

OPERATION MANUAL



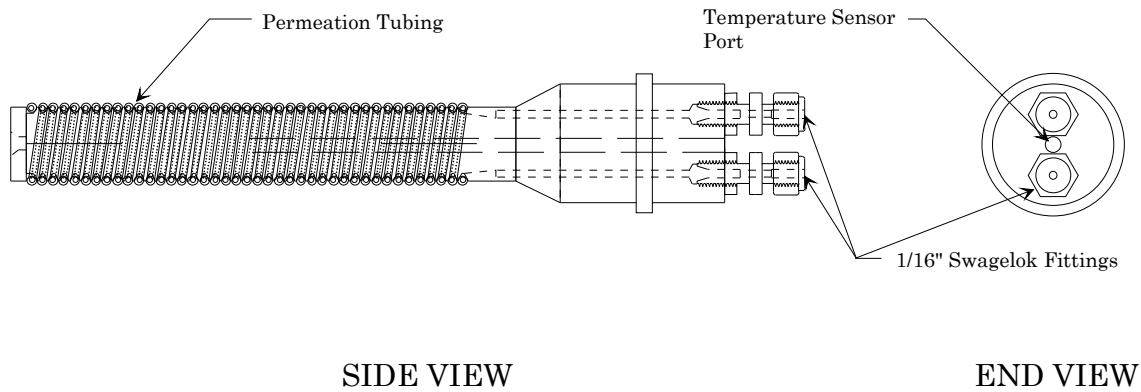
SUPPORTED CAPILLARY MEMBRANE SAMPLER

SCMS*

*U.S. Patent No. 5,317,932

Introduction

The basic Supported Capillary Membrane Sampler (SCMS) probe is shown in Figure 1 below:



SCMS PROBE DETAIL VIEW

FIGURE 1

The probe is designed to function in either a flowcell (Appendix A) or line/tank insertible (Appendix B) configuration. In operation, a carrier gas (typically nitrogen) enters the SCMS through 1/16" tubing from a mass flow controller, flows through the permeation tubing (typically silicone rubber), and exits the SCMS through a second 1/16" tube which is connected to the desired analytical instrumentation. As the outer wall of the permeation tubing is in direct contact with the sample stream, molecules of various species are transported from the bulk sample to the outer wall of the polymer tube. These molecules then dissolve into the polymer material, permeate through the tubing to the inner wall, and desorb from that wall into the flowing carrier gas. The effectiveness of this pervaporation process is governed largely by the mass transport of the sample molecules to the tubing outer surface, the solubility of the sample molecules in the polymer, the vapor pressures of the specific molecules involved, and the temperature.

Installation

A typical SCMS installation is shown in Figure 2 below:

