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Evaluation of the bias associated with the use of a Nafion® dryer in the analyses of certain polar and nonpolar organic compounds

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EVALUATION OF THE BIAS ASSOCIATED WITH THE USE OF A NAFION® DRYER IN THE ANALYSES OF CERTAIN POLAR AND NONPOLAR ORGANIC COMPOUNDS

by

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STATEMENT BY AUTHOR

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ABSTRACT

Recovery rates of certain polar and non-polar volatile organic compounds were evaluated for bias associated with the use of a Nafion® dryer in the analyses of environmental samples. Analyses of dryer inlet verses dryer outlet concentrations of specific compounds were used to assess the extent of Nafion® bias. A select group of 22 polar and 6 non-polar compounds, as well as historical data from other authors was used to develop a stepwise multiple regression model to aid in predicting recovery rates. Specific compound physical parameters used in this model include water solubility, hydrogen bonding capacity, and dipole moment. The overall R squared or predictive value of this model is 0.7885. Typical recovery rates of non-polar and extremely polar compounds are 100% and <10% respectively. Compounds that possess moderate intermolecular interactions (aldehydes, ethers, esters, and ketones) resulted in recovery rates between 10% and 100%.

1 INTRODUCTION

The ability of environmental professionals to characterize occupational exposures has greatly improved in the last decade. Technological advancements in analytical chemistry have opened the door to increasingly sensitive and accurate methods of analysis. With the advent of mass spectrometry, one's ability to fingerprint or scan a single sample for multiple compounds has become possible.

From an industrial hygiene standpoint, the sampling and analyses of ambient air encompasses a wide spectrum of techniques which are compound specific. Yet, only a handful of methods can be used for the collection and analysis of groups of compounds. Current techniques used for the sampling and analysis of volatile organic compounds (VOC's) and semi-volatile organic compounds (SVOC's) found in ambient air utilize several methods; 1) SUMMA passivated stainless steel canisters for whole air collection, 2) solid sorbent materials, or 3) liquid filled impingers. In each of these three general methods, condensing the sample must be done before analytical analysis.

Sample collection by solid sorbent or impinger incorporates the condensing phase during sample collection. These two methods are typically compound specific and require prior knowledge of the environment to be sampled.

In the case of whole air sampling with SUMMA canisters, the condensing phase is implemented after sample collection. The condensing phase involves cryogenic trapping of the sample prior to gas chroma- tography (GC) or gas chromatography/mass spectometry (GC/MS) analysis. The Environmental Protection Agency (EPA) Method TO-14 (EPA, 1-988) clearly outlines this methodology.

In May of 1988 the EPA introduced compendium method TO-14, which may be used to determine the concentration of volatile organic compounds found in ambient air. The method is based on SUMMA passivated canister sampling and cryogenic trapping and GC or GC/MS analysis. This method includes not only VOC's, but also some selected SVOC's (compounds too volatile for impinger collection and not volatile enough for solid sorbent collection).

An important feature of EPA Method TO-14 is the use of a reduced temperature trap. The reduced temperature trap or cryogenic trap consists of a 0.32 centimeter outside diameter (O.D.) nickel tubing loop packed with 60-80 mesh glass beads. This nickel trap is wrapped around a tube heater and then enclosed inside a stainless steel insulated shell. Coolant is fed into the shell where vaporization of the cryogen provides cooling. When rapidly heated, the trap produces a narrow band of condensed sample which is then introduced onto the GC column.

Low molecular weight compounds that possess higher boiling points than the temperature of the trap will pass through the trap while all others will condense on the glass beads. Typical coolants used for cryogenic trapping include liquid argon (bp. -185.7 ^{o}C) and liquid nitrogen (bp. -195.8 ^{o}C). However, if the relative humidity of the sample stream is high enough, and the volume of air passing through the trap is large enough, water vapor can collect and freeze in the trap. Clogging of the trap with ice can result in dysfunction of the system. In order to combat this problem, EPA Method TO-14 requires that a Nafion® (Du Pont) tube dryer available through (Perma Pure Products) be installed between the sample inlet and the cryogenic trap.

Nafion® permeable membrane tubing (a copolymer of tetrafluoroethylene and fluorosulfonyl monomer) is coaxially mounted within a larger tubing. See figures 1.1 and 1.2. The sample stream is passed through the interior of the Nafion® tubing, allowing water to permeate through the walls of the Nafion® into a countercurrent dry air purge stream which flows through the annular space between the Nafion® membrane and the outer tubing.

Because the described TO-14 method employs a Nafion® permeable membrane dryer to "selectively" remove water vapor from the sample stream, certain polar organic compounds may also permeate concurrent with the water molecules, thus introducing possible bias. The EPA recognizes this problem and suggests in the method that the analyst quantitate the nature and magnitude of the method bias for certain compounds.

EPA method TO-14 includes a list of 40 compounds, (Table 1.2), that can be analyzed by this technique without apparent bias introduced by the Nafion® dryer. These compounds are all nonpolar aromatic and halogenated hydrocarbons possessing boiling points between -30 and 213^{o}C.

The EPA recommends that an analyst determine the bias of this method for certain compounds. Therefore, addition of other compounds to this list is possible under the assumption that each laboratory documents recovery ratios for the analysis of each compound. It is important to note that the methodologies developed for EPA method TO-14 were conducted in Research Triangle Park, North Carolina, where ambient conditions, mainly relative humidity, may be higher than the norm. Many areas of the country or the world for that matter have much less relative humidity. Samples containing relative humidities of less than 50% may not require drying before cryogenic trapping. In desert climates the relative humidity rarely exceeds 25%. Air samples containing low humidity do not require pre-drying of the sample prior to cryogenic trapping.

Table 1.1 - EPA method TO-14 list of compounds.

Vinyl Chloride
Vinylidene Chloride
1,1,2-Trichloro
-1,2,2-Trifluoroethane
Choroform
1,2-Dichloroethane
Benzene
Toluene
Dichlorodifluoromethane
Methyl Chloride
1,2-Dichloro
-1,1,2,2-Tetrafluoroethane
Methyl Bromide
Ethyl Chloride
Dichlorofluoroethane
Dichloromethane
1,1-Dichloroethane
cis-1,2-Dichloroethylene
1,2-Dichloropropane
1,1,2-Trichloroethane

Perchloroethylene
Benzyl Chloride
Hexachloro
-1,3-Butadiene
Methyl Chloroform
Carbon Tetrachloride
Trichloroethylene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethyl Benzene
o,m,p-Xylene
Chlorobenzene
1,2,4-Trichlorobenzene
1,2-Dibromoethane
1,1,2,2-Tetrachloro
-ethane
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
o,m,p-Dichlorobenzene

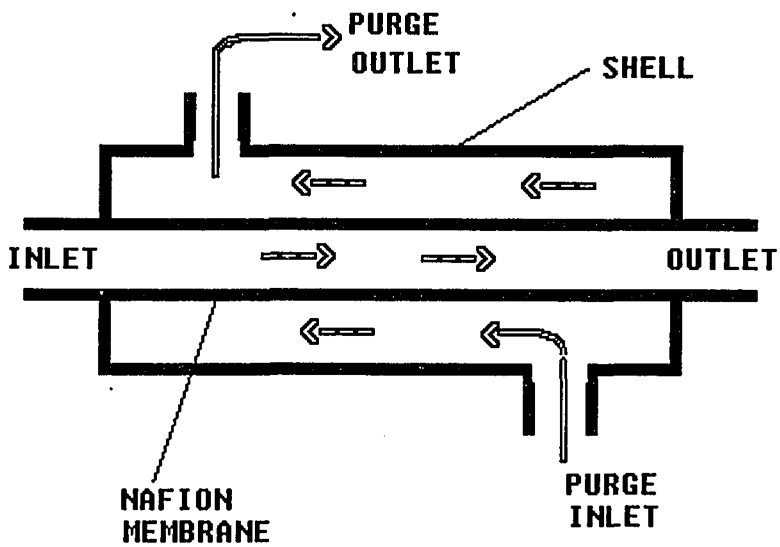


Figure 1.1 - Configuration of Nafion dryer.

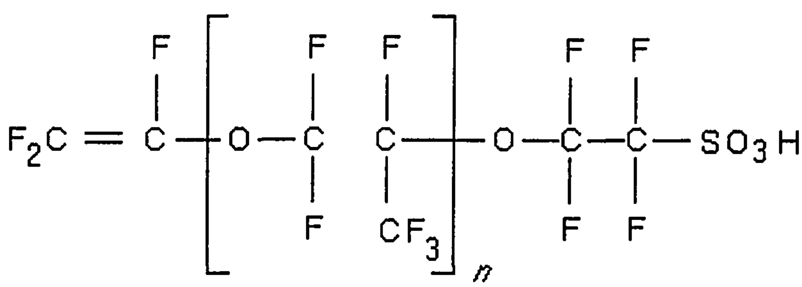


Figure 1.2 - Structural formula of Nafion ($-SO_3H$).

2 BACKGROUND

Many investigators have documented the use of Nafion® dryers for the removal of water vapor or liquid prior to chemical analyses. Most research data that are based on the use of Nafion® dryers are limited to aliphatic and aromatic hydrocarbons (excluding polar compounds such as ketones, alcohols, ethers, and esters). Several published papers have focused on the ability of Nafion® dryers to remove polar compounds. However, only a small number of compounds were evaluated.

