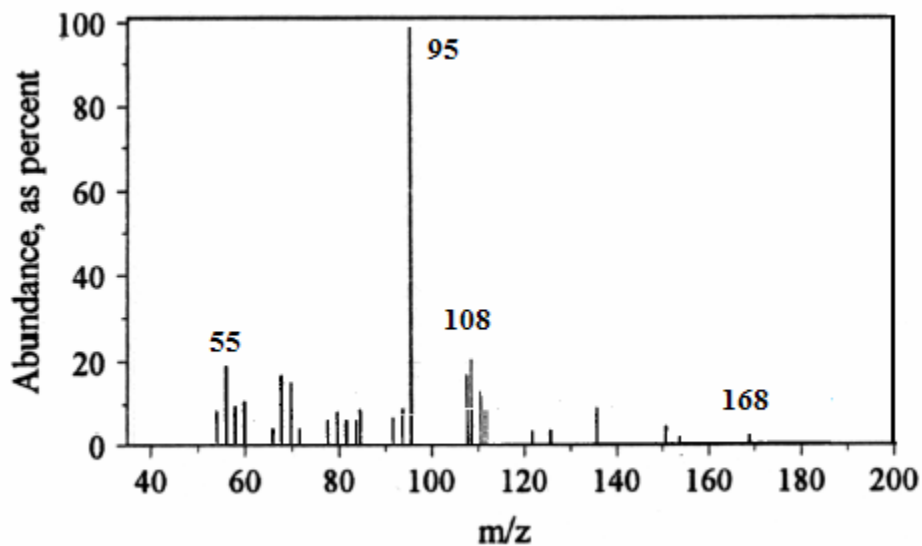


Figure-1.2: Mass Spectrum of 2-MIB

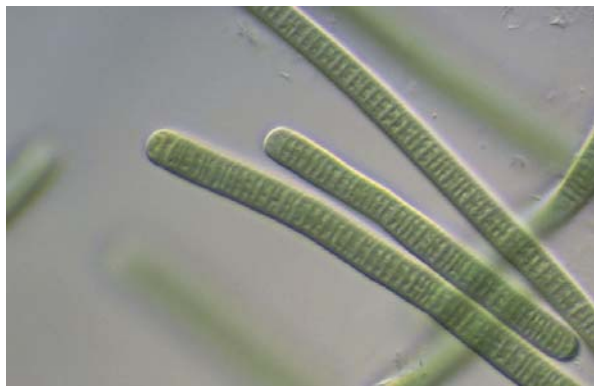


Figure-1.3: *Oscillatoria tenuis*

The off-flavor of canned mushrooms (Whitfield et al., 1983), musty wheat grains (Wasowics et al., 1988; Jelen et al., 2003), and fish (Lloyd and Grimm, 1999) are due to the presence of 2-MIB. It is also discussed that the main aroma compound in Robusta coffee is 2-MIB. 2-MIB is found in Arabica and Robusta coffee at 20 to 1280 ng/L concentrations, depending on the analysis method (Vitzthum et al., 1990). The analyses made on the roasted Robusta coffee proved the presence of 2-MIB and this was explained by microbial contamination (Blank and Grosh, 2002).

Geosmin

Geosmin is produced by both cyanobacteria and actinomycetes (Gerber and LeChevalier, 1965; Safferman et al., 1967; Scholler et al., 2002). It has an earthy odor, which can be defined as dirt, corn silk, and beet. Customer complaints start at concentrations around 7 ng/L (Simpson and MacLeod, 1991). Odor threshold for geosmin is 1 to 10 ng/L at 45°C (McGuire et al., 1981; Rashash et al., 1997). The intensity of the earthy odor is reduced by the presence of chlorine (Worley et al., 2003). It has a molecular weight of 182.3 g/mol, density of 0.95 g/mL at 20°C,

water solubility of 5.5×10^{-5} mg/L and Henry's Law constant of 0.0023 at 25°C (Lalezary et al., 1984; Pirbazari et al., 1992). Geosmin is produced both intracellularly and extracellularly and its release to the water occurs mainly when the algae producing it die and decompose. Geosmin can not be removed by conventional water treatment operations. It can be partially removed by adsorption onto powdered or granular activated carbon (GAC) (Sontheimer et al., 1988; Lalezary et al., 1988; Kirk et al., 2004) which will not be an adequate treatment if the problem is severe. Oxidation with chlorine, potassium permanganate, or chlorine dioxide is a common water treatment process which cannot eliminate odorous algal metabolites such as 2-MIB and geosmin (Dietrich et al., 1995; Peterson et al., 1995). Ozone and hydrogen peroxide are advanced oxidants that can eliminate 2-MIB, but the efficiency depends on the water quality (Nerenberg et al., 2000). A study by Kim et al. (1997) showed that by using a GAC filter and post-ozonation, taste-and-odor compounds were removed below threshold odor number (TON). Another long-term control measure that is used in United States is application of copper sulphate to surface waters to prevent the algal blooms (Sklenar and Horne, 1999).

Chemical name of geosmin is *trans*-1,10-Dimethyl-*trans*-9-decalol. Its chemical formula is $C_{12}H_{22}O$. The CAS number for geosmin is 19700-21-1.

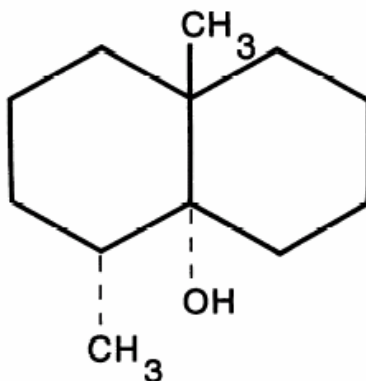


Figure-1.4: Molecular Structure of Geosmin

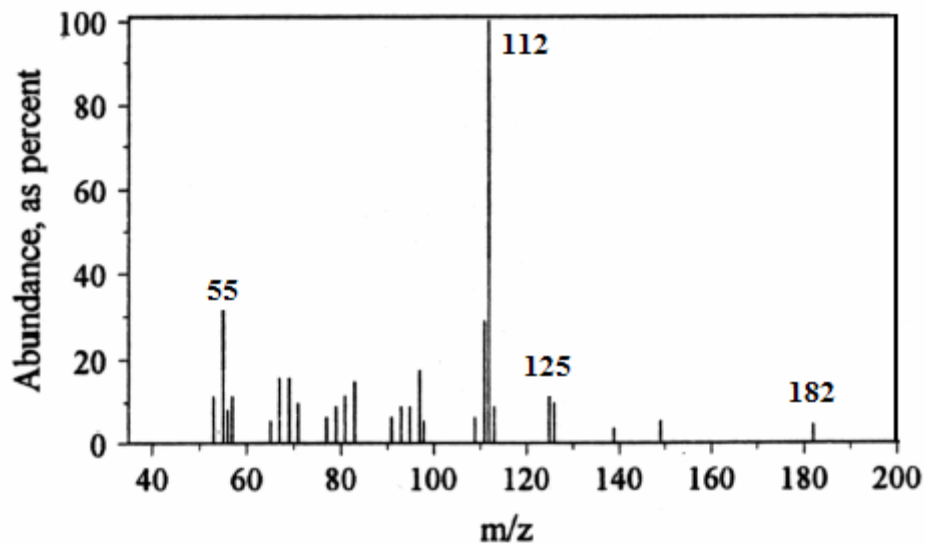


Figure-1.5: Mass Spectrum of Geosmin



Figure-1.6: *Anabaena flos-aquae*

After the detection of an earthy taste and odor in red and white wines, wine samples are analyzed. The results from GC-olfactometry following the extraction of the compound from the samples gave the same odor, which is perceived at tasting. The studies with the GC/MS identified the compound that is responsible for the earthy taste and odor as geosmin (trans-1,10-

dimethyl-trans-9-decalol). Further studies have shown that the compound was also present in the fresh grape juices, suggesting the growth of microorganisms on the grapes (Darriet et al., 2000).

Although red beet is one of the popular vegetables in Europe, its production is low in USA because of the earthy flavor. It is found out by the studies using headspace SPME method, that the compound responsible for the characteristic earthy flavor of the red beets is geosmin. It is found at 10 to 27 ug/kg concentration in beets depending on the cultivar. Due to lack of a quantitative method, it was not known if geosmin is synthesized by microorganisms in soil and taken up by the beets or produced by the beet itself. Studies conducted to solve this issue conclude that red beets are able to synthesize geosmin endogenously (Lu et al., 2003a; Lu et al., 2003b). Geosmin is also observed in fish, dry beans, and canned mushrooms (Buttery et al., 1976b; Lloyd and Grimm, 1999; Maga, 1987).

Geosmin and 2-MIB were isolated and analyzed by SPME-GC/MS from the wheat grains. Geosmin concentrations were found to be at 0.01 to 7.57 ug/kg concentrations. 2-MIB was found at a lower concentration; 0.15 ug/kg. It is observed that the earthy musty odors develop because of the microbial growth due to the inappropriate storage of the grains (Jelen et al., 2003).

Nonadienal

Nonadienal is produced by chrysophytes (Rashash et al., 1995). It has a cucumber, melon odor at 2 ng/L, and has a fishy, waxy odor at 13 ng/L concentration (Rashash et al., 1997). Nonadienal occurs in natural waters at low ng/L concentrations (Burlingame et al., 1992). It has a molecular weight of 138.2 g/mol, density of 0.87 g/mL at 20°C, and Henry's Law constant of 0.0045 at 25°C (Weaste and Astle, 1979; Zander et al., 1997). Oxidation by permanganate or chlorine can remove the cucumber odor of nonadienal (Dietrich et al., 1995).

Chemical name of nonadienal is trans, cis-2,6-Nonadienal and its chemical formula is C₉H₁₄O. The CAS number for nonadienal is 557-48-2.

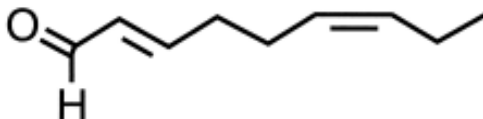


Figure-1.7: Molecular structure of nonadienal

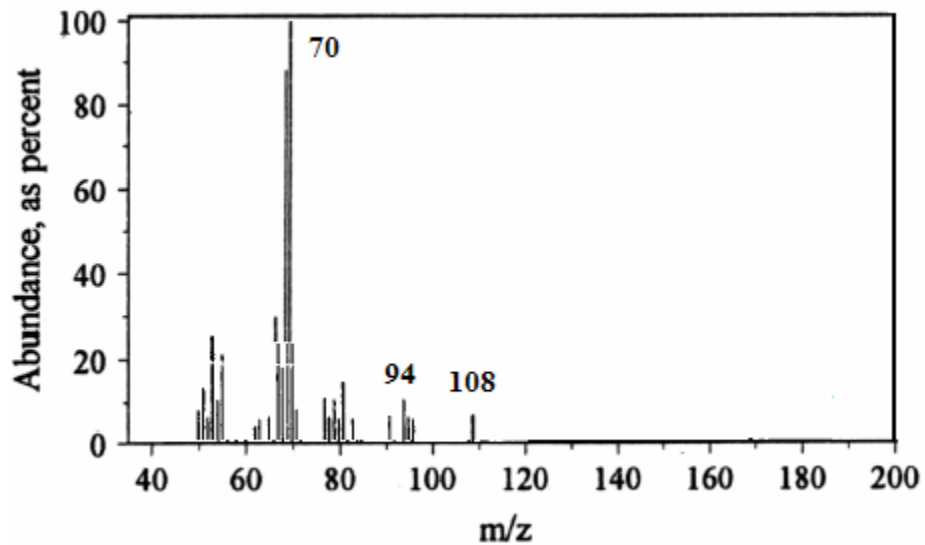


Figure – 1.8: Mass spectrum of nonadienal

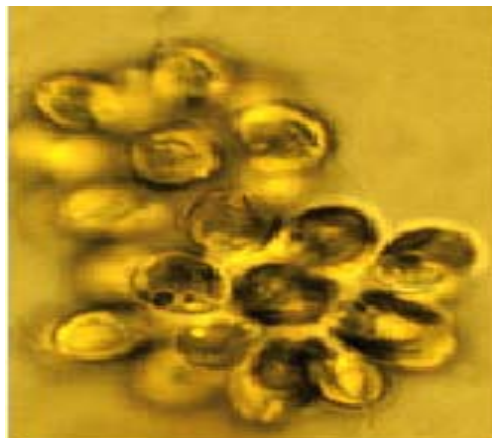


Figure – 1.9: *Synura petersenii*

Studies show that nonadienal is one of the volatile compounds that are isolated and identified from blended cucumber tissue (Forss et al., 1962; Whitfield et al., 1991; Harris et al., 2001, 2002). It is also stated that nonadienal is the chief odor compound from the cucumbers (Schieberle et al., 1990).

Using a headspace SPME method for the analysis of volatile compounds in cantaloupes, 135 volatile compounds are identified including nonadienal. It had the highest concentration in immature samples, and a decrease is observed with the increasing harvest maturity (Beaulieu and Grimm, 2001).

Powdery mildew, which affects both the foliage and berries, is an important disease for the vineyard. The leaves are covered with fungus resulting in aroma defects in grapes and wines. GC/MS and GC/olfactometry are two of the techniques used to determine the main odorants of the diseased grapes. Nonadienal was found to be one of these odorants (Darriet et al., 2002; Pallotta et al., 1998).

In fresh fish, the concentrations of the volatile compounds are very low. Even at small concentrations, some of these volatiles have a strong odor. To analyze the volatiles in the fish tissue, a dynamic headspace sampling method is used in conjunction with MS. The results show that nonadienal is present at the tissues of salmon and mackerel (Refsgaard et al., 1999).