TYPICAL SCMS PROBE/FLOWCELL-GC INSTALLATION

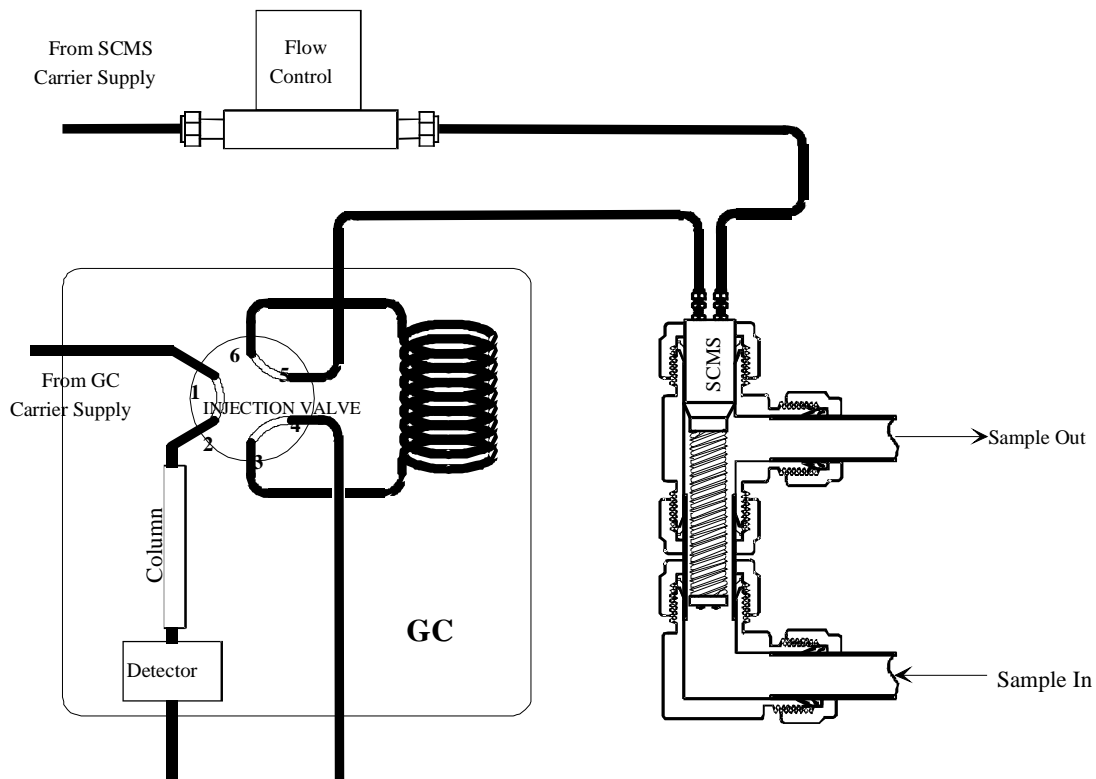


FIGURE 2

The equipment required for operation is:

1. **Regulated carrier gas supply for the SCMS.** The recommended carrier gas is nitrogen (argon and/or helium are not recommended, as they tend to permeate out through the membrane very rapidly and cause the formation of large amounts of bubbles on the membrane outer surface, and disrupting mass transport from solution to membrane).
2. **Carrier gas flow control.** The recommended flow control is a mass flow controller with a flow control range of 0-20 cc/min.

3. **Transfer lines** from the gas supply and flow-control to the SCMS and back to the injection valve of the GC. Stainless steel tubing, 1/16" o.d. by 0.030"i.d. is recommended. In some cases, use of stainless steel tubing will result in problems with adsorption of some species on the tubing walls. If such proves to be the case, nickel tubing is recommended (available from Valco Instrument Co. 1-800-367-8424)
4. **Temperature sensor and transmitter.** It is necessary to know the temperature of the sample stream in order to compensate the system for changes in concentration of the analyte in the carrier with respect to temperature. Such compensation is necessary to obtain quantitative results. The temperature sensor may be incorporated into the body of the SCMS (a port to allow this is provided), or the sensor may be incorporated separately in the flow path of the sample.

Optional equipment

Optional equipment may include:

1. **Temperature controller** and means for heating of transfer lines. For some species, adsorption on transfer line walls may be eliminated by heating the transfer lines. If the SCMS is to be used with water samples at elevated temperatures, heating the transfer lines may be necessary to prevent condensation of water (water WILL permeate through the membrane into the flowing carrier) in the sample lines, and condensation of liquid water is possible.
2. **Calibration vessel/system.** It is desirable to have a closed vessel to generate standards. In the case of a flow-cell system, a pump is also needed to circulate the standard from the vessel to and through the flow cell. The pump should be capable of pumping sufficient volume to establish turbulent flow in the flow cell (~1 ft/sec). In the case of a probe installation, a closed, stirred vessel into which the SCMS probe can be inserted is needed. The probe should be mounted off-center of the vessel at the point of maximum linear velocity of the stirring action. Both calibration vessel (SCMS-CV) and flow-cell (SCMS-FC) are available from Global FIA.

See Figure 3 below for a schematic of the calibration vessel.