(Baker,1974) utilized a Nafion® dryer system in measuring trace impurities in air by infrared spectroscopy. The procedure was as follows: A 70 liter sample bag of ambient air was connected to a 70 inch tube bundle of Nafion® membrane (Perma Pure, model PD 500-72), which was connected to the inlet of a compressor. The outlet of the compressor was connected to a second 70 inch dryer, and then to an evacuated 20 meter cell mounted in the spectrophotometer. Dry nitrogen was used as the purge gas through the dryers at a flow rate of 8 liters/min.

Drying efficiency was determined by drawing room air through one of the dryers into the evacuated cell. Regardless of the original humidity, the dryer lowered it to

2% relative humidity (R.H.). Baker found that many inorganic gases and organic vapors were unaffected by the Nafion® dryer. However, certain compounds were partially or completely removed, along with the water. Table 2.1 lists recovery percentages for the compounds tested. Compound concentrations for the dryer test were specified as being in the 100 part per million range.

TABLE 2.1 - Percent of compound removed from a sample stream by a Nafion® dryer system as reported by Baker.

<10% REMOVED

INORGANICS
- $CO, CO_2, SO_2, CS_2, H_2S$

HYDROCARBONS
- ethylene
- octene-1
- benzene

CL-HYDROCARBONS
- $CHCL_3$, allyl chloride(3-chloro-1-propene)

F-HYDROCARBONS
- CF_4, F-113(1,1,2-trichloro-1,2,2-trifluoroethane)

ACID FLUORIDES
- COF_2, CF_3, COF

ESTERS
- amyl acetate

ALDEHYDES
- butylaldehyde
- acetaldehyde

ETHERS
- diethyl ether
- furan
- methyl vinyl ether
- hexafluoropropylene oxide

MISCELLANEOUS
- nitropropane

10-90% REMOVED

ESTERS
- ethyl acetate (15%)

ALDEHYDES
- benzaldehyde (75%)

ETHERS
- ethylene oxide (50%)
- propylene oxide (25%)

KETONES
- ethyl amyl ketone (20%)

NITRILES
- benzonitrile (50%)
- acetonitrile (75%)

MISCELLANEOUS
- nitrobenzene (30%)

>90% REMOVED

ALDEHYDES
- crotonaldehyde

ETHERS
- dioxane
- methylal
- tetrahydrofuran

KETONES
- acetone
- methyl isobutyl ketone

AMINES
- n-butyl amine

ALCOHOLS
- methanol
- t-butanol
- n-hexanol

ACIDS
- acetic acid

MISCELLANEOUS
- dimethylformamide

(Langhorst,1983) utilized a Nafion® dryer to remove water vapor during sample collection on sorbent tubes. Reduced adsorption of organics on the solid sorbent was attributed to humidity effects on the solid sorbent material. Water molecule adsorption onto the sorbent material reduced the effective area for organic compounds to bind. Humidified samples (>80% R.H.) collected on solid sorbent material showed excessive breakthrough and reduced collection efficiency. Langhorst included a Nafion® dryer device in the sample train upstream from the sorbent tube. This configuration reduced the amount of water vapor reaching the sorbent tube and thereby increased it's collection efficiency.

Langhorst tested two configurations of a Nafion® dryer enclosed in a small container. One system utilized a container filled with dry air and the second config- uration used a container filled with desiccant. In both devices, the dry air and desiccant had a relatively short service-life. The life-span of a Nafion® dryer device is directly related to the osmotic differential that can be maintained between the air on the inside of the membrane and the dry air surrounding the Nafion® tubing. As the osmotic differential is reduced, the drying capacity of the Nafion® also becomes reduced. The dryer device filled with desiccant proved far superior to the air filled device in removing water vapor for extended periods. The air filled device was effective for only one hour, while the desiccant filled device proved effective for up to 10 hours.

Recovery rates for certain compounds tested with the Nafion® dryer devices were nearly 100% for aliphatic, aromatic, and chlorinated hydrocarbons. Compounds that have high boiling points were found to have lower recoveries. This reduction in recovery was hypothesized to result from condensation or adsorption onto the wall of the Nafion® tubing. Lowered recoveries were also observed for polar compounds.

Table 2.2 - Percent recovery of compounds from a Nafion® dryer system as reported by Langhorst.

COMPOUND	% RECOVERY
n-ALKANES	
C-7	100
C-8	100
C-9	101
C-10	99
C-11	106
C-12	102
C-13	99
C-14	100
C-15	93
C-16	70
C-17	70

Table 2.2 - Continued.

COMPOUND	% RECOVERY
1-ALKENES	
C-7	100
C-8	100
C-9	101
C-10	101
C-11	102
C-12	100
C-13	98
C-14	92
C-15	82
C-16	88
C-17	89
AROMATIC HYDROCARBONS	
benzene	100
toluene	102
ethyl benzene	103
n-propyl benzene	104
n-butyl benzene	100
n-hexyl benzene	103
n-octyl benzene	94
n-decyl benzene	46
CHLOROBENZENES	
chlorobenzene	100
1,3-dichlorobenzene	100
1,4-dichlorobenzene	100
1,2-dichlorobenzene	100
1,3,5-trichlorobenzene	100
1,2,4-trichlorobenzene	102
1,2,3-trichlorobenzene	100
1,2,4,5-tetrachlorobenzene	100
1,2,3,4-tetrachlorobenzene	100
pentachlorobenzene	100
hexachlorobenzene	100
OTHERS	
phenol	43
biphenyl	91
phenyl ether	86
3-ethylbiphenyl	44
4-ethylbiphenyl	36

(Frankel,1976) described an automatic continuous gas chromatographic monitor capable of selectively measuring 0.1 parts-per-billion (ppb) of bis(chloromethyl)ether (BCME) in air samples. The monitor utilized gas phase enrichment on a solid adsorption material (Tenax GC) and subsequent thermal elution. As this experiment continued into the summer months, a significant drop in the permeation standard occurred. Suspecting that moisture was collecting on the adsorber, due to the high humidity (70-90% R.H.), a Nafion® dryer was installed in front of the adsorbent. Continuous drying was accomplished by passing the moist sample stream at 500 milliliters per minute (ml/min) through the dryer with a 1500 ml/min purge flow rate of dry air. Under normal operating conditions, complete recovery of BCME was achieved when the relative humidity of the sample areas was as high as 95%. It was also found that acetic acid, which occasionally interfered with BCME, was removed by the Nafion® dryer.

(Foulger,1979) utilized the combination of a Nafion® permeable membrane and conventional desiccants to dry ambient air samples prior to GC analysis. A static drying system was developed for field use due to a limited supply of adequate purge gas. The dryer system was fabricated as tubular elements from a one-meter length of Nafion® 815 tubing and enclosed in a plastic container with removable nylon end caps. This container was then filled with desiccant (13X molecular sieve or magnesium perchlorate). Performance of the dryer was continuously monitored to determine the lifetime of the dryer before the desiccant needed replacement. Samples of ambient air were analyzed for F-11 (trichloromonofluoromethane), carbon tetrachloride, and methyl chloroform with and without the dryer system. The ambient temperature was 20 °C and the relative humidity was 68%. Experimental results showed no loss of these compounds when the dryer was used, and that the water content of the ambient air was reduced to less than 1% R.H.

Chromatographic separation of C2 - C10 hydrocarbons in a single analysis using a 60 meter SE-30 fused silica capillary column and subambient temperature programing was reported by Cox and Earp (Cox,1982). Chromatographic retention times and normalized photo-ionization detector/flame-ionization detector (PID/FID) responses were presented for alkanes, alkenes, dienes, alkynes, aromatics, aldehydes, ketones, saturated and unsaturated chlorinated hydrocarbons, and sulfur-containing hydrocarbons. Removal of water vapor was accomplished with a 24 inch Nafion® dryer (Perma Pure Products). Sample flow rates through the dryer were 100 ml/min with a purge rate of 1000 ml/min of ultra-high purity (UHP) air. The dryer was heated to 60 °C and purged for 10-15 minutes between analyses. Spiked air samples containing parts-per-million (ppm) levels of the selected compounds were analyzed by direct injection into the cryogenic trap using a 5-ml gastight syringe. The Nafion® dryer functioned well in the removal of water vapor and provided good recoveries for all aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, and aldehydes which were tested. However, low recoveries of alcohols and variable recoveries of ketones were obtained. The paper did not address the influence of the Nafion® dryer on recoveries of specific compounds. The data was reported as a toluene normalized ratio between the PID and FID detector responses.

(Burns,1983), reported that when a Nafion® permeable membrane was used to dry samples of organic gases emitted by vegetation, the dryer caused rearrangement of several monoterpenes and removal of several important oxygenated compounds from the samples. A dryer system was fabricated as previously described (Foulger,1979), in which a one meter length of Nafion® 815 tubing was placed in a plastic cylinder filled with 13X molecular sieve. Chromatographic data of vegative emissions dried with the Nafion® dryer showed more peaks than in undried samples. From the initial analyses it appeared that one or more of the compounds in the samples were reacting or rearranging in the dryer, yielding new compounds. Upon removal of the dryer, it was found that the injection system had become contaminated and was still reactive to the standards. The reactivity of the injection system lasted for several days after the dryer was removed. During this time the analytical system was continuously purged with dry helium. Over the course of the study, it was found that the reaction products changed every time the dryer was removed. Each time the dryer was removed the injection system was cleaned before reinstallation of the dryer. Several oxygenated compounds, which have been identified in vegetative emissions, were studied to determine if these compounds reacted with or were removed by the dryer. However, the authors did not include these results. The dryer results are listed in Table 2.3.