ODOR TESTING IN WATER INDUSTRY

Odor Perception by Humans

The sense of smell is a crucial factor in the human sensation of comfort. The studies show that smell perception is extremely complex and is sole to each individual and changes over time due to the changes of the physical condition and the individual's memory of exposures to similar odors. There are two types of olfactory sensitivities known; specialist and generalist. Generalist olfaction involves vague receptors, and the responses from all of the receptors are processed to obtain the information. Specialist olfaction is limited to a few particular odorants. When the olfactory receptors, which are located at the top of the nasal cavity, are exposed to odor molecules, a stimulus is formed and as a result, smell reaction occurs. The olfactory center in the brain receives the signals, and creates and compares the odor impression with the person's odor memory. The odor memory is based on the person's individual perceptions and social background (Hudson, 2000).

Henry's Law

Before reaching to the receptors, the odorant molecules should dissolve in the mucus. Henry's Law determines the extent, which the odorant molecules can dissolve. Henry's Law states that the solubility of a gas in liquid is a function of the partial pressure of the gas above that liquid. In other terms, the concentration of the gas in the liquid is proportional to the concentration in the atmosphere with the Henry's Law Constant describing the relationship.

Every compound has a unique Henry's Law constant, m (dimensionless), or K_h (pressure-mass per volume) at a specific temperature and pressure and the constant is a key property to predict the environmental behavior of the compound (Altschuh et al., 1999). The equations corresponding to the above two constants are given below;

$$C_{\text{air}} = m * C_{\text{water}}$$

$$P_v = K_H * C_{\text{water}} \quad \text{where;}$$

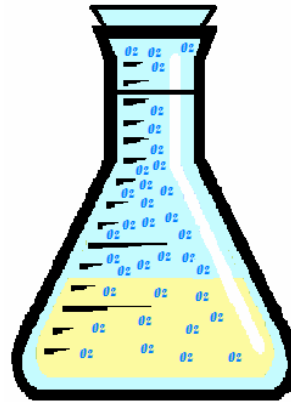
C_{air} : concentration in headspace, (mass/volume)

C_{water} : concentration in water, (mass/volume)

P_v : partial pressure in vapor phase

K_H : Henry's Law constant

m : dimensionless Henry's Law constant



Because Henry's Law constants are temperature dependent, the van't Hoff equation can be used to calculate Henry's Law Constants at various temperatures when one of the Henry's Law Constants at a specific temperature and the enthalpy of the reaction are known. The van't Hoff equation is given below;

$$\ln (m_1 / m_2) = (\Delta H_{\text{soln}} / R) * [(1/ T_2) - (1/ T_1)] \quad \text{where;}$$

m_1 : dimensionless Henry's Law Constant at T_1 ($^{\circ}\text{K}$)

m_2 : dimensionless Henry's Law Constant at T_2 ($^{\circ}\text{K}$)

ΔH_{soln} : enthalpy of the reaction (joule/mole)

R : universal gas constant (8.314 joule/mole. $^{\circ}\text{K}$)

Factors affecting Henry's Law constant values include temperature, pH, compound hydration, compound concentration, complex mixtures, dissolved salts, suspended solids, dissolved organic materials, and surfactants (Staudinger and Roberts, 1996; Lee et al., 2004).

Henry's Law constants have a very broad and important application area. In the environmental engineering point of view, those values are required for remediation systems and transport calculations (Bierwagen and Keller, 2001). Because they are very important, researchers have been trying to develop and improve methods to determine the Henry's Law constants for the compounds of interest.

Solid phase microextraction method is used by Bierwagen and Keller in 2001 for methyl tert-butyl ether, and by Dewulf et al. in 1999 in combination with equilibrium partitioning in closed systems method. The closed loop stripping method was used to determine the constants for taste and odor compounds including 2-MIB and geosmin (Lalezari et al., 1984). With static headspace sampling method the constants can be determined. This method is used by van Ruth et al. in 2001 for the compounds in foods, by Robbins et al. in 1993 to determine the constants of volatile and semi volatile compounds, and Peng and Wan in 1997 for high volatility organic compounds.

Kato and Nishiumi (2002) used headspace gas chromatography to measure the constants of hydrofluorocarbons in alcohols. Ramachandran et al. (1996) used headspace-GC method with varying headspace to liquid ratio to determine the air-water partitioning of toluene, chlorobenzene, and methylcyclohexane. Nirmalakhandan et al (1997) used a different method;

quantitative structure activity relationship model to determine Henry's Law constants and the effect of temperature on the constants and observed that the constants increase with increasing temperature over the range of 10 to 55°C while Brennan et al. (1998) compared and evaluated structure activity relationship model to property activity relationship model to gather more reliable Henry's Law constant data.

Effect of Dissolved Fulvic Acid and Temperature on Henry's Law Constant

Fulvic acid, a low molecular weight natural organic substance that is derived from humus, is soluble in water under all pH values. A study by Chiou et al. (1986) concluded that the water solubilities of selected organic compounds and pesticides increased by presence of dissolved humic and fulvic acids. The solubility of a compound in pure water may be considered as a definite physical constant, but the possible modification of apparent solubility and physical state of the compound by presence of impurities should be considered to determine the behavior under natural conditions. Previous studies show that the solubilities of many hydrophobic compounds are enhanced significantly by low concentrations of dissolved natural organic matter. However, the increase in solubility depends on the polarity and molecular size of the dissolved organic matter (DOM). The decrease in Henry's Law constants may also be related to the cosolute effects such as changed solvency of the matrix or direct solute interaction.

Anderson (1992) studied the effects of surfactants and humic acid on Henry's Law constants of some organic pollutants and observed a noticeable decrease in constants due to the increase of apparent water solubility of the hydrophobic compounds studied.

SENSORY TEST METHODS

Flavor Profile Analysis (FPA)

The FPA method as developed for the food industry (Caircross and Sjöstrom, 1950) and adapted by the Metropolitan Water District of Southern California (Krasner et al., 1985; Suffet et al., 1988; AWWA, 1993). FPA uses a trained panel of at least 4 people to describe the tastes and odors by their intensities and characteristics, based on the standards, by reaching to a consensus (Krasner et al., 1985; Rashash et al., 1997).

In FPA, the sample is given to the trained panel. After tasting and smelling, each panelist rates the sample in terms of its descriptor(s) and intensity(ies). The results are collected by the panel leader and if there is an inconsistency among the results, the panel discusses the differences to reach to a consensus. The descriptor or in other words the character note of the sample is any identifiable characteristic recognized while rating the sample. To rate the intensity a seven-point scale is used: 1 represents the threshold value and the even numbers between 2 and 12 are used for the intensity ratings (Krasner et al., 1985; AWWA, 1993).

Threshold Odor Number (TON)

The TON method has been used to quantify the intensity of an odor in the water sample by serially diluting it with odor-free water until an odor cannot be detected. The method being very simple can also be clumsy. It involves the use of a lot of glassware for the dilutions, and

only an overall odor rating is obtained for a sample without any intensity information (Mallevalle and Suffet, 1987).

TON is calculated from the ratio of sample volume plus dilution volume to the sample volume where the sample volume is 200 mL. The test is conducted generally with only one analyst at 40°C and 60°C. As mentioned above, TON is not a measure for the intensity; it is a measure of persistence of an odor. The method is not used to describe the odors since dilution changes the odor quality.

Attribute Rating Method

The attribute rating method is a new and practical method that uses the discriminative sensory analysis to find out the difference between the standard and the sample. It is straightforward, and the costs are minimal for the training, set up and implementation. The only things required to perform the test is one chemical standard, odor-free water, a water bath, Erlenmeyer flasks, and the human nose.

The method requires sensory analysts who are trained to rate the intensity of a specific odor of the sample by comparing it with a standard having a predetermined intensity. The analyst rates the sample having either more, the same, or less intensity compared to the standard (Lawless and Heymann, 1998; Meilgaard et al, 1999; Dietrich et al., 2004b).

Distribution Rating Method

As one of the surveys of the water utilities revealed, the number one cause of taste and odor complaints is the distribution system (AWWA, 1993). Based on the result of the survey and the studies made, considerable amounts of taste-and-odor compounds accumulate in the distribution system and a sensory method targeted to this phenomenon is appropriate. The rating method evaluates the odors in the sample coming from the distribution system by comparing it to a control that represents the ideal water (water leaving the treatment plant). The sensory analyst is expected to distinguish if the smell of the waters are the same or different (Meilgaard et al., 1999). If they are found out to be different, the difference is described and rated. The test is complete if they smell the same. The rating method is easy to conduct, and the training of the panelists only takes a few hours (Dietrich et al., 2004c).

Two-of-Five Test

The two-of-five odor test is used to determine if there is a difference between two water samples by applying a forced-choice approach. There are five flasks used which of two contains the test sample and the remaining three contains the control water. The sensory analysts that are going to be used should be screened and trained on the sensory testing and basics of the human senses. The analysts sort the flasks into groups of two and three according to their odor characteristics within 5 minutes even they have to guess. If the grouping is correct, the sample water is considered to be different. The test is concluded by describing the difference by choosing one of the common odor attributes from the list.

Because the two-of-five odor test uses the sorting method, it would be correct to say that the probability of guessing the different two flasks is very low because the sorting tests are powerful in statistical point of view. This yields a more reliable result when compared to the other sensory tests that also use guessing. The limit of the sorting tests is the fatiguing effect that results in only one sampling at a time (Dietrich et al., 2004d).

Uses of Odor Testing

Sensory tests are very useful tools for the water industry. Their low cost and easy to conduct properties combined with the ability of early detection of something wrong with the water makes them advantageous over the chemical analyses. Sensory tests can be used for water and wastewater quality monitoring, early warning of something wrong either with the water supply or distribution system, early action taking before affected water gets to the consumers, and responding to consumer complaints quickly by sampling their tap water. Sensory studies, such as TON, were useful to find a relationship between the water temperature, concentration of the taste-and-odor compound, and the concentration of the residual chlorine, which can be used as a tool to solve the consumer dissatisfaction problem (Ito et al., 1988). FPA have been used to assist in detecting the off-flavors in drinking water by The Metropolitan Water District of Southern California (Krasner et al., 1985).

CHEMICAL METHODS TO DETECT ODOROUS COMPOUNDS

Closed-Loop Stripping Analysis (CLSA)

Closed-loop stripping analysis method was developed by Grob and is mainly used for the analysis of the volatile organic compounds at parts per trillion to parts per billion levels (Bruchet, 2004). 1 liter of water sample is warmed up to 45°C and the volatile organic compounds (VOC) are stripped from the water by recirculating a stream of fine bubbled air. A filter containing 1.5 mg of activated carbon at 55 to 60°C removes the compounds from the air, and then the organics are extracted from the filter with about 25 uL of carbon disulfide for further analysis. The CLSA method is modified by using a GC/MS in order to isolate 2-MIB and geosmin from the water sample (Krasner et al., 1981; Bruchet, 2004)

The CLSA method has been used successfully for a long time to obtain useful samples from water. Short processing times and low cost equipment requirement makes the method even more advantageous (Mallevalle and Suffet, 1987). Young and Suffet (1999) developed a new method including CLSA and SDE coupled with GC/MS to analyze the compounds causing taste and odor in drinking water, and Cotsaris et al. (1995) used SDE to identify the odorous metabolites of algae in River Seine.

Gas Chromatography (GC)

After the samples of the organic compounds of interest are obtained at the desired volume, the gas chromatography is used to separate the analytes. When gas chromatography is combined with the mass spectrometry, a large variety of compounds at parts per trillion to parts per billion levels can be detected. GC can also be combined with a flame ionization detector.

Because the partition coefficient is different for the mobile and stationary phases, GC can separate the compounds. The resulting chromatogram peaks are based on the concentration of the compounds injected. The retention time depends on the type of the organic compound. The type of column, its length and diameter, temperature program for the oven, detector type and carrier gas flow are important parameters that should be kept constant for reproducible results.

MS attached to the GC ionizes the compounds with an electron beam, and then by the quadrupole the different fragments are separated depending on their mass to charge ratio. By observing the resulting fragmentation pattern, the compound can be identified. GC combined with MS or FID is a very useful tool in separation of the organic compounds in a sample and identifying them (Mallevalle and Suffet, 1987).

Steam Distillation Extraction (SDE)

Steam distillation extraction method is mainly used by the food industry for food odor analysis (Buttery et al., 1976a), and modified to isolate the taste and odor causing organics in environmental samples. The method has good recoveries of VOCs (Nickerson and Lickens, 1966). When SDE is used in combination with CLSA, more information can be provided on taste and odor causing compounds. Young and Suffet (1999) developed a new method including CLSA and SDE coupled with GC/MS to analyze the compounds causing taste and odor in drinking water, and Cotsaris et al. (1995) used SDE to identify the odorous metabolites of algae in River Seine.

In SDE technique, the water sample and a solvent are heated separately, then mixed, and condensed together. The solvent is recovered since the condensate is separated into two phases. The extracts are ready to be analyzed with GC combined to MS or FID (Anselme et al., 1985).

Purge-and-Trap Technique

The purge and trap technique, after modification, became the basis for the standard protocols implemented by the USEPA. It is most applicable to low molecular weight, non-polar volatile compounds with low water solubility including geosmin and 2-MIB (Bruchet, 2004). The method is based on Henry's Law. The organic compound partitions to the headspace above the water sample and it is adsorbed onto the resin particles. Desorption from the resin trap is accomplished thermally and the analyte is injected to a chromatographic column for detection

(Mallevalle and Suffet, 1987). When the technique is coupled with GC-MS instruments, the detection limits for non- and moderately polar compounds are in 0.02 to 1 ug/L range (Bruchet, 2004).