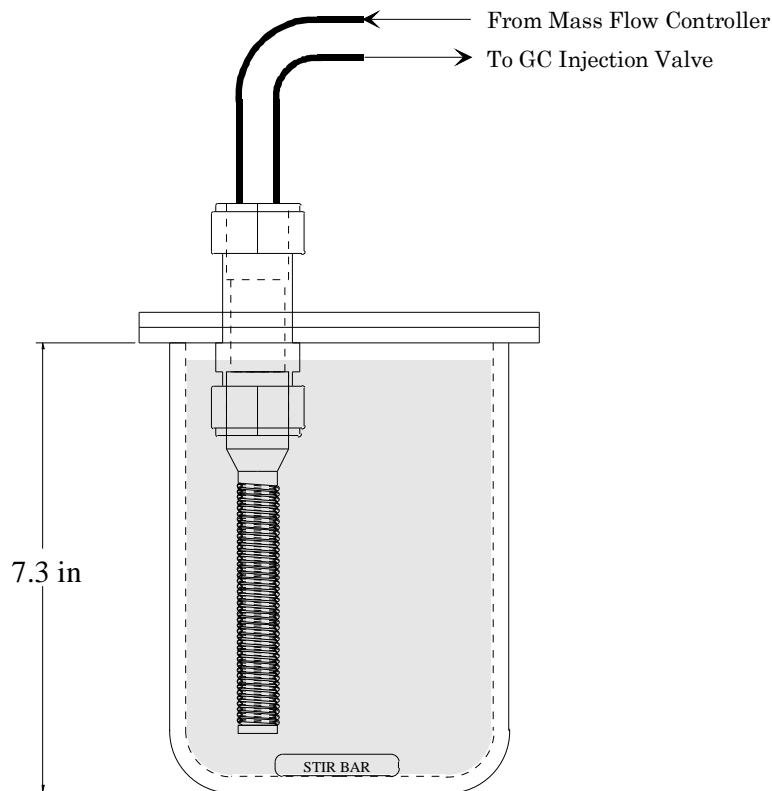


FIGURE 3-Calibration Vessel

Method Development for Specific Analytes:

1. Establish optimum carrier gas flow. Make up a standard solution of the desired concentration of the desired analyte and circulate it past the SCMS. Determine detector response at the highest flow rate (recommended 20 cc/min). Reduce the carrier gas flow rate and again determine detector response. Continue this until the detector response no longer increases with decreasing flow rate. At this point, the internal flow rate is sufficiently low that the carrier gas reaches vapor-liquid equilibrium with the analyte in solution. Plotting these data show that a "plateau" is reached of vapor phase analyte concentration vs. flow rate. For many compounds of environmental interest (benzene, chloroform, PDC, EDC, and others) the "plateau" flow rate is around 5-6 cc/min. Typical curves for several compounds are shown below.