TABLE 2.3 - Compound removal from vegetative samples tested by a Nafion® dryer system as reported by Burns, et al..

COMPOUND	AMOUNT REMOVED
cyclopentanone	all
cyclopentanol	all
1-penten-3-ol	all
3-pentanone	all
n-hexanal	partial
trans-2-hexenal	partial
3-hexen-1-ol	all

** The alcohols and ketones were completely removed. The aldehydes were partially removed or held up in the dryer and appeared in the next several runs.

The methodology used in reduced temperature preconcentration of VOC's was tested by using a specially designed system for automated sampling and analysis (McClenney,1984). McClenney, et al., determined that collection and recovery of selected VOC's were approximately 100% and the integrity of sample components were unaffected by the use of a Nafion® dryer. Nafion® (Perma Pure Products) tube dryers of 30 and 120 centemeters in length were tested. Both lengths of dryers showed similar results and only the data for the 30 cm dryer were reported. Sample flow through the Nafion® tube was set within the range of 15-60 ml/min with a countercurrent purge flow of approximately 200 ml/min of dry zero-air. Results of analyses run with and without the Nafion® dryer showed essentially no sample loss for compounds detected by an ECD.

TABLE 2.4 - List of compounds tested through a Nafion® dryer system as reported by McClenney, et al..

trichlorotrifluoroethane	cis-1,3-dichloropropene
chloroform	1,2-dibromoethane
methylchloroform	tetrachloroethylene
carbon tetrachloride	hexachlorobutadiene
trichloroethylene	

Reduced-temperature trapping has several limitations which must be considered when designing a sampling and analytical system. (Holdren,1985), tested a Nafion® dryer (Perma Pure Products) to determine if water vapor could be selectively removed from humidified samples containing 16 target compounds. These experiments focused on collection and recovery efficiencies of organic compounds and potential interference or artifact effects from co-collected ozone and nitrogen dioxide gases. A comparison was made between analytical results for samples that were temporally stored and real-time analyses. The Battelle laboratory conducted the real-time analyses, and the stored samples were analyzed by a separate EPA laboratory.

The Battelle laboratory conducted a comparison test between dry and humidified samples that were analyzed with and without the Nafion® dryer. The resulting recoveries have been condensed and are reported as a ratio of recoveries.

$$\frac{dD/dB}{hD/hB} = \text{ratio of \% recovery}$$

Where,

dD = concentration of dry sample analyzed with dryer
dB = concentration of dry sample analyzed without dryer
hD = concentration of humidified sample analyzed with dryer
hB = concentration of humidified sample analyzed without dryer

TABLE 2.5.A - Battelle laboratory results of recovery ratio's for compounds tested through a Nafion® dryer system as reported by Holdren, et al..

COMPOUND	% RECOVERY RATIO
trichlorotrifluoroethane	100/101
chloroform	100/100
1,2-dichloroethane	100/96
methylchloroform	98/105
benzene	102/98
carbon tetrachloride	102/101
trichloroethylene	101/98
cis-1,3-dichloropropene	105/102
toluene	101/101
1,2-dibromoethane	107/105
tetrachloroethylene	100/100
chlorobenzene	117/96
o-xylene	101/101
benzylchloride	170/104
hexachlorobutadiene	104/93

** Humidified samples were 83% R.H. at 23 °C. A 5 ml sample loop was employed in order to analyze all samples without threat of water clogging the system.

Because the methodology used by the EPA laboratory for analysis of the stored samples involved cryogenic preconcentration, all humidified samples were analyzed with the dryer installed in the analytical system. The results are presented as recovery ratios in table 2.5.B.

$$\frac{dD/dB}{hD/dB} = \text{recovery ratio }\%$$

TABLE 2.5.B - EPA laboratory results of recovery ratio's for compounds tested through a Nafion® dryer system as reported by Holdren, et al..

COMPOUND	RECOVERY RATIO
vinyl chloride	97/96
dichloroethylene	99/102
trichlorotrifluoroethane	100/102
chloroform	100/100
1,2-dichloroethane	98/100
methylchloroform	101/101
benzene	96/93
carbon tetrachloride	99/102
trichloroethylene	99/101
cis-1,3-dichloropropene	98/101
trans-1,3-dichloropropene	99/105
toluene	99/98
1,2-dibromoethane	99/101
tetrachloroethylene	99/101
chlorobenzene	101/101
benzylchloride	100/113
hexachlorobutadiene	110/107
o-xylene	99/96

Review of the data presented from both laboratories show high recovery rates for both dry and humidified samples for all compounds tested. Comparison between laboratory data shows almost identical results for all compounds. Recovery rates for chlorobenzene, benzylchloride, and hexachlorobutadiene resulted in >10% recovery differences between dry samples and humidified samples for the Battelle lab. Data from the EPA laboratory does not coincide with the Battelle data for these three compounds.

In a survey of household indoor air by Pleil, et al.

(Pleil,1985), air samples collected in SUMMA passivated canisters were analyzed by cryogenic preconcentration and GC analysis. Prior to preconcentration, the sample stream was dried with a Perma Pure (Model MD-125-48T) dryer to avoid column or trap blockage due to water or ice formation. No mention was made of the recovery rates expected from the Nafion® dryer. However, since standardization was conducted with the dryer included in the analytical system, the authors must have assumed that the recovery rates are identical for a wide range of compound concentrations. Table 2.6 lists the compounds included in the analytical evaluation.

TABLE 2.6 - Compounds tested through a Nafion® dryer system as reported by Pleil, et al..

CALIBRATED COMPOUNDS	OTHER RECOGNIZED COMPOUNDS
propane	F-11
o,m,p-xylene	(trichloromonofluoromethane)
vinyl chloride	F-12
benzyl chloride	(dichlorodifluoromethane)
vinylidene chloride	F-13
chlorobenzene	(monochlorotrifluoromethane)
F-113	F-22
hexachloro-1,3-butadiene	(monochlorodifluoromethane)
chloroform	1,2-dichloropropane
1,2-dichloroethane	bromoform
methyl chloroform	o,m,p-dichlorobenzene
benzene	allyl chloride
carbon tetrachloride	1,1,2,2-tetrachloroethane
trichloroethylene	1,1,2-trichloroethane
cis-1,3-dichloropropene	methylene chloride
trans-1,3-dichloropropene	ethyl benzene
toluene	1-bromo-3-chloropropane
1,2-dibromoethane	methyl chloride
tetrachloroethylene	

In an industrial environment, the presence of compounds in high concentration may mask the ppb-level concentration of targeted compounds when analyzed by non-specific detectors such as the ECD and FID. (Pleil,1986), investigated this problem for 42 targeted nonpolar compounds collected in SUMMA passivated canisters (Table 2.7). The analytical system utilized cryogenic precon- centration and GC/MS (quadrupole mass selective detector) analyses. To eliminate water vapor from the sample stream, a Nafion® dryer was included. The authors recognized that the Nafion® dryer discriminates against polar compounds, therefore, no polar compounds were tested.

TABLE 2.7 - List of 42 non-polar compounds analysed by a GC/MS system which included a Nafion® dryer. Pleil, et al..

F-12	1,1,2-trichloroethane
chloromethane	toluene
F-114	1,2-dibromoethane
vinyl chloride	tetrachloroethylene
bromomethane	chlorobenzene
chloroethane	ethylbenzene
F-11	o-,m-,p-xylene
vinylidene chloride	styrene
dichloromethane	1,1,2,2-tetrachloroethane
allyl chloride	4-ethyltoluene
F-113	1,3,5-trimethylbenzene
1,1-dichloroethane	1,2,4-trimethylbenzene
cis-1,2-dichloroethylene	o-,m-,p-dichlorobenzene
chloroform	benzyl chloride
1,2-dichloroethylene	1,2,4-trichlorobenzene
methyl chloroform	hexachlorobutadiene
benzene	carbon tetrachloride
cis-1,3-dichloropropene	trans-1,3-dichloropropene
1,2-dichloropropane	trichloroethylene

(Pleil, 1987), investigated the use of Nafion® permeable membrane dryer systems in the analysis of 15 volatile organic compounds (Table 2.8). This paper also described a dryer cleanup procedure that can be implemented during the non-sampling period of a GC analysis cycle. Individual dryers showed no significant difference in drying efficiency. Data for the 15 VOC's of interest, listed below, showed no effect of this procedure on sample integrity and some improvement in run-to-run precision was observed.

TABLE 2.8 - Compounds used by Pleil, et al. for demonstrating clean-up procedures when using a Nafion® dryer.

vinyl chloride	cis-1,3-dichloropropene
vinylidene chloride	trans-1,3-dichloropropene
F-113	1,2-dibromoethane
chloroform	tetrachloroethylene
1,2-dichloroethane	chlorobenzene
methyl chloroform	benzyl chloride
carbon tetrachloride	hexachlorobutadiene
trichloroethylene	

The use of a Nafion® dryer has also been applied to analytical systems used for the analysis of water samples (Cockran,1988)(Cockran,1988)(Cockran,1989). The obvious advantage of these methods is the increased speed of analysis. When the Purge/Whole Column Cryotrapping method is utilized with a Nafion® dryer, a wider variety of column stationary phases can be implemented. The Nafion® dryer was shown to reduce the time required in the purge/GC method utilized in cryogenic focusing. However, memory problems with the dryer were observed. Compounds tested include nonpolar species of halocarbons, alkanes, and aromatics.