Sampling is one of the most important issues that should be considered for accurate results. Samples should be headspace free, and biological or chemical reactions that may occur should be prevented by adding reagents or refrigerating the samples (Grob and Kaiser, 1982).

Liquid-Liquid Extraction (LLE)

Liquid-liquid extraction is a simple and widely used method for extracting semi-volatile compounds from liquid samples, which have low molecular weights and having different polarities. Two immiscible liquids are used to separate the analytes of different polarities. A batch operation is developed to analyze the organic compounds in drinking water. LLE is used in combination with MS or FID to analyze the mass of organic compounds (Yohe et al., 1980). LLE is useful when measuring the chemical tastes that are associated by synthetic contaminants and medicinal odors caused by chlorophenols or iodoforms (Bruchet, 2004).

Microextraction and Gas Chromatography-Ion-Trap Detection-Mass Spectrometry

Bao and his colleagues (1997) developed a simple, easy and sensitive method for analysis of taste and odor compounds in water. The compounds examined included geosmin and 2-MIB. Water samples were salted and extracted by microextraction using hexane. Gas

chromatographic-ion-trap detection-mass spectrometry (GC-ITD-MS) was used to analyze the extracts. The method detection limit for geosmin and MIB was 1 ng/L.

Olfactory-GC

When GC-MS is used for analysis of an extract from one of the methods above, up to 150 peaks can be detected and the researcher has to relate the identified compounds to the original sample's overall odor. This problem was solved by Bruchet and his colleagues (2004) by employing a sensory-GC-MS. The method is very useful because a human nose is very sensitive. The odor and the mass spectrum are obtained simultaneously, allowing the analyst to determine the corresponding compound to a GC peak. Important cases were solved with this technique by identifying the correct compound responsible for the off taste-and-odor.

WHAT IS SOLID PHASE MICRO EXTRACTION?

Solid phase microextraction was invented by Pawliszyn in 1989, and it is commercially available since 1994 (Arthur and Pawliszyn, 1990). It is a modern alternative to the at hand sample preparation technology because it has a low cost, eliminates the use of solvents, shortens the analysis time, is highly sensitive and makes the automation of sample preparation possible. The only drawback of the method is its limit for the fiber saturation. This problem can be overcome by diluting the samples. SPME was initially used for water sampling, later it started to be used in environmental, pharmaceutical, forensic and toxicology applications (Pawliszyn, 1997, Potter and Pawliszyn, 1992, Pawliszyn, 1999).

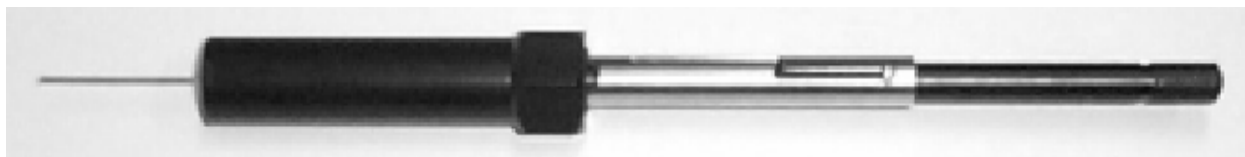


Figure-1.10: SPME Holder

Principles of SPME and its Devices

SPME is very easy to use and suitable method for both on-site analysis and process monitoring. The basic equipment of SPME is a syringe-like device; a fused silica fiber, usually coated with a polymeric phase, connected to a stainless steel tube. The film thickness of fibers range from 7 to 100 μm , and they are 1 cm long. The tube is mounted in a holder that has an adjustable depth gauge. The plunger is stabilized by the z-shaped slot.

During SPME sampling, the needle is inserted to the vial, the plunger is lowered, and the fiber is exposed to the sample solution or headspace. The analytes are allowed to partition into the fiber for a predetermined time. After the sampling is completed, the fiber is retracted into the syringe needle. Then the fiber is exposed to the hot GC injection port where the analytes are thermally desorbed and transferred into the GC column. The fiber is left in the GC inlet for some time to allow complete desorption.

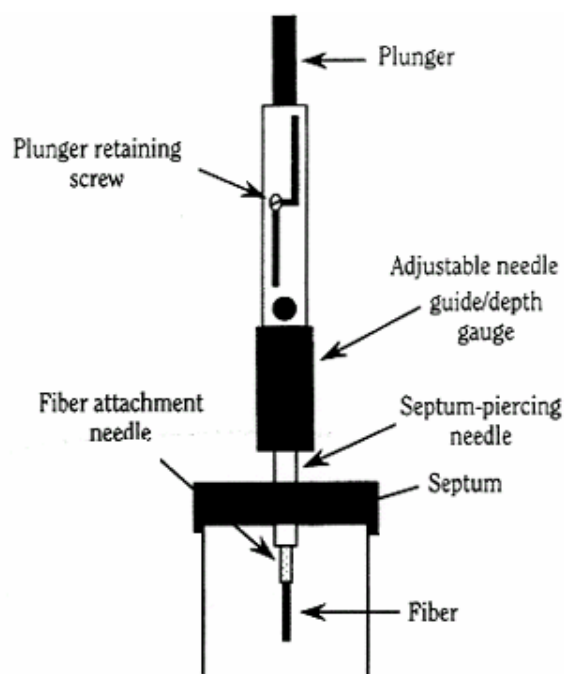


Figure – 1:11: Headspace Sampling with SPME

The first step for the most appropriate sampling is to select the right fiber. The fiber coating is selected based on film thickness and polarity (Wercinski, 1999). Typical film thickness (7 to 100 μm) determines the speed of extraction and capacity. Thicker films result in capacity increase but then the speed of extraction decreases. A thick film may cause the retaining

of the analyte from one sample in the fiber so that it may interfere with the other sample. The most important concern is the selectivity of the fiber. The polarity of the fiber determines its selectivity. Similar polarity of the fiber and the analyte yield the best results. Carboxen/Divinylbenzene is an example of a polar fiber whereas Polydimethylsiloxane is a non-polar fiber. To meet the requirements in every field, different coatings with different thicknesses and polarities are manufactured and are available commercially.

Fibers containing heterogeneous phases such as Polydimethylsiloxane/Divinylbenzene are made by hand coating in several steps. This fiber is a blend of porous particles with a liquid polymer. This fiber is highly porous and retains analytes for a long enough time to enable trace level analyses. The fiber is suitable for polar analytes.

The analytes are extracted by two means; adsorption and absorption. PDMS/DVB type of fibers has a porous solid side as the main extracting phase. Therefore, the extraction is via adsorption. Adsorption is a competitive process because there are a limited number of sites where analytes can attach on the surface of the solid. If there are no sites left for the attachment of the analyte, the fiber is saturated. Saturation phenomenon is an important issue for a linear relationship. Therefore, the sample should have low concentration of the analytes (Gorecki, 1999).

Determination of Amount of Analyte Extracted at Equilibrium

SPME is an equilibration process between the three phases; fiber coating, headspace, and matrix. If loss of mass of analyte by biodegradation or adsorption on walls of flasks is negligible, the equation below can be written;

$$C_o V_s = C_f^\infty V_f + C_h^\infty V_h + C_s^\infty V_m \quad \text{where;}$$

C_o : initial concentration of the analyte in the sample matrix,

C_f^∞ , C_h^∞ , and C_s^∞ : equilibrium concentrations of the analyte in the coating, the headspace, and the sample matrix respectively,

V_f , V_h , and V_s : volumes of the fiber coating, the headspace, and the sample matrix respectively.

The coating/gas distribution constant is defined as $K_{fh} = C_f^\infty / C_h^\infty$ and the gas/sample matrix distribution constant is defined as $K_{hs} = C_h^\infty / C_s^\infty$. The mass of the analyte absorbed by the coating $n = C_f^\infty V_f$ can be calculated from;

$$n = [K_{fh} K_{hs} V_f C_o V_s] / [K_{fh} K_{hs} V_f + K_{hs} V_h + V_s] \quad \text{and,}$$

$$K_{fs} = K_{fh} K_{hs} = K_{fg} K_{gs} \quad \text{where;}$$

K_{fg} : the fiber/gas distribution constant, and

K_{gs} : the headspace/sample matrix distribution constant hence;

$$n = [K_{fs} V_f C_o V_s] / [K_{fs} V_f + K_{hs} V_h + V_s]$$

As can be derived from the equation above, the amount of analyte extracted does not depend on the location of the fiber in the system. The fiber can be placed anywhere in the system provided that the volumes of the fiber coating, headspace, and matrix are kept constant. Because $V_f \ll V_s$, K_{fs} is small and hence the amount of analyte extracted is calculated from;

$$n = K_{fs} V_f C_o$$

The equation above indicates that the amount of analyte extracted does not depend on V_s provided that $K_{fs} V_f \ll V_s$. This enables SPME technique to be used in field sampling (Pawliszyn, 1999).

Physical Effects that Affect SPME

Many parameters should be taken into consideration for reproducible and reliable results with the SPME method. These can be named as; humidity in the matrix, temperature, type of the analyte, sampling time, condition of the injector, fiber positioning during sampling, analyte losses (adsorption on the walls and septa, permeation through septa), stability of GC/MS response, moisture in the needle, sample matrix components (using the same agitators, and solvents), and sample volume. These parameters highly interfere with the results obtained with the SPME method. To ensure the reproducibility and reliability of the results, the parameters mentioned above should be kept constant (Pawliszyn, 1999).

Headspace Analysis Using SPME

In SPME-Headspace sampling, the liquid or solid sample is placed in a vial with a headspace and sealed. After the equilibrium between the sample and the headspace is established, the fiber is inserted into the vial without contacting the sample. If the analyte is volatile, it is easily and quickly concentrated in the headspace and hence on the coating of the fiber. This shortens the time of extraction (Zhang and Pawliszyn, 1993; Chai and Pawliszyn, 1995).

The ideal case for a quantitative analysis would be the complete transfer of the analyte to the SPME fiber. Since quantitative transfer is impossible for SPME, a better approach would be to seek a linear relationship between the amount of extracted analyte, and its initial amount in the sample. This relationship helps to predict the concentration of the analyte in the sample matrix by just analyzing the amount sorbed to the fiber.

In headspace sampling, there are three phases involved; fiber coating, headspace and sample matrix. The analyte diffuses from sample matrix to the headspace and then to the fiber coating. The equilibrium between the phases depends on the sampling conditions and the nature of the analyte. The analysis can be conducted at non-equilibrium situations, and the amount of analyte extracted will be depending on the sampling time. If the sampling time is held constant, there will be a linear relationship between the amount of analyte extracted and the initial amount of the analyte in the sample matrix (Pawliszyn, 1999).

SPME is a widely used technique for analysis of geosmin and 2-MIB in water samples. In a study by Lloyd, 1998, a method was developed using SPME/GC/FID for rapid quantitative analysis of 2-MIB and geosmin. Watson in 1999, coupled SPME with GC/MS to monitor taste and odor compounds in surface waters and concluded that the method was very useful in identification and monitoring of the taste and odor compounds of interest in surface waters. In another study by Watson in 2000, headspace SPME method is used to analyze trace levels of geosmin and 2-MIB in source and drinking waters. Because geosmin and 2-MIB are not only found in drinking water but also some foods, SPME is also used by food scientists to determine the quantities of the mentioned compounds. In a study by Lu, 2003(a), headspace SPME is used to determine the amount of geosmin in red beets. In order to reveal the compounds responsible for fresh cucumber flavor, again SPME is used in combination with GC/FID (Harris et al., 2001) Treves et al. (2001), employed SPME to determine octanol-air partition coefficients of hydroxy alkyl nitrates. Lee et al. (2003) used SPME to evaluate the partition coefficient of important environmental pollutants, and concluded that the conventional method, liquid-liquid partition (LLP), was underestimating the coefficient. SPME method was also valuably used in food industry to determine and analyze the flavor compounds. Jung and Ebeler (2003), Rocha et al. (2001), Jelen et al. (1998), and Yang and Pepard (1994) are some examples of such studies.

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CHAPTER II
DETERMINATION OF TEMPERATURE DEPENDENT HENRY'S LAW CONSTANTS
OF ODOROUS CONTAMINANTS AND THEIR APPLICATION TO HUMAN
PERCEPTION

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ABSTRACT

A new method was developed to determine Henry's Law constants at varying temperatures and to calculate enthalpies of reactions for volatilization of aqueous compounds. The method was applied to 2-methylisoborneol, geosmin, and *trans*-2, *cis*-6-nonadienal, which are three of the major odorous compounds found in water. The method used static headspace equilibrium in standard odor analysis flasks and SPME-GC/MS. Dimensionless Henry's Law constants were determined at 20, 25, 32, and 39 °C. Their values ranged from 0.002 to 0.02 and increased with increasing temperature. The study was continued by determining the effects of different concentrations of fulvic acid added to the aqueous media. Decreases of 5 to 40% in Henry's Law constants were observed when fulvic acid was present; however the decrease was not correlated with the fulvic acid concentration. Fulvic acid at any concentration caused a small decrease in constants for geosmin and 2-MIB, yet a more substantial decrease was obtained for nonadienal. Finally, the gas phase concentrations were predicted using measured Henry's Law constants for known aqueous concentrations of 2-MIB, geosmin, and nonadienal at 25 and 45 °C.

An increase in the gas phase concentration was not correlated to an increase in human perception as determined by a trained human panel. It is concluded that after some point, panelists were not able to perceive an increase in the odorant concentration. This has important implications for controlling nuisance odors in the environment.