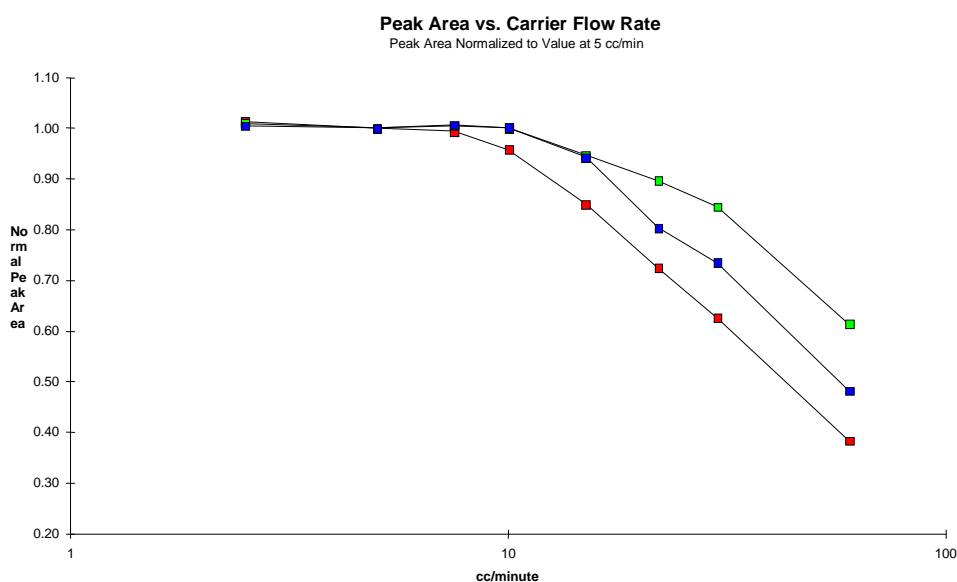


FIGURE 4 (Normalized) Detector Response vs. Carrier Flow

2. Establish temperature coefficient of response for each analyte. At the established v.l.e. (vapor-liquid-equilibrium) flow, obtain the detector response at different standard temperatures. In general, this temperature correction can be calculated using the response at a single sample temperature and the Antoine's constants¹ for the particular analyte, but the validity of any temperature correction so derived must be experimentally verified.

Helpful Hints and Suggestions:

Vapor-liquid-equilibrium vs. "Kinetic-Steady-State:

1. The preferred mode of operation is with the internal gas flow velocity sufficiently low to allow the desired analyte to reach true vapor-liquid equilibrium with the sample solution. This greatly simplifies system operation and calibration. In particular, operating in this flow regime renders the probe response independent of slight changes in carrier flow. It also makes it possible to use Henry's Law¹ and Antoine's Equation¹ to calculate the temperature coefficient for the particular analyte in order to correct for changes in concentration of the sample in the carrier gas with changing temperature.
2. It is possible to operate the probe at higher internal flow velocities (i.e. "off-the-plateau" of the internal carrier gas flow). This renders temperature compensation more difficult, as one must control the carrier gas flow rate very tightly, and

¹ Lange's Handbook of Chemistry, John A. Dean, Ed., McGraw Hill, Thirteenth Edition, c. 1985, p. 10-28 and 10-37-10-55.

determine a response matrix for both temperature and flow-rate variation. Under these conditions, the probe response becomes vulnerable to changes in the membrane that change the mass transfer rate of analyte molecules across the membrane.

3. It is important that the tubular pervaporation membrane not be internally overpressured, as this can result in membrane rupture. The maximum allowable internal pressure is dependent on membrane material. For the most widely used membrane material (silicone rubber), this maximum pressure should be no more than 10 psi. For polyethylene and PTFE membranes, the allowable pressures are higher—these membranes can safely handle overpressures of 100 psi (depending, of course, on process temperature). Internal overpressure must be distinguished from allowable EXTERNAL (i.e. process) pressure. All membranes will withstand 100 psi external pressure with no problem.

Alternate matrices:

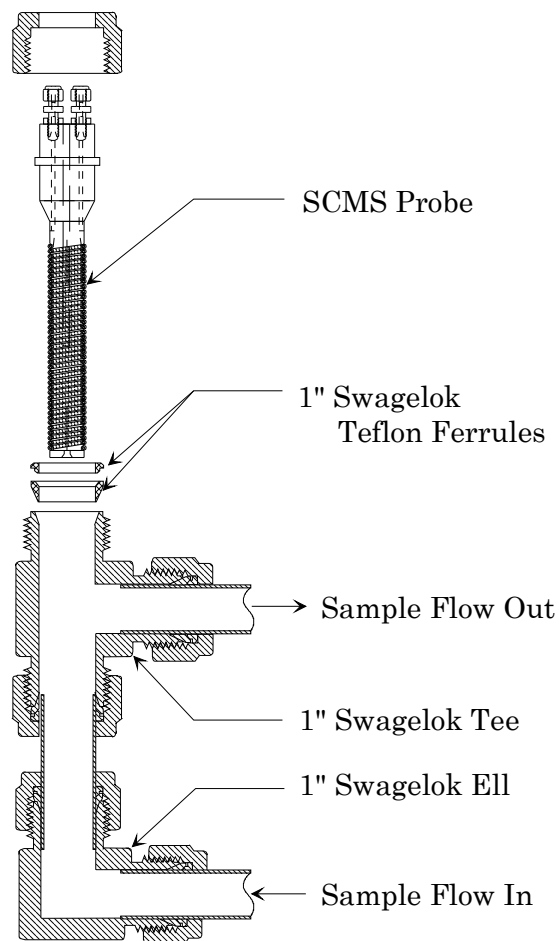
Most work thus far has been done for low levels of organics in aqueous streams, but the SCMS can certainly be used in other media. Analogous methods for calculating partial vapor pressures and temperature responses apply. For example, Appendix C illustrates the calculation and sources of data for use of the SCMS with an organic matrix (Diesel). If the Antoine's constants are not known, they can be determined experimentally from headspace studies.