Another example of water analysis by direct injection of samples for analysis of volatile organics was presented by Coutant and Keigley (Coutant,1988). They found that the bulk of the water vapor was removed within the first few centimeters of the Nafion® dryer. For the purpose of direct injection of water, adequate sensitivity was obtained by using a 50 microliter (μl) injection volume. Detection limits with this sample size were approximately 2 micro-grams/liter (μg/L). The limiting factor in determining sample size was not the volume capacity of the dryer but rather the dimensions of tubing fittings at the inlet end of the dryer. With samples larger than 50 μl, swelling of the Nafion® at the inlet end was sufficient to cause temporary blockage of the sweep gas passage. In no case was there any evidence for penetration of water vapor to the cryogenic trap.

Some recent attention has been focused toward the use of a CI/ITD (chemical ionization/ion trap detector) for the analyses of ambient air (Gordon,1989). Polar and nonpolar

VOC's were analyzed by water CI in the ion trap to evaluate the effects of humidified zero-grade air, dry zero-grade air, and Perma Pure dried air on simulated whole-air samples. Humidified samples were shown to affect chromatographic performance by increasing both the baseline current and the overall signal noise. By contrast, the baseline was flat and essentially zero for the dry air sample and the Perma Pure dried humidified air sample. The Perma Pure dryer also removed some of the polar compounds along with the water vapor.

All but three polar compounds were removed from the gas stream along with the water vapor. The exceptions were acetone, acrylonitrile, and 1-methyl-2-propanethiol. Both acetone and acrylonitrile are soluble in water. Thus, the small amount of acetone detected is most likely attributed to the fact that acetone was present at high levels in the original mixture. The disappearance of limonene from this sample is surprising, since it is insoluble in water and should have passed through the dryer into the GC column in much the same way as styrene or m-dichlorobenzene. The effects of humidified, dry, and Perma Pure dried air on the measured peak areas for the compounds of interest indicate no significant difference between the humidified and dry air samples. However, the results obtained for the Perma Pure dried samples were significantly lower for styrene and m-dichlorobenzene, which should have been unaffected by the dryer. The authors note that more work is needed to determine whether this behavior is due to instrument instability or the Nafion® dryer.

TABLE 2.9 - Detector response measured in area units for humidified, dry, and Perma Pure dried samples as reported by Gordon and Miller.

	AREA UNITS		
COMPOUND	humidified	dry	Perma Pure dried
acetone	7509	18570	70
acetonitrile	13398	15871	ND
acrylonitrile	5834	9811	1057
tetrahydrofuran	3602	7861	ND
ethyl acetate	12898	11365	ND
2-butanone	8695	8706	ND
1-methyl-2 -propanethiol	523	295	30
acrolein	141	480	ND
styrene	1782	3123	99
amyl acetate	406	92	ND
limonene	461	151	ND
m-dichlorobenzene	757	317	180
nitrobenzene	157	139	ND

The Tekmar Company reported an alternative method to sample drying (thermal desorption tubes) and has compared the analytical efficiencies of thermal desorption versus Nafion® dryer systems (Sensel,1990). Their experiments show that recoveries of ketones were extremely low and recovery of dichloromethane was low and very erratic. Analytical reproducibility of o-dichlorobenzene was very poor with a 40.8% RSD (relative standard deviation). Reproducibility of octane was fair at 8% RSD.

TABLE 2.10 - Recovery data and percent relative standard deviation for compounds tested through a Nafion® dryer system as reported by Sensel and Griffiths.

	NAFION® DRYER		
Compound	ngs	%recovery	%R.S.D.
acetone	159	N.D.	N.D.
dichloromethane	96	N.D.	N.D.
2-butanone	96	N.D.	N.D.
benzene	105	83.1	29
4-methyl-2-pentanone	96	N.D.	N.D.
octane	84	99.7	3.9
o-xylene	105	99.7	4.9
o-dichlorobenzene	156	106	11

Note: ngs = nanograms injected

SUMMARY OF FORCES THAT MAY AFFECT RECOVERY PERCENTAGES

The action of intermolecular forces and their effect on solubility involves electrostatic forces between; (1) two or more ions and dipoles,(2) an ion and a permanent dipole, and (3) an ion or a dipole and an induced dipole. Other forces to consider are hydrogen bonds and London forces.

The strongest intermolecular forces which are in action during the phenomena of polymer solubility are defined below.

Van Der Waals Forces

These are very short-range forces that attract all chemical species together. They arise when the attractive forces of protons and electrons within a molecule interact with neighboring atoms, molecules, or ions. The distance between molecules has an important effect on the strength of van der Waals forces. The distance at which attraction is greatest is defined as the van der Waals radius. As two molecules approach each other an attractive force develops between them. When the distance between two molecules becomes smaller than the van der Waals radius, the attractive forces between the molecules decreases, and a repulsive force begins to mount.

Continuous chain molecules can align themselves in zigzag chains, enabling the atoms of different molecules to assume positions to match the van der Waals radii. However, branched-chain molecules cannot approach one another closely enough for all the atoms to assume optimal van der Waals distances. For this reason, continuous-chain compounds have higher boiling points than branched compounds of the same molecular weight.

In comparison to intramolecular forces, van der Waal's forces are relatively weak; yet they are sufficiently strong to hold particles together in liquid or solid states. In general, as the number of protons and electrons in a molecule increases, the van der Waal's forces increase. Therefore, as molecular weight increases the van der Waal's forces also increase.

Dipole Forces

A second type of intermolecular attractive force is the result of the dysymmetry of charge that occurs when polar covalent bonds are present. Molecules that are negatively charged on one end and positively charged on the other are termed dipoles. Dipoles attract each other when the positive end of one molecule comes close to the negative end of another molecule.

In principle, any molecule containing two atoms of two or more elements of differing electronegativity could be a dipole. In some cases, the symmetry of the molecule causes two or more dipole bonds to exactly oppose each other. This molecule would be considered non-polar even though it contains polar bonds. The dipole force is strong in molecules containing small atoms - elements 1 through 9 (hydrogen - fluorine), although some compounds containing sulfur and chlorine also possess dipolar forces.

Molecular polarity is measured in terms of the dipole moment. The dipole moment is the vector sum of the direction as well as the magnitude of the bond moments. The dipole moment is a measure of the polarity of the molecule. This number tells us how strongly a molecule will be affected by electrical charges in its vicinity.

Dipole-Dipole Interactions

Except in a highly dispersed gas, molecules attract and repel each other. These attractions arise primarily from molecular dipole-dipole interactions. Non-polar molecules may attract each other by weak dipole-dipole interactions called London forces. London forces arise from dipoles induced in one molecule by another. Electrons of one molecule are weakly attracted to a nucleus of a second molecule; then the electrons of the second molecule are repelled by the electrons of the first. The result is an uneven distribution of electrons and an induced dipole.

Hydrogen Bonding

Another strong type of dipole-dipole interaction occurs between molecules containing a hydrogen atom bound to nitrogen, oxygen, or fluorine. In the liquid state, the molecules of these compounds have strong attractions for one another. A partially positive hydrogen atom of one molecule is attracted to the unshared pair of electrons of an electronegative molecule.

Compounds or groups of compounds containing only carbon and hydrogen cannot undergo hydrogen bonding. Hydrogen bonding is much weaker than typical covalent bonds, but substantially stronger than most dipole-dipole attractions. The reason for this difference is the size of the atoms involved. A hydrogen atom is small in comparison to other atoms and can occupy a position very close to the unshared electrons of an electronegative atom. A strong electrostatic attraction results. Atoms larger than hydrogen cannot occupy positions so near to each other; consequently, dipole-dipole attractions between other atoms are weaker.

For all substances, boiling point increases with molecular weight due to increasing van der Waals attractions. However, a hydrogen bonded compound has a higher boiling point than would be predicted from molecular weight alone. In addition, the water solubility of hydrogen bonded compounds decrease as molecular weight increases. For example, the solubility of alcohols in water is directly related to hydrogen bonding between the alcohol group and the surrounding water. The hydrocarbon portion of an alcohol is hydrophobic, while the -OH end is hydrophilic. As the length of the hydrocarbon chain of an alcohol increases its water solubility decreases. Branching, or a decrease in length of the hydrophobic region, results in increased water solubility. For example, 1-butanol is only slightly soluble in water, but t-butyl alcohol is miscible in water.

PHYSICAL ASPECTS OF NAFION® PERMEABLE MEMBRANES AND THEIR MECHANISMS OF ACTION

The Nafion® permeable membranes are a group of ionomers consisting of hydrophobic fluorocarbon backbone chains, with hydrophilic perfluorinated ether side chains terminated by sulfonic acid groups or corresponding alkali salts (Kyu,1982), (see Figure 1.2). The Nafions® are semi-crystalline polymers with a low degree of crystallinity, which is related to the equivalent weight. As equivalent weight increases, the degree of crystallinity increases, as well as the size of the ionic clusters. Nafion® ionomers that possess low equivalent weights and sulfonic acid groups show the largest hydration capacity.