Key words: *Henry's Law constant, taste-and-odor, 2-MIB, geosmin, nonadienal, drinking water, SPME-GC/MS, fulvic acid, FPA*

INTRODUCTION

Understanding the fate, transport, and sensory perception of environmental odorous compounds is critical to producing acceptable flavored drinking water and controlling the odorants in natural waters. Undesirable odors in drinking water are a global problem, which has been identified in the Americas, Australia, Europe, Africa, and Asia (1, 2, 3). Three of the most common source water related odor problems in drinking water are earthy odors caused by geosmin, musty odors caused by 2-methylisoborneol (2-MIB), and cucumber odors caused by trans,cis-2,6-nonadienal (nonadienal). Consumer acceptance of drinking water is crucial to the success of the drinking water industry, which spends millions of dollars to deal with taste-and-odor problem (4). Although consumers can detect and may accept changes in hardness, temperature, color, chlorine concentration, or salinity in their tap water, they often take offense to off tastes-and-odors in drinking water and natural waters used for recreation (1, 5).

2-Methylisoborneol, produced by both cyanobacteria and actinomycetes (6, 7) has a musty odor that can be defined as damp basement (8). There is a range of concentrations at which people with a normal sense of smell can detect 2-MIB. For aqueous solutions, the human odor threshold value is in the range of 2-20 ng/L at 45°C (9), and customer complaints in drinking water start at about 12 ng/L (10). Geosmin, or *trans*-1,10-dimethyl-*trans*-9-decalol, is produced by both cyanobacteria and actinomycetes (7, 11). It has an earthy odor, which can be defined as dirt, corn silk, and beet (9). Customer complaints start at concentrations around 7 ng/L (10) and the odor threshold for geosmin is in the range of 6-10 ng/L at 45°C (9). In 1992, Mattheis and Roberts (12) identified geosmin as a metabolite of *Penicillium expansum* one of the fungi responsible for losses of fruits such as pears, apples, and cherries after harvest.

Both 2-MIB and geosmin are produced intracellularly and extracellularly. The release of the two compounds to waters occurs mainly when the source algae come to the stationary growth phase or die and decompose (13). Geosmin and 2-MIB occur in water at concentrations at few ng/L concentrations (14) to greater than 800 ng/L (15). Neither compound is well removed by conventional water treatment operations, but both can be partially removed by adsorption onto granular activated carbon (GAC) (16, 17) or powdered activated carbon (PAC) (18) which will not be an adequate treatment to remove odors if the problem is severe. Also if natural organic matter is present in the water, efficiency of treatment with PAC is decreased (19, 20). Oxidation with chlorine, potassium permanganate, or chlorine dioxide is a common water treatment process but it cannot eliminate odorous algal metabolites such as 2-MIB and geosmin (21, 22), because the tertiary alcoholic structures of the compounds make them resistant to oxidation (23). Advanced oxidation with ozone and hydrogen peroxide can effectively eliminate 2-MIB and

geosmin, but the efficiency depends on the water quality such as pH, alkalinity, and dissolved organic matter (24). Another control measure that is used in United States is application of copper sulphate to surface waters to prevent the algal blooms (25). The persistence of geosmin and 2-MIB in source and treated waters makes them a nuisance to consumers. However they are desirable components of many foods such as beets, corn, and coffee. The main aroma compound in Robusta coffee is 2-MIB and it is found in Arabica and Robusta coffee at 20 to 1280 ng/L concentrations (26). Geosmin is responsible for the characteristic earthy flavor of the red beets and it is found at 10 to 27 ug/kg concentration in beets depending on the cultivar (27).

Nonadienal, or trans,cis-2,6-Nonadienal, is produced by *Synura petersenii*. It has a cucumber, melon odor between 2 to 13 ng/L, and the odor becomes fishy, waxy odor at higher concentrations (9). Nonadienal occurs in natural waters at low ng/L concentrations (28). Studies show that nonadienal is one of the volatile compounds that are isolated and identified from blended cucumber tissue (29, 30) and is the main component of cucumber-odor. The physical properties of the compounds are summarized in Table-2.1.

Table-2.1: Physical Properties of the Taste-and-Odor Compounds

Property	Geosmin	2-MIB	Nonadienal
OTC (ng/L)	6 – 10 ^{e, g}	2 – 20 ^{e, f}	2 – 13 ^{d, f}
m at 20°C	0.0023 ^{a, b}	0.0027 ^{a, b}	0.0045 ^g
Molecular Weight (g/mol)	182.31 ^{a, b}	154.25 ^{a, b}	138.21 ^h
Density at 20°C (g/mL)	0.949 ^{a, b}	0.929 ^{a, b}	0.868 ^c
Water Solubility at 20°C (mg/L)	150.2 ^{a, b}	194.5 ^{a, b}	---
Vapor Pressure (atm)	5.49 x 10 ^{-5 a, b}	7.26 x 10 ^{-5 a, b}	---

a. (49), b. (50), c. (52), d. (28), e. (53), f. (9), g. (51)

Odorous compounds can be monitored by sensory tests, which are important and increasingly used tools for the water industry and environmental applications (32). Their low cost and easy to conduct properties combined with the ability of quick detection of an off-odor in water makes them advantageous over chemical analyses. Sensory tests can be used for water and wastewater quality monitoring, early warning of problems with water supply or distribution system, assessing treatment and responding to consumer complaints quickly by sampling their tap water. For odorous compounds, it is important to understand the vapor phase concentrations that individuals can detect. This will allow for assessing the detectability of an odorant in the shower, household, or outdoors.

The Flavor Profile Analysis method was developed for the food industry (33) and adapted to the water industry to assess odors when samples are obtained from source or drinking (treated) water supplies (34, 35). FPA uses a trained panel of at least 4 people to describe the tastes and odors. After tasting and/or smelling a sample, each panelist rates the sample in terms of its descriptor(s) and intensity(ies). To rate the intensity a seven-point scale is used: 1 represents the threshold value and the even numbers between 2 and 12 are used for the intensity ratings. The Weber-Fechner Law is usually applied to yield a straight line for the relationship between the log concentration of the odorant and the FPA intensity. For geosmin and 2-MIB, a concentration of about 15 to 30 ng/L produces an FPA intensity of 4.

Because these compounds produce very noticeable odors at low ng/L concentrations, very sensitive analytical techniques are required to perform quantitative measurements. Solid phase microextraction is a widely used technique for analysis of geosmin, 2-MIB, and nonadienal in water samples (36) and food (27, 30, 37, 38).

In headspace sampling, there are three phases involved; fiber coating, headspace and sample matrix. The analyte diffuses from sample matrix to the headspace and then to the fiber coating. Equilibrium between the SPME fiber and the headspace depends on the sampling conditions and the nature of the analyte. The analysis can be conducted at non-equilibrium situations, and the amount of analyte extracted will be depending on the sampling time. For a constant sampling time, there is a linear relationship between the amount of analyte extracted and the initial amount of the analyte in the sample matrix (39). However, the three phase equilibrium system may yield erroneous results due to the disturbance of the equilibrium

between the gas and aqueous phases because of removal of the compound from the gas phase by sorption onto the SPME fiber. In that case equilibrium shifts, and more of the compound goes to the headspace and hence to the SPME fiber.

With the development of static headspace sampling, partitioning constants, such as Henry's Law constants, were measured for the compounds in foods (40), in water for the volatile and semi-volatile compounds (41), and high volatility organic compounds (42). Solid phase microextraction method was used by Bierwagen and Keller (2001) (43) for methyl tert-butyl ether and by Dewulf et al. (1999) (44) in combination with equilibrium partitioning in closed systems method which was limited to measure the constants of the compounds with m values greater than 0.06 and with a standard deviation in the range of 1 to 20 % for $n = 99$ replicates.

Henry's Law can be applied to relate vapor phase and aqueous phase concentrations of odorants. Every compound has a unique Henry's Law constant, m (dimensionless), or K_H (mol/L-atm) at a specific temperature and pressure, and the constant is a key property to predict the compound's environmental behavior (45). The equations corresponding to the above two constants are given below;

$$C_{\text{air}} = m * C_{\text{water}}$$

$$P_v = K_H * C_{\text{water}}$$

$$K_H \times R \times T = m \quad \text{where;}$$

C_{air} : concentration in headspace, (mass/volume)

C_{water} : concentration in water, (mass/volume)

P_v : partial pressure in vapor phase

K_H : Henry's Law constant (mol/L-atm)
m: dimensionless Henry's Law constant
R: universal gas constant (0.082057 L-atm/mol-°K)
T: temperature in °K

Because Henry's Law constants are temperature dependent, the van't Hoff equation can be used to calculate Henry's Law Constants at various temperatures. The van't Hoff equation is;

$$\ln (m_1 / m_2) = (\Delta H_{\text{soln}} / R) \times [(1/ T_2) - (1/ T_1)] \quad \text{where;}$$

m_1 : dimensionless Henry's Law Constant at T_1 (°K)

m_2 : dimensionless Henry's Law Constant at T_2 (°K)

ΔH_{soln} : enthalpy of the reaction (joule/mole)

R: universal gas constant (8.314 joule/mole.°K)

Henry's Law constants have very broad and important applications from remediation systems and transport calculations (43) to odor prediction (19). Researchers have been trying to develop and improve methods to determine the Henry's Law constants particularly at various temperatures and water quality conditions such as pH, alkalinity, and dissolved organic matter. Methods have evolved as analytical chemistry has evolved, moving from dynamic methods to static headspace methods with SPME-GC/MS detection.

Fulvic acid, a low molecular weight natural organic substance that is derived from humus, is soluble in water under all pH values and increases the water solubilities of selected organic compounds and pesticides (46). The solubility of a compound in pure water may be considered as a definite physical constant, but the possible modification of apparent solubility and physical state of the compound by presence of impurities should be considered to determine

the behavior under natural conditions. Previous studies showed that the solubilities of many hydrophobic compounds are enhanced significantly by low concentrations of dissolved natural organic matter and this would affect the value of K_H . Anderson (1992) (47) studied the effects of surfactants and humic acid on Henry's Law constants of some organic pollutants and observed a noticeable decrease in constants due to the increase of apparent water solubility of the hydrophobic compounds studied.

To understand the fate and sensory perception of the odorous compounds in natural and processed drinking waters, it is necessary to predict their vapor phase concentrations at different temperatures and water quality conditions. Henry's Law constants could do this if available and the temperature dependence for most of the compounds could be predicted.

The objectives of this study were to develop a headspace-SPME method for measuring the dimensionless Henry's Law constants for geosmin, 2-MIB, and nonadienal at selected temperatures; to use these data to calculate the enthalpy of reaction for gas-aqueous transfer and the Henry's Law constants at any temperature; and predict the gas phase concentrations of drinking water odorants and compare the results with the human sensory data.

MATERIALS AND METHODS

Reagents. The high-purity chemicals: geosmin (CAS 16423-19-1), *trans*-2, *cis*-6-nonadienal (CAS 557-48-1), 2-methylisoborneol (CAS 2371-42-8), benzaldehyde (CAS 100-52-7) were purchased from Supelco (Bellefonte, PA). Nanopure[®] ultrapure water (Barnstead/Thermolyne, model #D4744, Dubuque, IA) was used as reagent water for the experiments.

Optima grade Methanol (CAS 67-56-1; Fisher Scientific) was used for the preparation of the standard solutions. 5% Dimethyl dichlorine silane (DMDCS) in toluene (CAS 75-78-5) and 99.5% toluene were purchased from Sigma-Aldrich Chemical (St. Louis, MO). Suwannee River Fulvic Acid reference material was obtained from International Humic Substances Society.

SPME-GC/MS Analysis. Solid Phase Microextraction holders consisted of 65 μm PDMS/DVB crosslinked fibers (Supelco, Bellefonte, PA) were used at a manual sorption and desorption mode. Sorption time was 10, 20, or 30 minutes depending on the experiment: all standards and samples were sorbed for the same time for a given experiment, and desorption time for all compounds was 3 minutes. An Agilent 6890 Series GC System connected to Agilent 5973 Network Mass Selective Detector was operated in splitless mode with a 0.75 mm ID injection sleeve (Supelco, Bellefonte, PA), total helium flow of 24 mL/min, inlet temperature of 220°C, and 80 kPa pressure. J&W DB-5 capillary (30.0 m x 250 μm x 0.3 μm nominal) column with 325°C maximum temperature was used for all compounds.

For geosmin, the GC/MS was operated with an initial temperature of 100°C, ramped at a rate of 20°C/min to 210°C; m/z values 112, 125, and 182 were monitored in selective ion mode and geosmin eluted at 5.25 minutes. For 2-MIB, the GC/MS was operated with an initial temperature of 60°C, ramped at a rate of 20°C/min to 180°C; m/z values 95, 108, and 168 were monitored in selective ion mode and 2-MIB eluted at 5.39 minutes. For nonadienal, the GC/MS was operated with an initial temperature of 100°C, held at that temperature for 2 minutes, ramped at a rate of 20°C/min to 170°C; m/z values 41, 70, 94, and 108 were monitored in selective ion mode and nonadienal eluted at 4.59 minutes. For benzaldehyde, the GC/MS was operated with an initial temperature of 50°C, held at that temperature for 1 minute, ramped at a rate of 10°C/min to 160°C; m/z values 77, 105, and 106 were monitored in selective ion mode and benzaldehyde eluted at 4.29 minutes.