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Appendix A

Assembly of the SCMS in a Flow-Cell Configuration

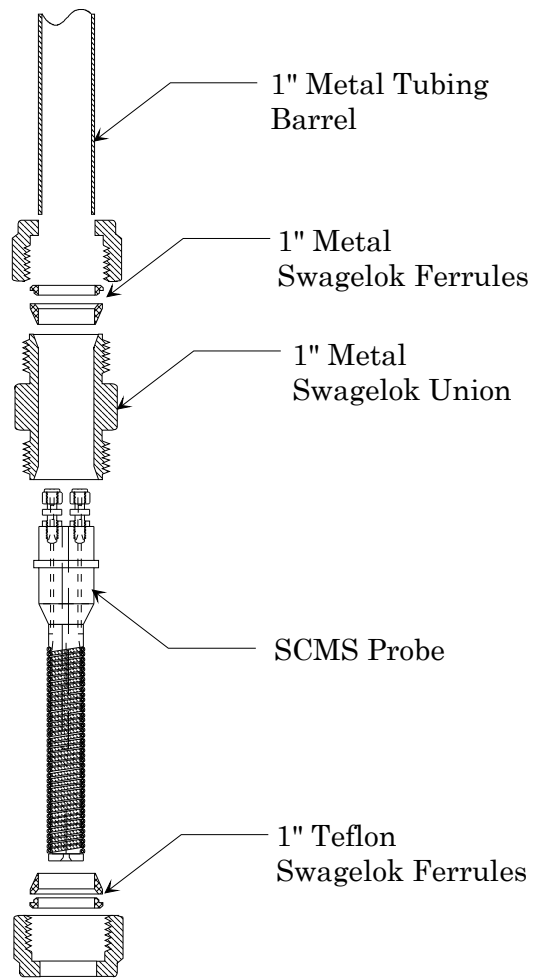
The SCMS is designed to fit and seal in 1" Swagelok fittings, hence the flowcell is constructed of such fittings. The SCMS "may" work using other fitting brands, but has not been tested with them. The ridge around the 1" diameter portion of the upper end of the SCMS is a "blowout preventer". For low-pressure systems (<100 psig), we recommend the use of Teflon ferrules, particularly with plastic versions of the SCMS.



ASSEMBLY VIEW - FLOWCELL

Appendix B

Assembly of the SCMS in an Insertion-Probe Configuration



INSERTION PROBE ASSEMBLY

Appendix C

Temperature Compensation

And

Antoine's Coefficients

Quantitative analysis with the SCMS requires compensation for temperature, as both the permeation rate across the membrane and the vapor pressure of various analytes are strong functions of temperature. If the SCMS is operated under VLE (vapor-liquid equilibrium) conditions—i.e. “on the plateau” of response vs. flow rate (FIGURE 4), then the concentration of the analyte(s) in the carrier exiting the SCMS is determined by Henry's Law, and Antoine's Equations.

Henry's Law states that the partial pressure of a species in a vapor space above the solution is proportional to its concentration in solution, and Antoine's Equations describe the partial pressure of a pure compound over its liquid form as a function of temperature.

It has been experimentally determined that for many compounds (at VLE flow) the form of the temperature variation of ppm levels of analytes is the same as that given by the corresponding Antoine's curve for the pure compound, divided by a simple dilution factor. The necessary dilution factor is determined by measurement of a prepared standard of the desired low concentration with the SCMS at some arbitrary (measured) temperature.