Studies of low-angle X-ray scattering and other physical properties of Nafion® (Yeo,1980)(Kyu,1982) suggest that hydrated Nafion® is a two-phase system, consisting of hydrated clusters of $-SO_3H$ groups embedded in the surrounding fluorocarbon medium. Hydration can be expressed as either uptake of water molecules per $-SO_3H$ group or as a percent increase in overall weight. In a saturated condition, 1100 EW Nafion® is fully hydrated when 19.6 water molecules per $-SO_3H$ group are present, or the overall weight of the membrane has increased by 32% (Hashimoto,1982).

An approach to equilibrium for the process of hydrating Nafion® from a dry state has been proposed by Komoroski and Mauritz (Komoroski,1982). In the dry state, water molecules are bound by electrostatic forces. Interaction between the organic polymer backbone and water molecules may initially inhibit the rate of swelling. The initially-arrived water molecules bind to the outer wall of the ionic cluster creating ionic solvation shells that result in little or no volume expansion of the polymer network. Once the solvation shells have become saturated, further uptake of water results in moving the association dissociation equilibrium toward increased water mobility. The driving force for swelling is the tendency for the water to dilute the polymer network. Differences between water activity in the interior and exterior of the membrane gives rise to an internal osmotic pressure that serves as the driving force for polymer chain network deformation.

As the water uptake proceeds, increased sidechain-water dissociation allows for more complete ionic hydration. The clusters begin to increase in size, as well as form inter-conecting channels throughout the polymer membrane. Maximal hydration is reached when the overall energy state for a given membrane water content (n moles per equivalent weight of Nafion®) equals the polymer chain retractive forces that resist expansion of the network. An equilibrium water content is eventually reached, at which point the osmotic pressure is balanced by the cohesive energy density.

Estimation of the solvent power of solvents is termed the solubility parameter. The solubility parameter is based on the energy needed to overcome all the forces holding the molecules together. A solvent dissolves the polymer if both components have the same or nearly the same solubility parameter. Conversely, when the solubility parameter of a solvent differs greatly from that of the polymer, solvation does not take place.

The original concept of solubility parameters was developed in 1916 by J.H. Hildebrand. During the mid-1950's Burrell (Burrell,1955)(CDIC,1957) made additional contributions to Hildebrand's work. With few exceptions, the solubility parameter can be calculated for all compounds based on molecular weight, density, and the heat of vaporization. The solubility parameter is defined as the square root of the cohesive energy density of a specific compound. The cohesive energy density equals the ratio of molar energy of vaporization minus RT, the work of expansion on vaporization, to the molar volume. Cohesive energy density is expressed as cal/cc units, and the solubility parameter is expressed as Hb (Hildebrand).

The Greek letter delta δ represents the solubility parameter of solvents, resins, and polymers. As a physical constant, the solubility parameter measures the force by which solvent molecules attract one another. If a liquid and a resin have the same or nearly the same solubility parameter values, then that liquid is a solvent for the resin. When matching parameter values, the effect of hydrogen bonding must be considered.

Solubility parameters have become increasingly important in formulating a wide variety of products. The use of these constants reduces the need for extensive experimentation. The parameters can also be utilized to indicate compatibilities between various resins and polymers (Mellan,1968).

A polymer is a large molecule formed by many small chemical units. In some cases these small units are linear in structure, more like a chain. In other cases these chains are branched or interconnected to form a three dimensional network. These polymers are held together by strong, primary chemical bonds and also by weak secondary forces of attraction between the molecules. The former are the ionic, covalent, coordinate and metallic bonds. The latter bonds are the dipole, induction and dispersion forces. Other factors which play an important role in solubility are the intermolecular forces, hydrogen bonds and polarity.

(Yeo,1980) investigated the solubility parameter of Nafion® (1100 EW) by the swelling technique. Data from swelling experiments show two distinct swelling envelopes for the Nafion® membrane. Yeo hypothesized that the association of the first envelope is with the organic backbone, while the second envelope is associated with the ion clusters of the membrane (Yeo,1980)(Yeo,1981).

The degree of swelling of a membrane exposed to a solvent is related to the closeness between the solubility parameters of the polymer and the solvent (Gee,1942), as well as the hydrogen bonding capability of the solvent (Burrell,1955).

The swelling of Nafion® in mixed solvents is greater than in pure solvents (Grot,1972). Grot postulated that this increase may be due to larger differences that occur in chemical potentials between the polymer and the solvent.

In contrast to many polymers, Nafion® exhibits two solubility parameter values. This feature is not common in other materials whose solubility parameters have been reported (Burrell,1975).

3 METHODS

Evaluation of the bias attributed to the use of a Nafion® dryer is based on data collected from new experimentation with a select group of 22 polar and 6 nonpolar compounds, (Table 3.1), as well as historical data from other authors. Analyses of dryer inlet verses dryer outlet concentrations of specific compounds will determine the extent of bias associated with the use of the Nafion® dryer.

Table 3.1 - List of compounds tested for recovery rates through a Nafion® dryer.

Ethyl Alcohol	Cyclohexanone
Methylene Chloride	n-Octane
Acetone	Ethyl Butyl Ketone
Isopropyl Alcohol	Diisobutyl Ketone
Tetrahydrofuran	Chlorobenzene
Ethyl Ether	Methyl Propyl Ketone
Methyl Ethyl Ketone	n-Propyl Acetate
Isobutyl Alcohol	Methyl Isobutyl Ketone
Ethyl Acetate	Perchloroethylene
n-Butyl Alcohol	Cyclohexanol
1,4-Dioxane	n-Butyl Acetate
Trichloroethylene	Toluene
Isopropyl Alcohol	Isoamyl Acetate
m-Xylene	Methyl Amyl Ketone

The evaluation of bias associated with the use of a Nafion® dryer in the analysis of certain volatile organic compounds is rooted in the concentration differential related to the percent recovery from the dryer. A known concentration of a specific compound is introduced into the dryer and the effluent is measured for comparison. In order to quantitate the percent recovery, calibration of the analytical system must include a calibration curve as well as duplicate analyses for each compound to be tested. Accuracy and precision of the methodology and associated analytical equipment used in this experiment are evaluated in this manner. Development of a calibration curve and precision data for each compound allows for a statistically stronger analysis of the experimental data regarding recovery values.

ANALYTICAL EQUIPMENT

A Hewlett Packard Gas Chromatograph model 5890 equipped with a Flame Ionization Detector was used for all analyses. Integration of the GC signal was performed by a JCL-6000 chromatographic program run on a IBM type PC. All peak areas were determined by the computer. Identification of individual compounds was done manually based on comparison of retention times.

Due to the variety of compounds tested, two chromatographic columns were required. Both columns were 6′x 1/8" packed stainless steel. For compounds with higher boiling points, 0.1% SP-1000 on 80\100 carbopack C packing was used; and for lower boiling point compounds, 10% FFAP on 80\100 Supelcoport was used as packing. Both the SP-1000 and the FFAP column packing have a combination of carbowax and substituted terephthalic acid phase type.

All sample collection and GC injections were made with Dynatech Precision Gas-Tight Syringes. Syringe sizes were chosen depending upon the desired injection size and limited to the range of greater than 10 percent or less than 50 percent of the syringe volume.

CALIBRATION

A three point calibration curve ranging from 100 ppb to 2 ppm was produced for each compound included in the evaluation of a Nafion® Dryer. See Table 1.1.

Each calibration point is the result of two dilutions. The first dilution was made by injecting 1 μl. of high purity liquid standard (Chem Service,Inc.) into a 1.0 liter glass jar containing approximately 25 to 30 glass mixing beads. After introduction of the liquid standard into the glass jar, the jar was shaken for 60 seconds, thereby allowing the glass beads to mix the internal vapor. This procedure resulted in a million fold dilution or a concentration of approximately 300 ppm (depending upon the compound). A second dilution was made by removing 5 ml of calibration air from the glass jar and injecting it into a 5.64 liter closed-loop dynamic mixing chamber. The resulting concentration in the dynamic mixing chamber was approximately 200 ppb. Additional calibration points included concentrations of approximately 800 ppb and 2.0 ppm (depending upon the compound). Each calibration point was separately made up as outlined above. Calibration curves for each compound were replicated three times to insure the reproducibility of the standard mixture. For each concentration (200 ppb, 800 ppb, and 2 ppm), three replicate injections were analyzed. A total of 9 analyses were made at each calibration point, three for each calibration mixture.

Precision was assessed by replicating injections of the median calibration concentration, resulting in 34 total data points for the calibration of each compound.

A 1 ml. injection volume into the gas chromatograph was used for each calibration curve point. Instrument range and attenuation parameters were set at the most sensitive level (Range=0, Attenuation=0). Appendix A lists calibration data, column type, and column temperatures and flow rates.

DRYER TEST

A Nafion® dryer was evaluated for bias associated with the removal of certain compounds from a spiked air sample. Evaluation of the Nafion® dryer was based on the difference between compound concentration up-stream and down-stream of the dryer.

A Nafion® dryer (model number MD-125-48F) was obtained from Perma Pure Products,Inc., for the testing.