Glassware. The same flasks used for odor analysis (Standard Methods 2150) were also used for measurement of odorant partitioning in this research. Kimax[®] 500 mL wide mouth Erlenmeyer flasks (Fisher Scientific) were modified to have narrow longer mouths to minimize the loss of compound, septum sampling ports (equivalent to a VOA vial cap) on the sides to insert SPME fiber into the flask and a stopcock valve at the bottom to remove the liquid from the flask after the equilibrium between the gas and liquid phases was reached to reduce the system to a two phase equilibrium between the gas phase and the SPME fiber (Figure-2.1). All of the flasks were silanized and washed with Sparkleen[®] (Fisher Scientific) detergent. Standard solutions of each compound were prepared in methanol at 4, 2, 1, 0.5, 0.25, 0.1, 0.04, 0.02, 0.01, and 0.002 mg/L concentrations.

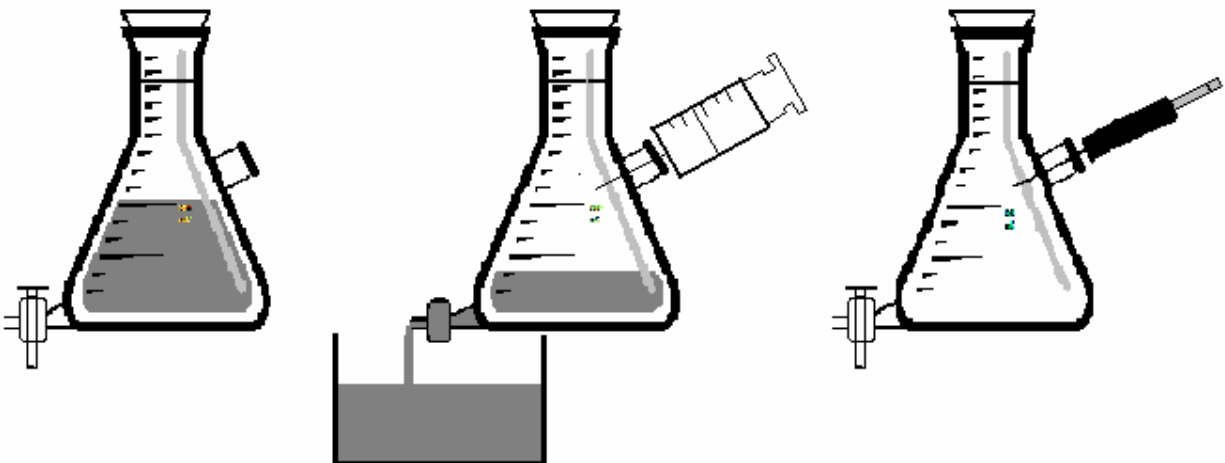


Figure-2.1: Schematic of the flasks: Equilibration, removing the water, SPME sampling

Henry's Law Constants. For each temperature, all glassware, reagent water, and odorant solutions were stored and prepared in a constant temperature room adjusted to the desired temperature (20, 25, 32, or 39°C). The conditions used to measure m simulated those standard odor analyses recommended for Flavor Profile Analysis, namely 200 mL of odorant solution in a 500 mL Erlenmeyer flask. To determine Henry's Law constant, a known mass of odorant and 200 mL reagent water were added to the Erlenmeyer flask, the odorant was allowed to equilibrate between the gas and aqueous phase for 1 hour. The flask was emptied by opening the stopcock valve at the bottom and injecting clean purified air with a glass syringe through the sampling port on the side, then the gas phase concentration was measured by SPME-GC/MS, and the remaining aqueous concentration was calculated by difference (Figure-2.1). The reason for emptying the flask was to obtain a two phase system while sampling with SPME and eliminating the effect of affected partitioning constants between the gas-aqueous, and gas-fiber phases. If the liquid was not removed, the initial equilibrium obtained between the gas and aqueous phase would be disturbed by the removal of the compound from the gas phase by the SPME fiber and

more of the compound would go into the gas phase and hence into the fiber leading to erroneous results for the gas phase concentration.

Concentrations of 20, 30, 100, or 200 ng/L were prepared by adding 4, 6, 20, or 40 μL of a 1 mg/L odorant solution into a silanized 500 mL Erlenmeyer flask containing 200 mL of reagent water. The flasks were shaken and allowed to equilibrate for 1 hour. The aqueous phase was removed by displacement. The silanized glassware assured that the aqueous solution was readily and completely removed.

After no aqueous solution remained, the concentration of odorant in the gas phase was determined by adsorption to the SPME fiber and desorption into the GC/MS as previously described. To quantify the mass of odorant on the fiber, a standard curve was prepared using gas phase odorant concentrations in 500 mL silanized flasks. The change in concentration because of displacement of water with clean air was taken into consideration and corrected with a factor calculated by the ratio of volume change.

The standard curves for each compound at desired temperatures (20, 25, 32, and 39°C) were determined by preparing different concentrations at gas phase in the flasks by injecting 10 μL of 0.04, 0.02, 0.01, and 0.002 mg/L concentrated standard solutions and letting a sorption time of 10, 20, or 30 minutes. The amount of compound that is sorbed onto the fiber is analyzed by GC/MS, and linear curves were obtained for all three compounds at all temperatures.

Fulvic Acid. To determine the effect of presence of fulvic acid on Henry's Law constants, the method described above was repeated at 25°C for all three compounds. Concentrations of 2, 5, and 8 mg/L Suwannee River Reference Standard fulvic acid in reagent water were placed into silanized 500 mL Erlenmeyer flasks to a volume of 200 mL. The procedure described above for measuring Henry's Law constants was applied for each compound at 100 ng/L and 200 ng/L.

Method Validation. For the justification of the method, benzaldehyde was used. The method described above was applied at 20°C to measure the Henry's Law constant of benzaldehyde.

Statistical Analysis. Excel one-way ANOVA was performed with an alpha value of 0.05 as the significance level to determine if there was a difference between the Henry's Law constants with and without fulvic acid and Bonferri multiple comparison was performed to determine if there was a difference between the Henry's Law constants at different fulvic acid concentrations in reagent water.

RESULTS AND DISCUSSION

Method Validation. In this section the data obtained for 2-MIB at 20 °C at 30 and 100 ng/L concentrations and for 20 minutes sorption time is presented. The data for sorption curves for 3 replicates and four different temperatures (20, 25, 32, and 39 °C) is shown in Figure-2.2. As can be seen from the graph, the data points of the sorption curve were linear and the best line

drawn by using Excel has the equation as $\text{Mass} = (\text{Area} - 48.7) / 20778$ with r^2 being equal to 0.9988. For all three compounds, the sorption curves at all temperatures yielded linear data points and the lines drawn through them had r^2 values very close to 0.99.

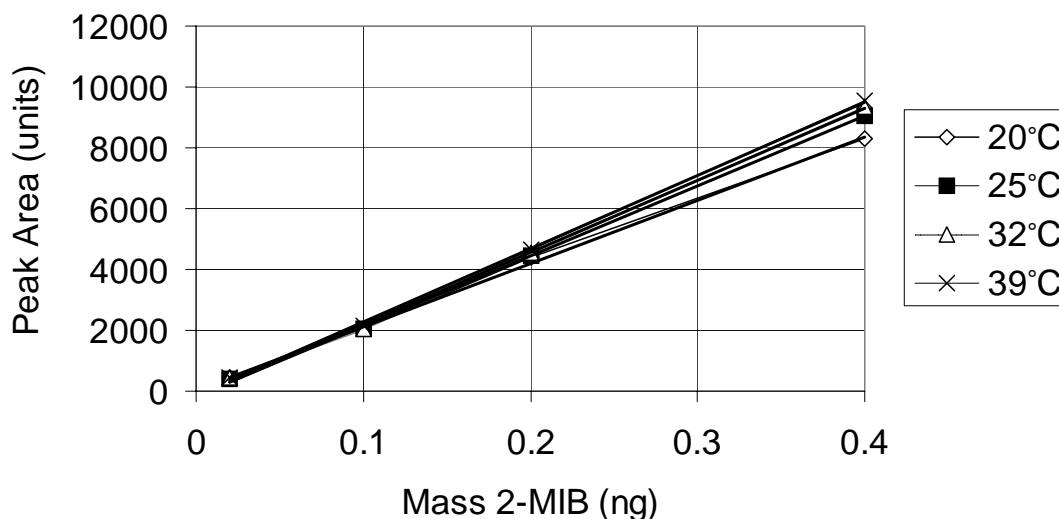


Figure-2.2: Sorption Curve for 2-MIB at 20, 25, 32, and 39°C for 20 minutes sorption time

The measured Henry’s Law constants’ data for 2-MIB at 20°C are summarized in Table-2.2. When the results were compared to the results of a similar study made by Lloyd et al. (36), it was observed that the standard deviation and coefficient of variations were similar.

Table-2.2: SPME/GC/MS Data for 2-MIB at 20°C

Concentration (ng/L)	Mean Peak Area ¹	Coefficient of Variation (%)
30	422 ± 33	4.98
100	1273 ± 172	8.60

¹ n = 5 replicates, mean ± standard deviation

When the reagent water in the flask was expelled and replaced with clean air, the concentration of the odorant in the flask decreased. To overcome this dilution effect, the peak area values obtained from SPME-GC/MS were multiplied by 550/350. The initial headspace volume was 350 mL, and when the water was removed it became 550 mL. Hence the corrected peak area values for 2-MIB at 30 and 100 ng/L are 663 and 2000 area units respectively. The equation found from the sorption curve was then used to calculate the mass of odorant in the headspace. For example, for 30 ng/L concentration the corrected peak area value is 663 and by using the equation “Mass = (Area - 48.7) / 20778” the mass of odorant is calculated as 0.0296 ng. Similarly for 100 ng/L, the mass of odorant is 0.0939 ng. Then the mass in the reagent water after equilibrium was reached is calculated from the difference between the initial mass of odorant added to the flask and the mass of odorant in the gas phase. The initial mass of odorant added to the flasks were 6 and 20 ng, and the mass of odorant in aqueous phase is calculated as 5.97 and 19.906 ng for 30 and 100 ng/L concentrations respectively. The dimensionless Henry’s Law constants are calculated as the ratio of the concentration of the odorant in the headspace to the concentration of the odorant in the aqueous phase. Therefore, the Henry’s Law constant for 2-MIB at 20°C for 30 ng/L concentration is calculated as $(0.0296 \text{ ng} / 350 \text{ mL}) / (5.97 \text{ ng} / 200 \text{ mL}) = 0.0028$, and the constant for 100 ng/L concentration is calculated as 0.0027. The above calculations explained here are based on the average area units. But in our calculations, each area value for five replicates was taken individually and Henry’s Law constants for each value was calculated. Consequently, the standard deviations for 30 and 100 ng/L could be calculated as 0.0003 and 0.0002 respectively. These calculation steps were repeated for all temperatures, all concentrations, and all odor compounds to calculate and then predict the Henry’s Law constants. When all of the constants were calculated, the enthalpy of each reaction was calculated by using

all combinations of two Henry's Law constants at all temperatures. By using Excel's Goal Seek function, the Henry's Law constants were predicted to obtain a common enthalpy value. This was accomplished by entering the enthalpy value found by van't Hoff equation to the "set cell" box, entering the "to value" box a common (average of all calculated) enthalpy determined, and entering one of the m values to the "by changing cell" box.

As can be seen from Figure-2.2, the slope of the sorption curves for all temperatures were very close, yielding comparable percent sorption values to the SPME fiber. For geosmin the percent sorption was approximately 20% for 30 minutes sorption time, for 2-MIB 16% for 20 minutes sorption time, and for nonadienal it was approximately 3.5 % for 10 minutes sorption time with the 65 μm PDMS/DVB fiber. This demonstrates that at low nanogram levels the percent sorption is constant regardless of the increasing concentration of odorants, and the fiber is not saturated.

The method is further validated in experiments with benzaldehyde. At 20°C the measured Henry's Law constant was 0.00086 and this value was very comparable with the constants given in literature 0.00084 (48, 49).

Henry's Law Constants for Odorants. Henry's Law constants for geosmin, 2-MIB, and nonadienal were determined in reagent water at 20, 25, 32, and 39°C. For all of the compounds the constants increased with the increasing temperature. In Figure-2.3, measured Henry's Law constants at four different temperatures for the three compounds of interest are shown. The enthalpy of the reaction for each compound was determined by van't Hoff equation by using

combinations of two Henry's Law constants at different temperatures. To obtain a common enthalpy value for each compound, Excel's "Goal Seek" command was used to predict the Henry's Law constants. In the goal seek function, the van't Hoff equation was used and the enthalpies were calculated in excel, the goal set for the command was to obtain a common enthalpy value by adjusting the Henry's Law constants. As can be seen from Table-2.3, the Henry's Law constants measured analytically and predicted empirically by Goal Seek using the common enthalpy were very close. Also the measured constants were comparable to the 20°C constants found in literature, for example for 2-MIB the m was measured to be 0.028 and the m given in the previous research report was 0.0027. The Henry's Law constants and enthalpies for geosmin and 2-MIB, and the constants' increase with temperature were very similar. This may be because of similar molecular structure and physical-chemical properties. For nonadienal the increase in constants with increasing temperature was less than geosmin and 2-MIB. The enthalpy values for all three compounds, measured and averaged analytically and predicted empirically, are given in Table-2.4.