The form of Antoine's Equation is often expressed as:

$$\log p = A - B/(t + C)$$

where p = (partial) pressure of the compound in the gas phase at equilibrium with pure condensed phase (in torr)

t = temperature (deg. Celsius)

A , B , and C are compound-specific constants

To develop a temperature correction curve, an actual measurement is taken of a sample

at a known temperature (either from an artificial standard solution, or a process grab sample), and a curve plotted through that point with the same slope as the Antoine's equation for the compound(s) of interest.

Table of Antoine's Constants for Selected

Environmentally Important Compounds

<u>Compound Name</u>	<u>Constant A</u>	<u>Constant B</u>	<u>Constant C</u>
<u>ALIPHATICS</u>			
methane	7.19309	451.64	268.49
ethane	6.82915	663.72	256.68
ethylene	6.74419	594.99	256.16
propane	6.80338	804	247.04
propene	6.77811	770.85	245.51
butane	6.80896	935.86	238.73
isobutane	6.91048	946.35	246.68
pentane	6.85296	1064.84	233.01
2-methylpentane	6.83910	1135.410	226.57
3-methylpentane	6.84887	1152.368	227.13
cyclopentane	6.88676	1124.162	231.36
hexane	6.87601	1171.17	224.41
cyclohexane	6.84130	1201.53	222.65
heptane	6.89677	1264.90	216.54
octane	6.91868	1351.99	209.15
nonane	6.93893	1431.82	202.01
decane	6.94365	1495.17	193.86

<u>AROMATICS</u>	<u>Constant A</u>	<u>Constant B</u>	<u>Constant C</u>
benzene	6.90565	1211.033	220.790
toluene	6.95464	1344.800	219.48
ethylbenzene	6.95719	1424.255	213.21
styrene	7.14016	1574.51	224.09
n-propylbenzene	6.951.42	1491.297	207.14
n-butylbenzene	6.98317	1577.965	201.378
sec-butylbenzene	6.94219	1533.95	204.39
tert-butylbenzene	6.92255	1505.987	203.490
o-xylene	6.99891	1474.679	213.69
m-xylene	7.00908	1462.266	215.11
p-xylene	6.99052	1453.430	215.31
1,2,4-trimethylbenzene	7.04382	1573.267	208.56
1,3,5-trimethylbenzene	7.07436	1569.622	209.5
biphenyl	7.24541	1998.73	202.733
naphthalene	7.01065	1733.71	201.86
acenaphthylene	na	na	na
acenaphthene	7.72819	2534.234	245.576
fluorene	7.7618	2637.1	243.2
anthracene	7.67401	2819.63	247.02
fluoranthene	6.373	1756	118
chrysene	na	na	na
pyrene	5.6184	1122.0	15.2
benzo(a)pyrene	na	na	na
<u>CHLORINATED ORGANICS</u>	<u>Constant A</u>	<u>Constant B</u>	<u>Constant C</u>
bromobenzene	6.86064	1438.817	205.4412
bromochloromethane	6.49606	942.267	192.587
bromoform	7.0372	1735.32	195.42
carbon tetrachloride	6.87926	1212.021	226.41
chloroethane	6.986.47	1030.01	238.61
chloroethene	6.98117	905.01	239.48
chloroform	6.4934	929.44	196.03
o-chlorotoluene	7.36797	1735.8	230.0
dibromomethane	6.72148	1280.82	201.75
1,2-dichlorobenzene	7.14378	1704.49	219.42
1,3-dichlorobenzene	7.0401	1607.05	213.38
1,4-dichlorobenzene	7.0208	1590.9	210.2

1,1-dichloroethane	6.9770	1174.02	229.06
1,2-dichloroethane	7.0253	1271.3	222.9
1,1-dichloroethene	6.972.2	1099.4	237.2
cis-1,2-dichloroethene	7.0223	1205.4	230.6
trans-1,2- dichloroethene	6.9651	1141.9	231.9
dichloromethane	7.4092	1325.9	252.6
1,2-dichloropropane	6.9807	1308.1	222.8
1,1,1-trichloroethane	8.6434	2136.6	302.8
1,1,2-trichloroethane	6.95185	1314.41	209.2
trichloroethene	6.518.3	1018.6	192.7
tetrachloroethene	6.97683	1386.92	217.53