The Nafion® dryer specifications are as follows:

- Length = 48 cm.
- Internal Diameter = 2.65 mm.
- Internal Area = 8.33 mm^2.
- Internal Volume = 0.4 cm^3.
- Equivalent Weight (EW) = 1100 (sulfonic acid)

LOW PPM TEST

A low ppm "test" concentration of each compound was produced in a sample bag by following a two step dilution procedure similar to that outlined in the previous calibration procedure. The first dilution was made by injecting 10 μl. of high purity liquid standard into a glass jar containing approximately 25 to 30 glass mixing beads. The jar was then shaken for 60 seconds to insure complete mixing. Five ml. of the jar air was then injected into an aluminized sample bag as the bag was filled with 5 liters of dry zero-air. This bag provided a constant low ppm (approximately 2 ppm) concentration air source for the Nafion® Dryer.

The sampling train (Figure 3.1) consisted of the Nafion® Tube Dryer connected to the aluminized sample bag on one end and to a MSA (Mine Safety Appliance Company) model S small volume vacuum pump on the other end. Dry zero-air (<10% R.H.) was used as the counter current purge gas for the Dryer. During testing, the sample flow rate through the dryer was 60 ml/min and the purge flow rate was 300 ml/min. Flow rates for the vacuum pump, bag air, and purge air were calibrated with a Gilian Primary Flow Calibrator model number P/N-D008268 (Gilian Instrument Corporation).

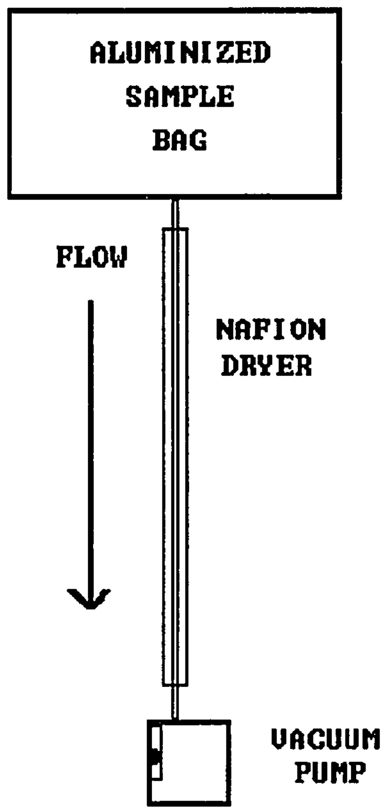


Figure 3.1 - Configuration of the Nafion sampling train.

Between the sample bag and the Nafion® tubing, a short section of stainless steel tubing (1/8" OD) was connected to a small section of rubber tubing (1/8" ID) to allow for sampling. The rubber tubing was slipped over the male barbed fittings on the valve of the sample bag and the stainless steel tubing, allowing each to butt up against the other. This technique limited the surface area of rubber in contact with the sample stream. The other end of the stainless steel tubing was connected to the Nafion® dryer by a nylon fitting.

Collection of a sample involved slightly stretching the rubber tubing between the barbed fittings, thus allowing a syringe needle to penetrate into the sample stream. The needle was pushed into the sample line in the up-stream direction or towards the bag. This further reduced any effects caused by the rubber tubing.

Sampling of the outflow end of the Nafion® dryer was similar to that of the inflow. A small section of rubber tubing connected the dryer to the vacuum pump. The sampling syringe needle was inserted into the rubber tubing in the up-stream direction towards the dryer.

HIGH PPM TEST

The high ppm "test" concentration was made up at approximately 200 to 500 ppm. As in the low ppm test, an aluminized sample bag served as the test chamber. Five μl. of high purity liquid standard were injected into the bag inlet as the bag was filling with 5 liters of zero-air.

The sample train and sampling methodology for the high ppm test was identical to the low ppm test procedure.

DECONTAMINATION AND QUALITY CONTROL

SAMPLE BAG

Cleaning of the sample bag occurred prior to each test session. Decontamination of the sample bag involved a series of filling and evacuation steps. Filling the bag with zero-air, followed by evacuation with a vacuum pump (25 L/min) was one step. This procedure was repeated 10 to 20 times, or until GC analysis insured that the bag was clean.

NAFION® DRYER

Decontamination of the Nafion® Dryer involved exposing both the inside and outside of the dryer to dry zero-air while heating the dryer assembly. A countercurrent flow pattern was formed where the incoming zero-air travelled in the opposite direction to spiked-air flow through the dryer. Zero-air flow rate was set at 1000 ml/min for the decontamination phase. The dryer was placed in an oven set at 70 degrees centigrade for a minimum of 15 minutes. Decontamination of the dryer was verified by GC analysis of the dryer tube and purge annulus effluent.

SAMPLE SYRINGES

Decontamination of all syringes was accomplished by cleaning with Alconox detergent and oven baking at 80°C for a minimum of 30 minutes. Each syringe was certified clean by GC analysis of zero-air prior to sample collection.

4 RESULTS

GC CALIBRATION

Calibration data and associated calibration curves for 28 compounds tested with the Nafion® dryer are given in Appendix A. Included in Appendix A are the masses of each compound injected into the GC, the concentration of each standard mixture, integrated peak area units for each analysis, peak area unit means, peak area unit standard deviations, percent coefficient of variation between trials, and GC column types and oven temperatures.

Calibration standard concentrations for each compound ranged from 0.124 ppm for diisobutyl ketone to 3.73 ppm for ethyl alcohol, and injected masses ranged from 0.63 ng. (nanograms) for n-octane to 14.4 ng. for perchloroethylene. All injection volumes used for calibration purposes were 1000 μl.

The coefficient of variation for all standard concentrations ranged from 0.05 percent for isopropyl ether with 6.48 ng. injected to 18.3 percent for ethyl ether with 0.7 ng. injected. The average overall percentage coefficient of variation for all 28 compounds was 4.8 percent.

Calibration curves were developed by linear regression of the total data collected for each compound. Each calibration curve represents 27 total data points collected in three trials of 9 separate analyses. The formula for each regression line and its corresponding "R" value is included on each individual graph. This formula was used for the calculation of compound concentrations based on area unit data collected in the testing of the Nafion® dryer. The "R" value describes the goodness of fit for the regression line to the data.

All analyses used for GC calibration purposes, precision evaluation, and testing of the Nafion® dryer were conducted using batches or groups of compounds. Compounds in a single batch were selected such that no one compound should interfere or coelute with another. Chromatographic peaks for all compounds in a single batch were sufficiently separated so that no overlap of adjacent peaks was evident throughout the concentration range of calibration standards. Therefore, compound identification was easily accomplished by comparing relative retention times, and bias associated with peak area integration would not be influenced by overlapping peaks. Compounds listed in Appendix A are grouped by column type and oven temperature. The order of chromatographic elution for any single batch of compounds is identical to the order in which those compounds are listed in Appendix A.

In order to evaluate precision of the analytical technique, ten duplicate analyses were run for each batch of compounds. These results are listed in Appendix B. Included in Appendix B are the peak area units from each analysis, sample means, standard deviations, and the percent coefficient of variation for each of the 28 compounds. The overall percent coefficient of variation is 3.4 percent, with a low of 1.2 percent for toluene and a high of 8.6 percent for n-octane.

NAFION® DRYER DATA

Nafion® dryer test data are given in Appendix C. High and low part per million concentrations for all 28 compounds listed in Table A.1 were tested through the Nafion® dryer. Appendix C includes: GC injection volumes for Nafion® dryer inlet and outlet samples, detector response in area units, the average peak area units for three duplicate analyses, calculated compound concentrations based on calibration curve regression formulae, and percent recoveries. Percent recovery for each compound was calculated by dividing the outlet compound concentration by the inlet compound concentration and then multiplying that value by 100. Less than values (ie. < 0.1) represent the analytical detection limit for that specific compound, which is directly related to the amount of sample injected into the GC.

Low ppm concentrations ranged from 0.12 ppm for methyl amyl ketone to 3.26 ppm for ethyl alcohol. Injection volume size for the low part per million tests ranged from one to five ml.

High ppm concentrations ranged from 66 ppm for ethyl butyl ketone to 1349 ppm for n-butyl acetate. Injection volume size for the high ppm test ranged from 100 μl. to 1.0 ml. Reported injection volumes include appropriate dilution factors. For example, the reported injection size of 0.002 ml. for the dryer outlet sample analyses of m-xylene equals a 200 μl. injection size with an applied dilution factor of 1 to 100.

SUMMARY DATA

The following graphs are given in Appendix D: percent recovery verses hydrogen bonding, percent recovery verses dipole moment, percent recovery verses log of water solubility, hydrogen bonding verses log of water solubility, dipole moment verses log of water solubility, and dipole moment verses hydrogen bonding. The data used to create these graphs is included in Appendix D. Experimental data and all historical data are included for an overall evaluation of a number of compounds tested against Nafion® dryer systems.

The ability of a compound to form hydrogen bonds is based on strong, moderate, and weak bonding capacities. Compounds that have strong hydrogen bonding capacities are given a value of three, (eg. methanol); moderate hydrogen bonding compounds are given a value two, (eg. acetone); and poor hydrogen bonding compounds are given a value of one, (eg. benzene).

All the graphs in Appendix D are based on the total available data, which include historical data from other authors as well as data from this experiment. The data base for the total sum of all compounds tested was limited by the availability of information on water solubility, dipole moments, and hydrogen bonding capacities. Historical data on compound recoveries from Nafion® dryers are given in Table D.2. However, physical data on some of the listed compounds were not available. Therefore, those compounds were eliminated from the data base used to produce the graphs in Appendix D.