Table-2.3: Measured and Predicted Henry's Law Constants Data for Three Compounds

Compound	Geosmin		2-MIB		Nonadienal	
	m_{measured}^1	$m_{\text{predicted}}^2$	m_{measured}	$m_{\text{predicted}}$	m_{measured}	$m_{\text{predicted}}$
Temperature (°C)						
20	0.0028 $\pm 0.0003^3$	0.0023	0.0028 ± 0.0002	0.0027	0.0036 ± 0.0001	0.0035
25	0.0054 ± 0.0005	0.0043	0.0042 ± 0.0002	0.0047	0.0044 ± 0.0002	0.0050
32	0.0096 ± 0.0004	0.0097	0.0090 ± 0.0003	0.0090	0.0083 ± 0.0005	0.0085
39	0.0213 ± 0.0007	0.0214	0.0199 ± 0.0007	0.0199	0.0140 ± 0.0003	0.0163

¹ n = 5 replicates

² Predicted using measured m values and Excel's Goal Seek

³ Standard deviation

Table-2.4: Measured and Predicted Enthalpy Data for Three Compounds (kJoule/mole)

Geosmin		2-MIB		Nonadienal	
$\Delta H_{\text{measured}}^1$	$\Delta H_{\text{predicted}}^2$	$\Delta H_{\text{measured}}$	$\Delta H_{\text{predicted}}$	$\Delta H_{\text{measured}}$	$\Delta H_{\text{predicted}}$
82.5 \pm 13.3	89	78.7 \pm 9.9	80	51.8 \pm 11.3	57.5

¹ Mean \pm Standard deviation for n = 6 values

² Predicted by Goal Seek

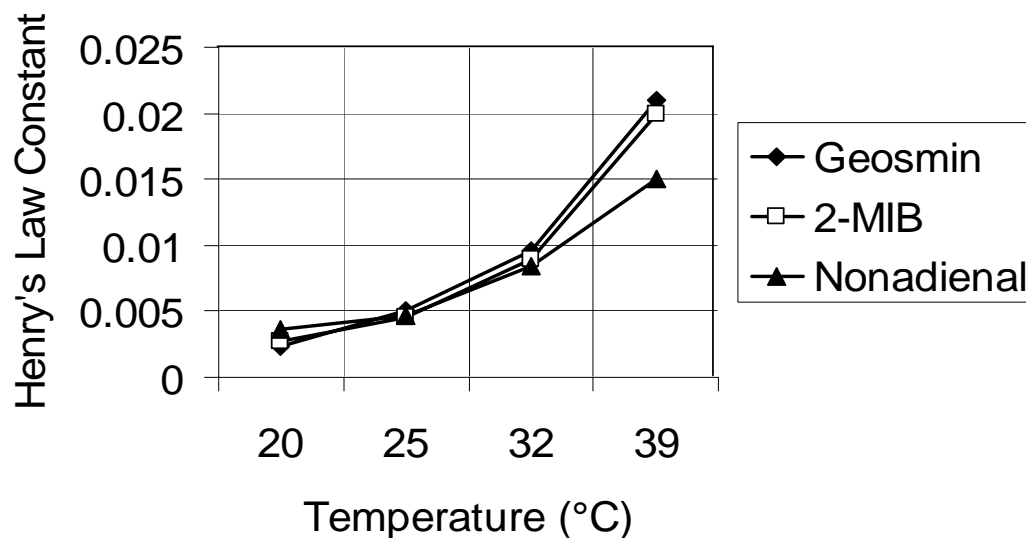


Figure-2.3: Effect of temperature on Henry's Law constants

Effect of Fulvic Acid. When mg/L quantities of fulvic acid was added to the reagent water containing 100 ng/L odorant, the measured Henry's Law constants were lower than the constants measured at 25°C in reagent water (Table-2.5). For geosmin the decrease in constant was about 25%, and about 5% for 2-MIB. Fulvic acid had a large effect on the measured value of m for nonadienal and reduced its value about 40%. The presence of the fulvic acid in the matrix likely increased solubilities of the compounds of interest. One-way ANOVA results ($p = 0.05$) indicated that there was a significant decrease in the constants but a Bonferri multiple comparison demonstrated that the decrease in m was independent of fulvic acid concentration. The decrease in the constants may be due to an increase in solubility of the compounds or a co-solute effect; interactions between the solutes such as adsorption or partitioning.

Table-2.5: Effect of Fulvic Acid on Henry's Law Constants at 25°C

Fulvic Acid (mg/L)	Geosmin	2-MIB	Nonadienal
0	0.0054 ¹ ± 0.0005 ²	0.0042 ± 0.0002	0.0044 ± 0.0002
2	0.0042 ± 0.0001	0.0040 ± 0.0003	0.00025 ± 7x10 ⁻⁶
5	0.0038 ± 0.0002	0.0040 ± 0.0001	0.00024 ± 7x10 ⁻⁶
8	0.0038 ± 0.0001	0.0040 ± 0.0002	0.00026 ± 10 ⁻⁵

¹ m_{measured} for n = 3 replicates

² Standard deviation

Human Perception of Odorants. The measured Henry's Law constants were used to predict the gas phase concentration of samples with known aqueous concentrations of odorants and which sensory analysis was performed. These data are represented in Figures-2.4 to 2.6 for geosmin, 2-MIB, and nonadienal, respectively. The results demonstrated that vapor phase concentration of the odorant increases with increasing temperature and concentration based on Henry's Law. But, the humans' ability to detect odors increased at a much lower rate than the increase in vapor phase concentration. Ultimately, at concentrations of about 100 to 200 ng/L, humans could not detect an increase in odor with increasing concentration of the odorant. At low concentrations, the Flavor Profile Analysis (FPA) ratings curve is steeper. The odor intensity data were obtained from Whelton and Dietrich, 2004 (3).

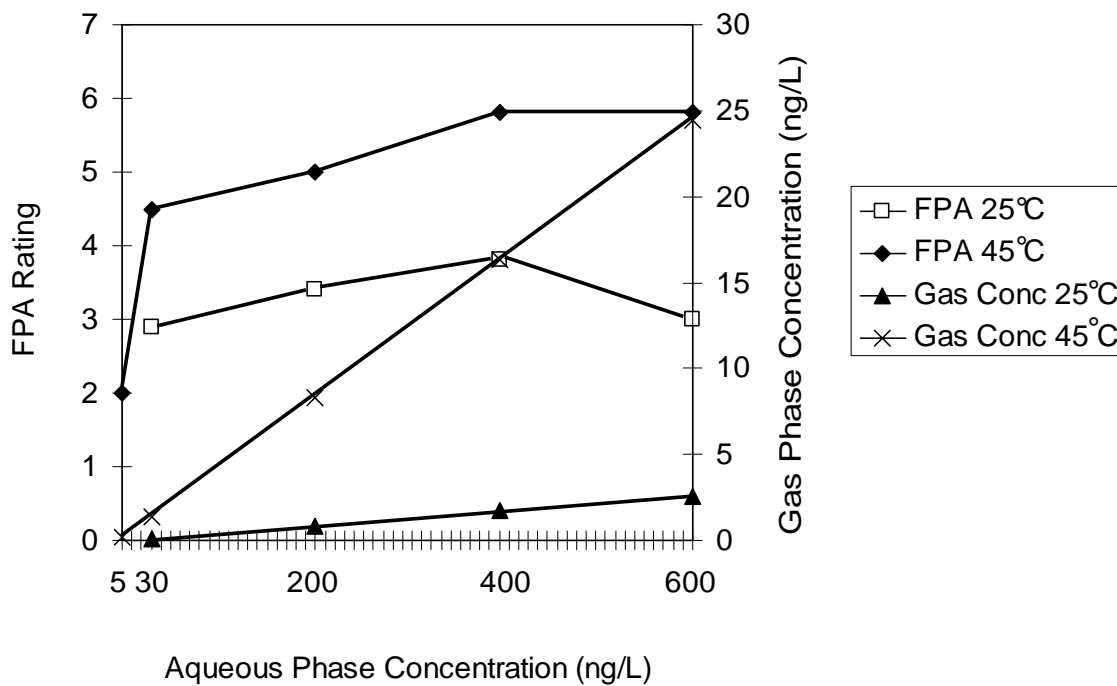


Figure-2.4: Gas Phase Concentration and FPA Rating Correlation for Geosmin

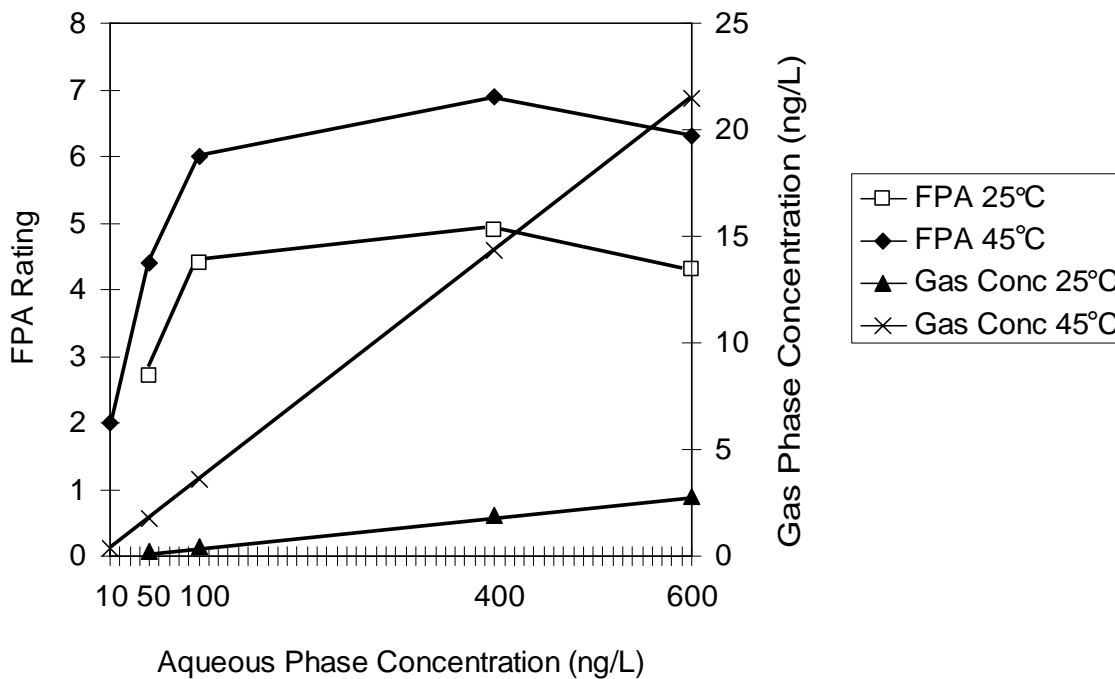


Figure-2.5: Gas Phase Concentration and FPA Rating Correlation for 2-MIB

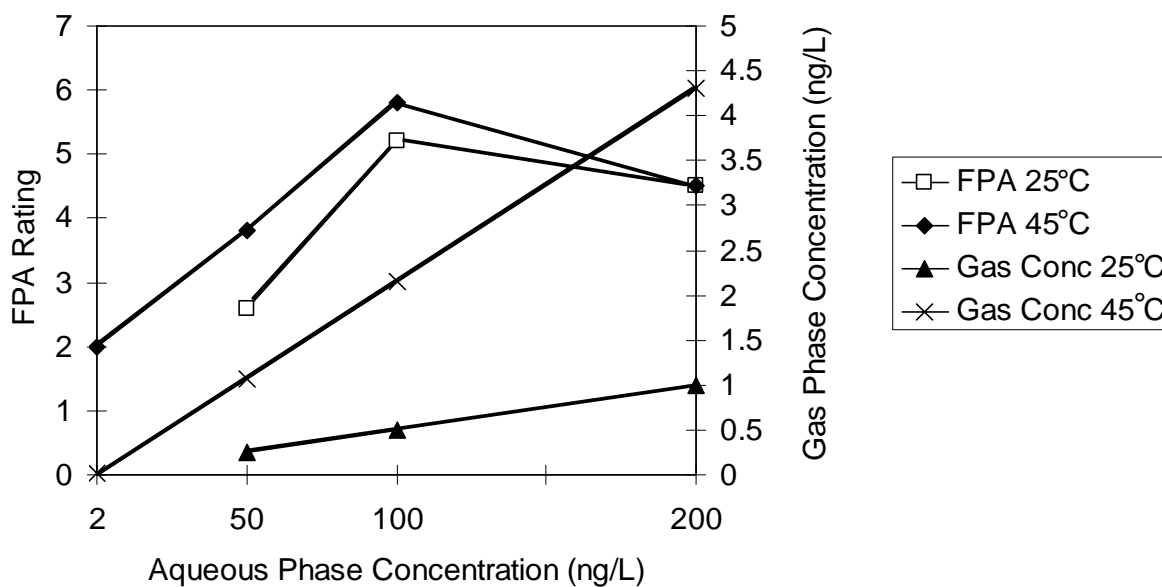


Figure-2.6: Gas Phase Concentration and FPA Rating Correlation for Nonadienal

CONCLUSIONS

The new static headspace-SPME method developed to measure Henry's Law constants under standard conditions for odor analysis is precise and reproducible at ng/L concentrations and different temperatures. The enthalpy of reaction calculated by using van't Hoff equation and the measured Henry's Law constants at different temperatures will allow Henry's Law constants to be calculated at any temperature. Presence of fulvic acid decreased the Henry's Law constants of these taste-and-odor compounds compared to the values in reagent water. However, as the concentration of the fulvic acid increased above 2 mg/L, the value of the Henry's Law constants did not change. Hence the effect of different water quality conditions, such as different pH values, salt concentrations, and dissolved organic matter concentrations, on Henry's Law constants may be investigated in future research. The gas phase concentration and the FPA

results correlated up to a point, but humans do not seem to be able to detect increased concentrations of geosmin, 2-MIB, and nonadienal at higher concentrations.