For a more complete listing of Antoine's Constants, see "Lang's Handbook of Chemistry", Editor John A. Dean, 13th Edition, McGraw-Hill Book Company ISBN 0-07-016192-5,

Table 10-8—Vapor Pressures of Various Organic Compounds, pp. 10-37 to 10-54.

Appendix D

Calculation of the Solubility of a Gaseous Component in a Liquid Hydrocarbon Solution

By

Joanne M. Wolcott

Ref: William D. McCain, Jr.: **The Properties of Petroleum Fluids**, PennWell Publishing Co., Tulsa, Oklahoma, 1990.

The calculation of the solubility of a gaseous component in a liquid hydrocarbon mixture at equilibrium conditions is based on solution theory. The simplest method of calculation assumes that the solution exhibits ideal behavior. Ideal behavior means that there is no special attraction between the components of a solution, all components are mutually soluble, there is no change in internal energy on mixing, and the molecular diameters of the components are the same. Hydrocarbon mixtures like those found in crude oils approximate ideal behavior. The solubility of a gaseous component in a liquid hydrocarbon can be calculated using the equation for the bubble point pressure, P_b

$$P_b = \sum z_i P_{vi}$$

Where z_i is the mole fraction of a liquid phase component and P_{vi} is the vapor pressure of that component. The mole fraction of a gas dissolved in a liquid mixture is determined by setting the bubble point pressure equal to the working pressure. For example, if we assume the following: operating conditions of 60 °F and 14.7 psia, diesel is composed of hydrocarbons in the range of C_{13} - C_{17} (pg. 2 of McCain's book), and we have one mole of a solution containing x moles CH_4 and $(1-x)$ moles of diesel, then the solubility of methane in diesel is given by the equation

$$14.7 \text{ psia} = (x \text{ moles } CH_4) P_{v \text{ CH}_4} + (1-x \text{ moles diesel}) P_{v \text{ Diesel}}$$

The vapor pressure of CH_4 at 60 °F is 4200 psia (from Fig. 2-7 (pg. 56) in McCain's book). Since the composition of diesel varies, it is impossible to accurately estimate the vapor pressure of the particular diesel used without determining its composition. We do know that the vapor pressures of C_{13-17} hydrocarbons are very low at 60 °F, and that vapor pressure decreases with decreasing temperature and increasing molecular weight (assuming that similar molecular structures are compared). The vapor pressure chart

in McCain does not go below 0.1 psia, and the vapor pressure of C_{13} is 0.1 psia at about 200 °F. The vapor pressure of n-octane, C_8 , is about 0.15 psia at 60 °F, while the vapor pressure of n-nonane, C_9 , is 0.1 psia at about 76 °F. Since C_{13} is considerably heavier than C_8 or C_9 , it is reasonable to assume that the vapor pressure at 60 °F is well below 0.1 psia but higher than zero. The following table shows the results of gas solubility calculations for methane, ethane, propane, and n-butane in diesel. n-Pentane would exist primarily in the liquid phase at 60 °F since the vapor pressure, 6.9 psia, is lower than atmospheric pressure. The solubility of a gas mixture in a liquid like diesel can't be calculated unless all but one of the actual gas concentrations is known; otherwise, you will have one equation with more than one unknown. It is important to note that the equation used in these calculations assumes that you have a closed system or conditions like those found in an oilfield separator.

Gas	P_{vi} (psia)	X_i assuming $P_{v \text{ Diesel}} = 0$ psia	X_i assuming $P_{v \text{ Diesel}} = 0.1$ psia
Methane	4200	0.0035	0.0035
Ethane	510	0.029	0.029
Propane	120	0.12	0.12
n-Butane	28	0.52	0.52