5 DISCUSSION

In this paper, the evaluation of bias associated with the use of a Nafion® permeable membrane dryer used in the analyses of polar and nonpolar volatile organic compounds involved historical data as well as new experimental data. Historical data regarding recovery rates from Nafion® dryer systems were incomplete and, therefore, certain compounds were chosen to fill gaps in known data.

It is clear from previous work from other authors that the Nafion® permeable membrane is a selective material that has limited uses in analytical chemistry. Scientists that use analytical methodologies that include a Nafion® dryer must carefully evaluate the applicability of that method for the analysis of specific types of compounds. The following discussion includes a summary of the total data base on recovery rates from Nafion®, interpretation of these recovery rates, and results from a statistical model developed to aid future researchers in determining the feasibility of using a Nafion® dryer for analytical purposes.

A summary of the data base (see Table D.1) reveals two distinct relationships between recovery rates from Nafion® dryers and certain classes of chemicals. Recovery rates for non-polar volatile organic compounds are typically upwards of 100 percent, and recoveries of extremely polar volatile organic compounds are typically less than ten percent. There are many compounds that fall into the middle ground; for example, ketones, ethers, esters, and aldehydes. It is these compounds that are of special interest. Moderately polar compounds, or more specifically, compounds that possess moderate abilities to form hydrogen bonds, are possible candidates for inclusion into analytical methods that utilize a Nafion® dryer.

Information collected in this investigation show that many or most of the slightly polar compounds that were tested exhibit gross effects of removal when the analytical system includes a Nafion® dryer. With proper documentation and knowledge of possible reductions in recovery rates, an analyst may choose to use a Nafion® dryer in specific laboratory procedures. Further, Nafion® membranes may prove to be an aid in eliminating interfering compounds from a specific analysis. For example, the direct injection of water or alcohol samples into an analytical system fitted with a Nafion® dryer will aid in the analysis of nonpolar compounds contained in the polar medium.

In this paper, hydrogen bonding capacities are categorized into three groups; 1) weak hydrogen bonding, 2) moderate hydrogen bonding, and 3) strong hydrogen bonding. Precise data on hydrogen bonding capacities are not available for many compounds. Other authors have recognized this fact. Therefore, specific characterization of hydrogen bonding itself may not be essential. General bonding categories are sufficient to estimate recovery rates from Nafion®. However, some compounds may possess hydrogen bonding capacities similar to compounds in an adjacent category. Therefore, the apparent influence of hydrogen bonding may hide or shade its true influence on interactions between specific molecules.

From the graph of water solubility verses hydrogen bonding (see Appendix D), we see that moderately water soluble compounds typically have lower hydrogen bonding capacities than miscible compounds. Compounds that are moderate hydrogen bonders are more water soluble than compounds with weak hydrogen bonding capacities. It is clear from the graph of hydrogen bonding verses percent recovery (see Appendix D) that compounds with high hydrogen bonding capacities also have lowered recovery rates from the Nafion® dryer.

The effect of dipole moment on recovery from the Nafion® is less clear. From the graph of dipole moment verses percent recovery, there appears to be a relationship between small dipole moments and higher recovery rates. It is less evident that large dipole moments are strongly related to lower recoveries. From the graph of hydrogen bonding verses dipole moment (Appendix D), there appears to be little relation between the two parameters for the compounds selected in this data base.

The compounds that fall into the middle ground are the most difficult to predict recovery rates from the Nafion® dryer. Recovery from the dryer is dependant on two scenarios; 1) the ability of compounds to interact with water molecules held in the Nafion® matrix and, 2) interactions between exogenous compounds and the Nafion® matrix. What is the quantitative effect of Nafion®-compound interactions on recovery percentages? Is scenario #1 the predominant scheme to be analyzed when evaluating the recovery rates from Nafion® dryers? Certainly, much of the evidence points in that direction. Therefore, water solubility may indeed be the best indicator for determining compatabilities between specific compounds and Nafion® dryers.

Referring to Appendix D, the plot of percent recovery verses log of water solubility shows that compounds with solubilities of less than 1 g/L predominately have recovery rates greater than 90 percent and compounds with water solubilities of greater than 1 g/L have lower rates of recovery. Only four compounds, (benzaldehyde, ethylene oxide, ethyl ether, and acetonitrile) have recoveries between 40 and 80 percent. Benzaldehyde possesses moderate hydrogen bonding capacity, a large dipole moment, and a water solubility of 3 g/L. Ethylene oxide possesses a moderate hydrogen bonding capacity, a moderate dipole moment, and is miscible in water. Ethyl ether possesses moderate hydrogen bonding, a moderate dipole moment, and water solubility of 8 g/L. Acetonitrile possesses low hydrogen bonding capacities, a large dipole moment, and is nearly miscible in water with water solubility of greater than 400 g/L. Each of these compounds has different factors determining its interaction with the Nafion® dryer. These four compounds exemplify the complexity of determining what factors are most important in estimating the reactivity of specific compounds with the Nafion® membrane. It is only through statistical analysis of recovery percentages for many compounds and their individual characteristics that we can further understand the micro-mechanics of this phenomenon.

It is important to note that the recovery percentage for ethyl ether, as reported by Baker (Baker,1974) is higher than the recovery percentages found in this experiment. Baker reported a recovery percentage of >90% for ethyl ether. This experiment resulted in recoveries of approximately 50%. Ethyl Ether was the only compound that exhibited significantly different recovery rates between historical data and the duplicate experiments included in this study. Since both the high ppm and low ppm tests for ethyl ether resulted in similar recovery rates, this author must assume that the value reported by Baker is in error. Unfortunatly, there are no additional data from a third source to validate this discrepancy.

A predictive model for recovery rates from a Nafion® dryer, based on known physical parameters listed in Table D.1, was calculated by the computer program Number Cruncher Statistical System (Hintze,1987). Computer calculation of the data base by stepwise multiple regression is based on hydrogen bonding capacity, dipole moment, water solubility, and recovery rates for specific compounds. For this model, the dependent variable is percent recovery, and the independent variables are hydrogen bonding, dipole moment, and the log of water solubility. The result is the following formula:

$$y = 140.53 - (40.16)(A) - (7.06)(B) - (4.10)(C) + 11.56$$

Where,

y = Estimated percent recovery from dryer.
A = Hydrogen bonding capacity (1,2, or 3).
B = Dipole moment.
C = Log of water solubility.

Parameter estimates for each variable, (eg. -40.16), precede each independent variable in the formula. The y intercept equals 140.53 and the additive error is 11.56. The overall R^2 or predictive value of this model is 0.7885. Individual or simple R^2 values are 0.7316 for hydrogen bonding, 0.5070 for water solubility, and 0.1676 for the dipole moment.

The solubility parameter (δ) is excluded from the model because it has no effect on predicting compound recovery from Nafion® dryers. The solubility parameter is specific for evaluating solubility potential between two or more compounds that are present in high concentration. Since water is typically in percent concentration in ambient air and all other compounds are in the ppm or ppb concentration range, the solubility parameter is not a significant predictor of recovery.

From the earlier discussion of the mechanisms of action within the Nafion® membrane, water content within the membrane is the driving force for all or most other interactions. It is the interaction of water molecules within the Nafion® membrane, the formation of solvent shells, and the eventual expansion of the ionic clusters within the Nafion® matrix which influence the overall recovery of specific compounds from the Nafion® dryer. The most predominant scheme involves water solubility, either by strong hydrogen bonding or by induced dipole-dipole interactions, whereby molecules are stripped from the sample stream and collected within the Nafion® membrane. These water soluble molecules become interrelated with water molecules within the Nafion® membrane, and as the ionic clusters expand, transport of these molecules along with the water molecules occur through interconnected clusters within the membrane. The initial force responsible for the flux of water and other molecules is dependent on the osmotic gradient which is attributed to the dehydrated Nafion® and further accentuated by the countercurrent flow of dry purge gas on the outside of the membrane. Molecules of water and their water soluble counterparts finally dissociate from each other, evaporate from the outside surface of the membrane, and are swept away by the dry purge gas.

Early experiments in this investigation with the Nafion® dryer showed a preponderance for contamination of the dryer with polar compounds that possess strong hydrogen bonding capacities or large dipole moments. Contamination of the dryer by polar compounds typically involves a long residence period. There was no evidence of contamination of the dryer by nonpolar or water insoluble compounds. Heating of the dryer for approx- imately 30 minutes at 80 °C, along with purging both the inside and outside of the dryer with dry zero-air, was sufficient to reduce the concentration of any contaminant below the GC detection limit. EPA Method TO-14 recommends this decontamination procedure prior to each analysis. It is important to note that if the Nafion® dryer recommended in EPA Method TO-14 does not effect recovery rates of the 42 compounds listed as viable for this method (Table 1.1), then the Nafion® dryer should not become contaminated. It is only when polar or water soluble compounds contact the Nafion® membrane that decontamination need be required.