The information gathered by this study may be used by personnel that deal with the taste-and-odor problems to understand the effect of water quality on Henry's Law constants and human perception of odorants. Also the Henry's Law constants found will allow for assessing the fate of these compounds in the water supplies or when water is used in the household or outdoors.

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APPENDIX A – DATA FOR HENRY’S LAW CONSTANTS

GEOSMIN

Sorption Data for Geosmin at 20°C for 30 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	916	43	4.66
0.1	4089	159	3.90
0.2	6643	106	1.60
0.4	11627	512	4.41

$$\text{Mass} = (\text{Area} - 879.78) / 27438$$

Henry’s Constant Data for Geosmin at 20°C for 30 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	1460	2294	254	11.07
200	2526	3969	419	10.56

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.05152	19.9485
200	0.20023	39.7998

Concentration (ng/L)	m	Standard Dev	CV
100	0.00148	0.00041	14.69
200	0.00288	0.00028	8.24

Sorption Data for Geosmin at 25°C for 30 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	938	87	9.28
0.1	4187	186	4.44
0.2	6783	162	2.39
0.4	13199	742	5.62

$$\text{Mass} = (\text{Area} - 586.29) / 31615$$

Henry's Constant Data for Geosmin at 25°C for 30 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
20	1022	1606	189	11.77
200	8987	14122	903	6.39

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
20	0.03226	3.96774
200	0.42814	39.5719

Concentration (ng/L)	m	Standard Dev	CV
20	0.00465	0.00097	20.86
200	0.00618	0.00047	7.61

Sorption Data for Geosmin at 32°C for 30 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	1149	163	14.19
0.1	4004	173	4.32
0.2	6719	182	2.71
0.4	12928	890	6.88

$$\text{Mass} = (\text{Area} - 688.04) / 30623$$

Henry's Constant Data for Geosmin at 32°C for 30 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
20	1587	2494	353	14.15
200	14595	22934	722	3.15

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
20	0.05898	3.94102
200	0.72646	39.2735

Concentration (ng/L)	m	Standard Dev	CV
20	0.00856	0.00170	19.86
200	0.01057	0.00035	3.31

Sorption Data for Geosmin at 39°C for 30 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	1234	142	11.51
0.1	4154	215	5.18
0.2	6899	194	2.81
0.4	13737	1102	8.02

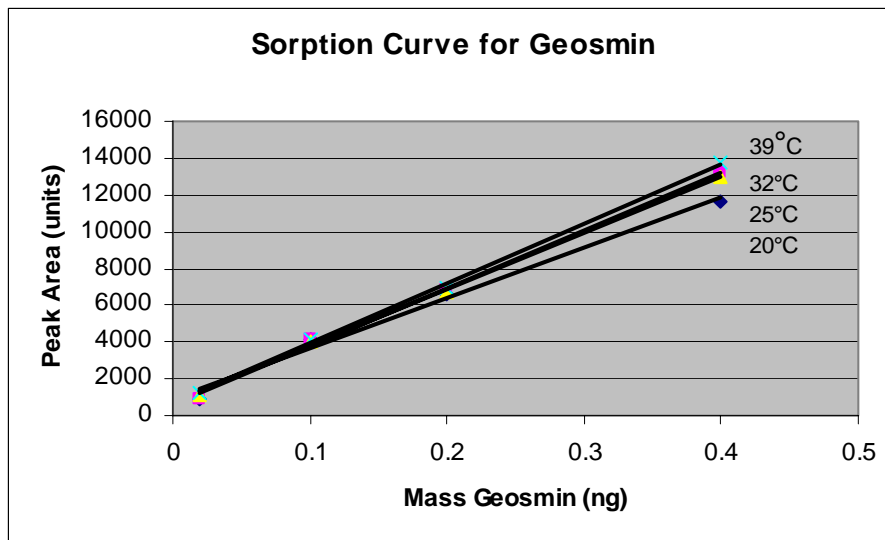
$$\text{Mass} = (\text{Area} - 646.36) / 32554$$

Henry's Constant Data for Geosmin at 39°C for 30 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
20	3386	5321	259	4.87
200	30535	47984	1398	2.91

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
20	0.14359	3.85641
200	1.45412	38.5459

Concentration (ng/L)	m	Standard Dev	CV
20	0.02128	0.00123	5.78
200	0.02156	0.00066	3.06



$$y_{20} = 27438x + 879.78$$

$$y_{25} = 31614x + 586.25$$

$$y_{32} = 30624x + 687.77$$

$$y_{39} = 32554x + 646.29$$

Enthalpy of Geosmin

T (°C)	m (analytical)
20	0.0028
25	0.0054
32	0.0096
39	0.0213

T (°C)	ΔH (kJ/mole)
20-25	95.36
25-32	62.11
32-39	90.07
20-39	75.77
25-39	76.29
20-32	95.36

Prediction

T (°C)	m (theoretical)
20	0.00231
25	0.00426
32	0.00973
39	0.02140

$\Delta H = 89$ kJ/mole

2-MIB

Sorption Data for MIB at 20°C for 20 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	448	42	9.38
0.1	2032	138	6.79
0.2	4377	251	5.73
0.4	8298	375	4.52

$$\text{Mass} = (\text{Area} - 48.4) / 20779$$

Henry's Constant Data for MIB at 20°C for 20 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
30	422	663	33	4.98
100	1273	2000	172	8.60

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
30	0.02956	5.97044
100	0.09394	19.9061

Concentration (ng/L)	m	Standard Dev	CV
30	0.00283	0.00030	10.63
100	0.00269	0.00023	8.56

Sorption Data for MIB at 25°C for 20 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	408	57	13.9
0.1	2066	189	9.13
0.2	4433	177	3.98
0.4	9065	342	3.77

$$\text{Mass} = (\text{Area} - 133.93) / 22927$$

Henry's Constant Data for MIB at 25°C for 20 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
30	734	1153	52	4.55
200	4347	6831	270	3.95

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
30	0.04444	5.95556
200	0.29209	39.7079

Concentration (ng/L)	m	Standard Dev	CV
30	0.00426	0.00022	5.19
200	0.00420	0.00017	4.06

Sorption Data for MIB at 32°C for 20 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	427	28	6.46
0.1	2052	318	15.5
0.2	4534	216	4.75
0.4	9345	339	3.63

$$\text{Mass} = (\text{Area} - 174.39) / 23689$$

Henry's Constant Data for MIB at 32°C for 20 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
30	1552	2438	151	6.18
100	4687	7365	205	2.79

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
30	0.09557	5.90443
100	0.30353	19.6965

Concentration (ng/L)	m	Standard Dev	CV
30	0.00925	0.00063	6.77
100	0.00881	0.00026	2.90

Sorption Data for MIB at 39°C for 20 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	437	28	6.34
0.1	2163	152	7.05
0.2	4647	154	3.30
0.4	9552	189	1.98

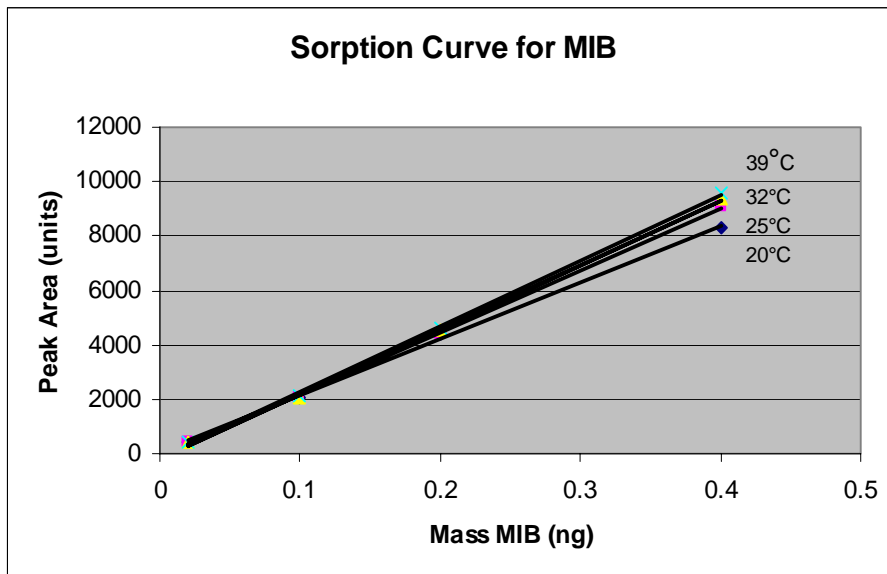
$$\text{Mass} = (\text{Area} - 147.44) / 24152$$

Henry's Constant Data for MIB at 39°C for 20 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
30	3272	5142	223	4.33
100	10000	15714	493	3.14

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
30	0.20868	5.79132
100	0.65600	19.3440

Concentration (ng/L)	m	Standard Dev	CV
30	0.02059	0.00078	3.81
100	0.01938	0.00064	3.28



Enthalpy of MIB

T (°C)	m (analytical)
20	0.00276
25	0.00423
32	0.00903
39	0.01999

T (°C)	ΔH (kJ/mole)
20-25	61.99
25-32	81.86
32-39	89.79
20-39	79.19
25-39	85.74
20-32	73.39

Prediction

T (°C)	m (theoretical)
20	0.00270
25	0.00462
32	0.00952
39	0.01900

$\Delta H = 78$ kJ/mole

T (°C)	m (theoretical)
20	0.00270
25	0.00470
32	0.00990
39	0.01999

$\Delta H = 80$ kJ/mole

NONADIENAL

Sorption Data for Nonadienal at 20°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	728777	14685	2.0
0.1	3632738	94753	2.6
0.2	7324379	97749	1.3
0.4	15129275	258360	1.7

$$\text{Mass} = (\text{Area} + 13024) / (4 \times 10^7)$$

Henry's Constant Data for Nonadienal at 20°C for 10 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	3116375	4897161	130039	4.2
200	6191464	9729443	167173	2.7

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.12568	19.8743
200	0.24649	39.7535

Concentration (ng/L)	m	Standard Dev	CV
100	0.00361	0.00015	4.1
200	0.00354	0.00009	2.7

Sorption Data for Nonadienal at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	461111	10913	2.4
0.1	2314801	71303	3.1
0.2	4569978	165327	3.6
0.4	9105421	267215	2.9

$$\text{Mass} = (\text{Area} - 23552) / (2 \times 10^7)$$

Henry's Constant Data for Nonadienal at 25°C for 10 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	1963730	3085862	88965	4.5
200	3932471	6179598	156647	4.0

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.15312	19.8469
200	0.30780	39.6922

Concentration (ng/L)	m	Standard Dev	CV
100	0.00441	0.00020	4.6
200	0.00443	0.00018	4.0

Sorption Data for Nonadienal at 32°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	483314	20088	4.2
0.1	2506667	40037	1.6
0.2	4829022	135439	2.8
0.4	9565852	249033	2.6

$$\text{Mass} = (\text{Area} - 61848) / (2 \times 10^7)$$

Henry's Constant Data for Nonadienal at 32°C for 10 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	3572804	5614407	220533	6.2
200	7247096	11388294	440273	6.1

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.27763	19.7224
200	0.56632	39.4337

Concentration (ng/L)	m	Standard Dev	CV
100	0.00804	0.00051	6.3
200	0.00821	0.00051	6.2

Sorption Data for Nonadienal at 39°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.02	429683	19823	4.6
0.1	2176456	176980	8.1
0.2	4475657	222695	5.0
0.4	9020890	440501	4.9

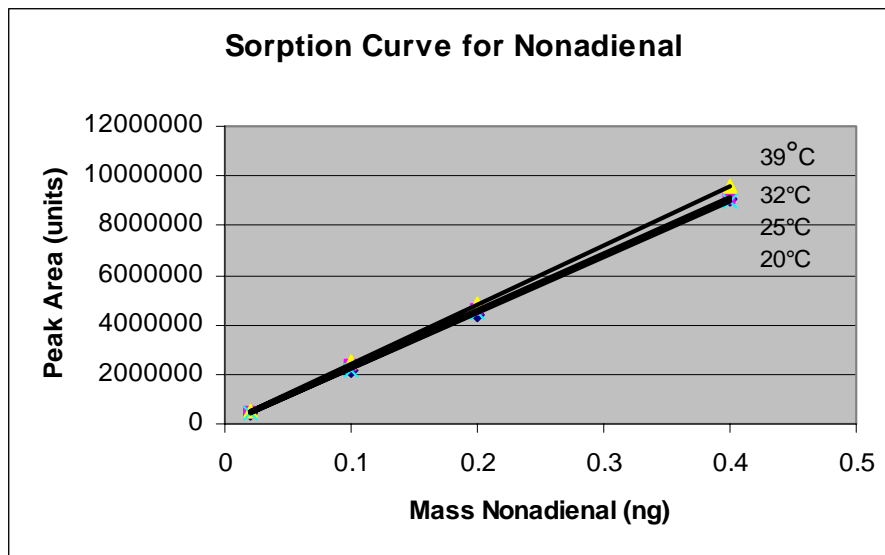
$$\text{Mass} = (\text{Area} + 53831) / (2 \times 10^7)$$

Henry's Constant Data for Nonadienal at 39°C for 10 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	6040783	9492659	150230	2.5
200	12254921	19257732	202057	1.6

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.47734	19.5227
200	0.96559	39.0344

Concentration (ng/L)	m	Standard Dev	CV
100	0.01397	0.00035	2.6
200	0.01414	0.00024	1.7



$$y_{20} = 4 \times 10^7 x - 13024$$

$$y_{25} = 2 \times 10^7 x + 23552$$

$$y_{32} = 2 \times 10^7 x + 61848$$

$$y_{39} = 2 \times 10^7 x - 53831$$

Enthalpy of Nonadienal

T (°C)	m (analytical)
20	0.00358
25	0.00442
32	0.00831
41	0.01405

T (°C)	ΔH (kJ/mole)
20-25	34.06
25-32	68.15
32-39	46.46
20-39	51.10
25-39	56.23
20-32	54.50

Prediction

T (°C)	m (theoretical)
20	0.00350
25	0.00500
32	0.00851
39	0.01630

$\Delta H = 57.5$ kJ/mole

BENZALDEHYDE

Sorption Data for Benzaldehyde at 20°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	8396	789	9.40
0.2	17168	351	2.04
0.4	35277	1298	3.68

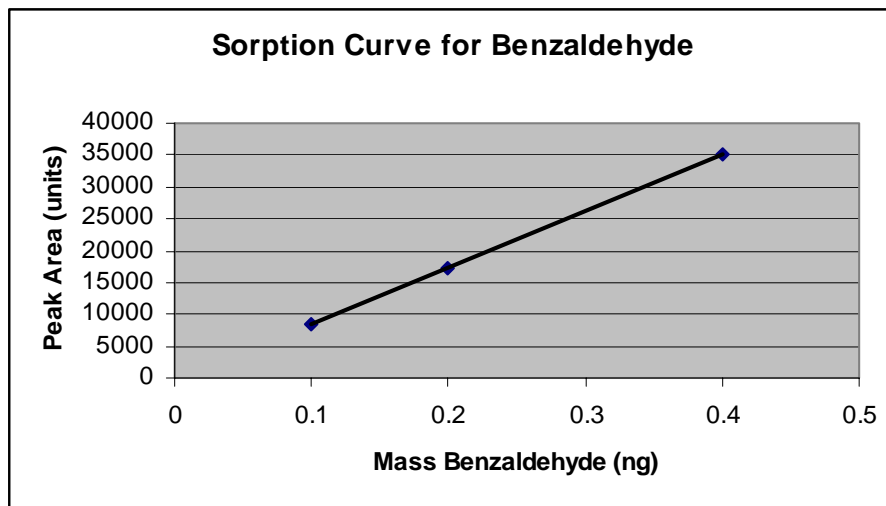
$$\text{Mass} = (\text{Area} + 658.5) / 89737$$

Henry's Constant Data for Benzaldehyde at 20°C for 10 minutes

Concentration (ng/L)	Average Area	Corrected Area	Standard Dev	CV
100	1299	2041	113	8.66
200	3003	4718	154	5.14

Concentration (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.03009	19.96991
200	0.05992	39.94008

Concentration (ng/L)	m	Standard Dev	CV
100	0.00086	0.00004	4.17
200	0.00086	0.00002	2.87



APPENDIX B – DATA FOR EFFECT OF FULVIC ACID

GEOSMIN

Sorption Data for Geosmin at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	1586	167	10.56
0.2	3145	218	6.92
0.4	6119	158	2.58

Mass = (Area – 98.8) / 15076

Henry's Constant Data for Geosmin at 25°C for 10 minutes

Conc. GSM (ng/L)	Conc FA (mg/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	2	1604	2521	174	10.85
100	5	1347	2117	146	10.84
100	8	1583	2488	227	14.34
200	2	2776	4362	372	13.41
200	5	2608	4098	298	11.43
200	8	2759	4335	367	13.30

Conc. GSM (ng/L)	Conc FA (mg/L)	Mass gas (ng)	Mass liq (ng)
100	2	0.16064	19.83936
100	5	0.13385	19.86615
100	8	0.15845	19.84155
200	2	0.28280	39.71720
200	5	0.26523	39.73477
200	8	0.28097	39.71903

Conc. GSM (ng/L)	Conc FA (mg/L)	m	Std. Dev.	CV
100	2	0.00434	0.0001	2.30
100	5	0.00385	0.0002	5.19
100	8	0.00378	0.0001	2.65
200	2	0.00407	0.0001	2.46
200	5	0.00381	0.0002	5.25
200	8	0.00381	0.0002	5.25

2-MIB

Sorption Data for 2-MIB at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	3867	189	4.89
0.2	7848	312	3.98
0.4	16167	488	3.02

$$\text{Mass} = (\text{Area} + 292.5) / 41085$$

Henry's Constant Data for 2-MIB at 25°C for 10 minutes

Conc. MIB (ng/L)	Conc FA (mg/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	2	3468	5450	267	7.70
100	5	3397	5338	189	5.56
100	8	3512	5519	221	6.29
200	2	7152	11239	656	9.17
200	5	7127	11199	785	11.01
200	8	7149	11234	512	7.16

Conc. MIB (ng/L)	Conc FA (mg/L)	Mass gas (ng)	Mass liq (ng)
100	2	0.13976	19.86024
100	5	0.13705	19.86295
100	8	0.14145	19.85855
200	2	0.28067	39.71933
200	5	0.27970	39.72030
200	8	0.28056	39.71944

Conc. MIB (ng/L)	Conc FA (mg/L)	m	Std. Dev.	CV
100	2	0.00402	0.0003	7.46
100	5	0.00394	0.0001	2.54
100	8	0.00407	0.0002	4.91
200	2	0.00404	0.0002	4.95
200	5	0.00402	0.0001	2.49
200	8	0.00404	0.0002	4.95

NONADIENAL

Sorption Data for Nonadienal at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	1252182	36784	2.94
0.2	3870308	58779	1.52
0.4	10312703	89342	0.87

$$\text{Mass} = (\text{Area} + 2 \times 10^6) / 3 \times 10^8$$

Henry's Constant Data for Nonadienal at 25°C for 10 minutes

Conc. NDL (ng/L)	Conc FA (mg/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	2	395832	622022	12672	3.20
100	5	341769	537066	17390	2.80
100	8	402856	633059	15375	1.57
200	2	2164874	3401945	92465	4.27
200	5	1993105	3132022	97233	4.88
200	8	2191853	3444340	132829	6.06

Conc. NDL (ng/L)	Conc FA (mg/L)	Mass gas (ng)	Mass liq (ng)
100	2	0.00874	19.99126
100	5	0.00846	19.99154
100	8	0.00878	19.99122
200	2	0.01801	39.98199
200	5	0.01711	39.98289
200	8	0.01815	39.98185

Conc. NDL (ng/L)	Conc FA (mg/L)	m	Std. Dev.	CV
100	2	0.00025	7×10^{-6}	2.80
100	5	0.00024	7×10^{-6}	2.92
100	8	0.00025	10^{-6}	2.80
200	2	0.00026	7×10^{-6}	2.69
200	5	0.00024	7×10^{-6}	2.92
200	8	0.00027	10^{-5}	3.70

APPENDIX C – DATA FOR EFFECT OF TAP WATER

GEOSMIN

Sorption Data for Geosmin at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	1555	91	5.88
0.2	3126	227	7.27
0.4	6239	500	8.02

$$\text{Mass} = (\text{Area} + 1.33) / 15605$$

Henry's Constant Data for Geosmin at 25°C for 10 minutes

Conc. GSM (ng/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	1349	2120	99	7.38
200	2825	4439	230	8.15

Conc. GSM (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.13593	19.86407
200	0.28456	39.71544

Conc. GSM (ng/L)	m	Std. Dev.	CV
100	0.00391	0.0003	7.43
200	0.00409	0.0003	8.20

2-MIB

Sorption Data for 2-MIB at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	2599	254	9.78
0.2	4959	204	4.11
0.4	9850	370	3.75

$$\text{Mass} = (\text{Area} - 153.67) / 24210$$

Henry's Constant Data for 2-MIB at 25°C for 10 minutes

Conc. MIB (ng/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	1874	2945	106	5.64
200	3847	6045	177	4.60

Conc. MIB (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.11529	19.88471
200	0.24335	39.75665

Conc. MIB (ng/L)	m	Std. Dev.	CV
100	0.00331	0.0002	6.32
200	0.00349	0.0002	4.72

NONADIENAL

Sorption Data for Nonadienal at 25°C for 10 minutes

Mass (ng)	Average Area (units)	Standard Deviation	Coefficient of Variation
0.1	1457728	71521	4.91
0.2	3579665	257244	7.19
0.4	6655137	306566	4.61

$$\text{Mass} = (\text{Area} + 80008) / (2 \times 10^7)$$

Henry's Constant Data for Nonadienal at 25°C for 10 minutes

Conc. NDL (ng/L)	Avg. Area	Corr. Area	Std. Dev.	CV
100	1283341	2016678	67434	5.25
200	2526437	3970116	131138	5.19

Conc. NDL (ng/L)	Mass gas (ng)	Mass liq (ng)
100	0.10483	19.89517
200	0.20251	39.79749

Conc. NDL (ng/L)	m	Std. Dev.	CV
100	0.00301	0.0002	5.08
200	0.00291	0.0002	5.11

APPENDIX D – DATA FOR FPA AND GAS PHASE CONCENTRATION

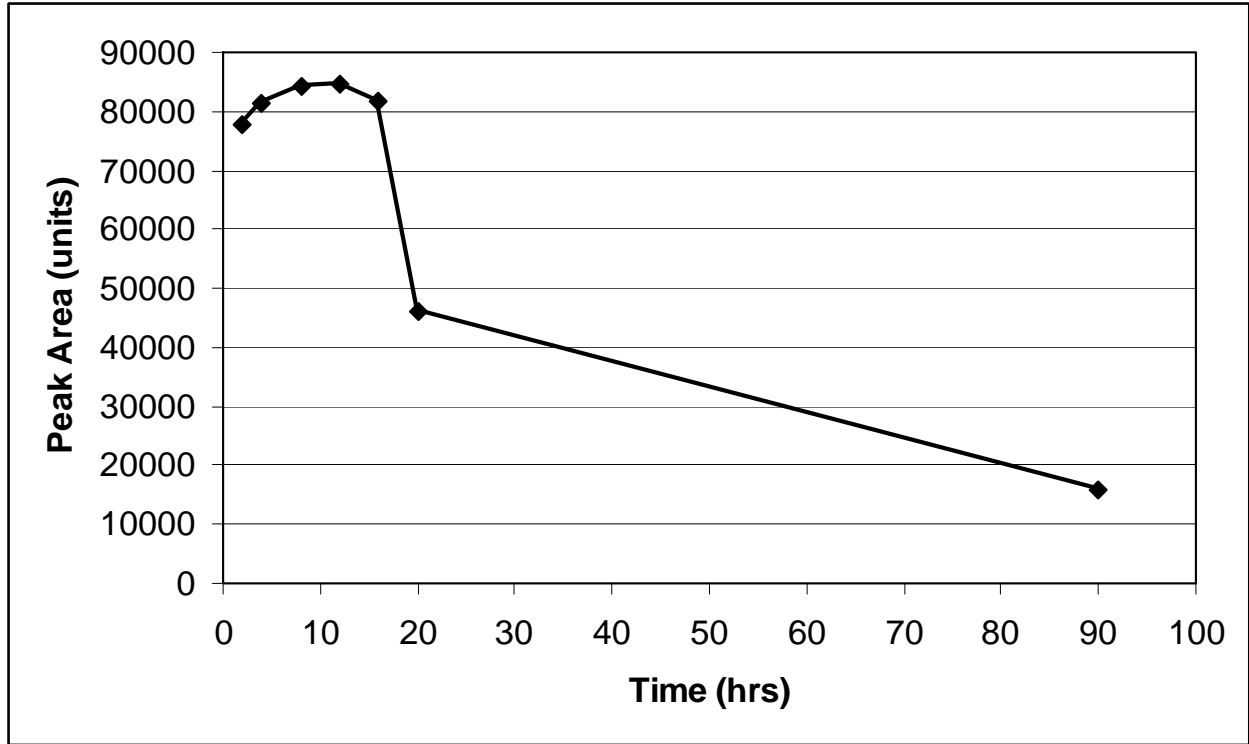
Compound	Aqueous Phase Concentration ¹ (ng/L)	Gas Phase Concentration ² (ng/L)		FPA Rating ³	
		25°C	45°C	25°C	45°C
Geosmin	30	0.13	1.22	2.9	4.5
	200	0.85	8.16	3.4	5.0
	400	1.70	16.32	3.8	5.8
	600	2.56	24.48	3.0	5.8
2-MIB	50	0.21	1.79	2.7	4.4
	100	0.42	3.58	4.4	6.0
	400	1.68	14.33	4.9	6.0
	600	2.52	21.49	4.3	6.3
Nonadienal	50	0.22	1.01	2.6	3.8
	100	0.44	2.02	5.2	5.8
	200	0.88	4.04	4.5	4.5

¹ Initial aqueous concentration added to Erlenmeyer flasks

² Gas phase concentrations are calculated using Henry's Law constants and enthalpies measured

³ FPA Data for Whelton and Dietrich, 2004

APPENDIX E – SPME FIBER SORPTION WITH TIME



Time (hrs)	Peak Area (units)
2	77701
4	81406
8	84275
12	84519
16	81834
20	45916
90	16014

VITA

Pınar Ömür was born on January 31, 1980 in Ankara, Turkey, as the first child of Ayla and İlhami Ömür. She has only one sister Ece, who is three years younger. Being a daughter of two engineers, Pınar received her B.S. degree in Environmental Engineering in Middle East Technical University (METU) Ankara, Turkey, in June 2002. She started doing her M.S. degree in January 2003 at Virginia Polytechnic Institute and State University. During her studies, she has been the research assistant of Dr. Andrea M. Dietrich. She received her Master of Science degree in Environmental Engineering in December 2004. She is planning to continue her studies in the PhD program in Environmental Engineering in Virginia Polytechnic Institute and State University.