In general, one may attribute reduced recovery rates from the Nafion® dryer to interactions between specific compounds and the water content within the sample. Mass transfer of molecules from the sample stream into the Nafion® matrix is largely driven by molecular forces between the predominant water molecules and the compound or compounds in low concentration. It would be incorrect to rule out any other interactions, such as bonding between specific compounds and the fluorocarbon backbone or the sulfuric acid tails of the Nafion® polymer. It is entirely possible that specific molecules do bond or adsorb onto the Nafion® polymer membrane. However, these types of interactions appear to be hidden by the massive flux of water molecules and their ability to co-transport other molecules through the tortuous paths of the inner Nafion® polymer.

In summary, this paper should provide environmental professionals as well as the analytical chemistry community with a concise collection of previous work regarding the use of Nafion® permeable membranes. Nafion® polymer membranes have many uses in analytical chemistry and environmental science which include, but are not limited to: 1) the use of a pre-dryer for sample collection with solid sorbent tubes, 2) pre-drying air samples collected in bags or SUMMA canisters before analyses by cryogenic trapping, and 3) direct injection of liquids into an analytical instrument what contain a Nafion® pre-dryer. Some insight was also presented about the mechanism of compound removal from sample streams by a Nafion® dryer. Several authors have experimented with the Nafion® membranes, and have determined what techniques apply. However, little is known of the specific physiochemical interactions between specific compounds, which are diluted in humid air or liquid samples, and the Nafion® polymers.

APPENDIX A - (Calibration data)

Table A.1 - Compounds tested and GC column types and temperatures.

Column = SP-1000

55 degrees isothermal

Ethyl Alcohol
Methylene Chloride
Acetone
Isopropyl Alcohol

120 degrees isothermal

Tetrahydrofuran
Ethyl Ether
Methyl Ethyl Ketone
Isobutyl Alcohol
Ethyl Acetate
n-Butyl Alcohol

150 degrees isothermal

1,4-dioxane
Trichloroethylene
Isopropyl Ether
Cyclohexanone

180 degrees isothermal

Methyl Propyl Ketone
n-Propyl Acetate
Methyl Isobutyl Ketone
Perchloroethylene

190 degrees isothermal

Cyclohexanol
n-Butyl Acetate
Toluene

Column = FFAP

40 degrees isothermal

n-Octane

80 degrees isothermal

Ethyl Butyl Ketone
Diisobutyl Ketone
Chlorobenzene

100 degrees isothermal

Isoamyl Acetate
m-Xylene
Methyl Amyl Ketone

Table A.2 - Calibration data for 28 compounds tested.

ETHYL ALCOHOL

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.7	0.373	4162	8258	5722	6033	1103.8	18.3
0.7	0.373	3916	8335	6038			
0.7	0.373	4014	7756	6093			
2.81	1.49	14322	13482	13826	13718	386.5	2.8
2.81	1.49	13901	13336	13058			
2.81	1.49	13918	14252	13363			
7.03	3.73	41672	40707	40761	40937	580.3	1.4
7.03	3.73	40880	41290	41139			
7.03	3.73	41551	39506	40931			

METHYLENE CHLORIDE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
1.16	0.335	3408	3475	3503	3465	201.7	5.8
1.16	0.335	3510	3652	3880			
1.16	0.335	3152	3307	3298			
4.65	1.34	11787	12325	12424	12141	71.4	0.6
4.65	1.34	11611	12229	12260			
4.65	1.34	11974	12392	12267			
11.64	3.35	29987	29245	28618	29082	434.4	1.5
11.64	3.35	29719	29229	28355			
11.64	3.35	30122	28262	28198			

ACETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.7	0.295	6090	5492	5905	5910	370.6	6.3
0.7	0.295	6008	6315	6030			
0.7	0.295	6449	5168	5732			
2.8	1.18	24623	24811	23512	24486	444.8	1.8
2.8	1.18	24100	24404	23904			
2.8	1.18	26378	24624	24020			
7.01	2.95	58612	58316	56020	57561	1073.3	1.9
7.01	2.95	58553	58247	55675			
7.01	2.95	58964	57486	56179			

S.D. - Standard Deviation
% C.V. - Percent Coefficient of Variation

Table A.2 - Continued.

ISOPROPYL ALCOHOL

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.69	0.283	6047	4856	7404	6333	1128.0	17.8
0.69	0.283	6366	5682	7512			
0.69	0.283	6656	5126	7351			
2.78	1.13	25024	24861	24987	24894	318.1	1.3
2.78	1.13	24464	24303	24554			
2.78	1.13	25534	25081	25236			
6.95	2.83	62920	66040	61338	63163	2004.5	3.2
6.95	2.83	64035	64583	61455			
6.95	2.83	62625	64635	60839			

TETRAHYDROFURAN

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.79	0.267	6649	7693	8174	7625	623.7	8.2
0.79	0.267	6777	7475	8874			
0.79	0.267	6550	7457	8972			
3.16	1.07	35331	34628	34794	34741	312.2	0.9
3.16	1.07	34991	34037	34834			
3.16	1.07	35090	34192	34768			
6.32	2.14	62799	62836	65758	63196	1825.4	2.9
6.32	2.14	62082	61874	65724			
6.32	2.14	60112	61794	65788			

ETHYL ETHER

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.63	0.209	7408	7278	6610	7170	208.6	2.9
0.63	0.209	7551	7053	7039			
0.63	0.209	7366	7179	7050			
2.52	0.84	26644	25481	25841	25785	308.7	1.2
2.52	0.84	26443	25018	25623			
2.52	0.84	26561	24987	25468			
6.3	2.09	63098	62754	63235	62272	1150.3	1.8
6.3	2.09	62423	61012	63426			
6.3	2.09	60729	60542	63232			

Table A.2 - Continued.

METHYL ETHYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.71	0.242	7930	8705	8047	8260	199.0	2.4
0.71	0.242	8072	8348	8511			
0.71	0.242	7838	8408	8480			
2.84	0.97	30265	29996	29796	29788	180.1	0.6
2.84	0.97	29629	29617	29805			
2.84	0.97	29815	29757	29413			
7.1	2.42	72935	72071	71100	71023	825.4	1.2
7.1	2.42	71593	69825	70915			
7.1	2.42	70361	69593	70813			

ISOBUTYL ALCOHOL

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.72	0.236	3957	6407	5825	5595	288.4	5.2
0.72	0.236	3867	6458	6648			
0.72	0.236	3932	6587	6674			
2.88	0.94	21944	25661	26397	24343	543.1	2.2
2.88	0.94	20815	24970	26389			
2.88	0.94	21919	25181	25814			
7.2	2.36	61044	59590	63304	60710	2771.1	4.6
7.2	2.36	60866	57414	63899			
7.2	2.36	59132	57637	63505			

ETHYL ACETATE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.79	0.221	4043	3483	3758	3712	157.3	4.2
0.79	0.221	4067	3334	3724			
0.79	0.221	4019	3399	3581			
3.16	0.88	14293	13498	14126	14021	292.1	2.1
3.16	0.88	14963	13704	13472			
3.16	0.88	14626	13412	14096			
7.9	2.21	29488	29299	29629	29219	568.5	1.9
7.9	2.21	30111	29216	28937			
7.9	2.21	29784	27854	28657			

Table A.2 - Continued.

n-BUTYL ALCOHOL

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.72	0.238	8141	8171	6447	7759	668.0	8.6
0.72	0.238	8420	8229	7350			
0.72	0.238	7761	8183	7125			
2.88	0.95	31294	32521	31532	31913	428.6	1.3
2.88	0.95	30679	32414	32123			
2.88	0.95	32423	32623	31612			
7.2	2.38	83303	80229	78793	79726	779.1	1.0
7.2	2.38	82014	77868	78743			
7.2	2.38	79624	77965	78995			

1,4-DIOXANE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.92	0.255	5415	5237	7157	5838	916.0	15.7
0.92	0.255	5318	4617	6734			
0.92	0.255	5244	5978	6846			
3.68	1.02	20505	22815	20861	21488	790.8	3.7
3.68	1.02	21035	22744	21571			
3.68	1.02	20899	22068	20890			
9.19	2.55	49892	53764	52011	51917	530.2	1.0
9.19	2.55	49753	52866	53090			
9.19	2.55	50231	53049	52599			

TRICHLOROETHENE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
1.31	0.243	5708	5814	5856	5848	483.3	8.3
1.31	0.243	5430	5164	6347			
1.31	0.243	5294	6425	6594			
5.24	0.97	20787	23271	22861	22114	682.8	3.1
5.24	0.97	21020	23549	22047			
5.24	0.97	21337	22593	21558			
13.1	2.43	54213	55963	55078	54993	297.4	0.5
13.1	2.43	53339	55846	55676			
13.1	2.43	53920	55354	55550			

Table A.2 - Continued.

ISOPROPYL ETHER

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.65	0.155	9838	9096	10153	9414	1063.0	11.3
0.65	0.155	9347	7194	10292			
0.65	0.155	9479	9254	10075			
2.6	0.62	35045	37100	35537	36066	722.2	2.0
2.6	0.62	35582	37052	35461			
2.6	0.62	35442	37148	36225			
6.48	1.55	85756	87544	87743	87387	466.4	0.5
6.48	1.55	86214	88591	88125			
6.48	1.55	85899	88826	87784			

CYCLOHEXANONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.84	0.209	5846	9540	9456	8277	352.8	4.3
0.84	0.209	5703	9057	9964			
0.84	0.209	5294	10134	9498			
3.36	0.84	37800	40859	39028	39635	1113.1	2.8
3.36	0.84	38224	40990	40927			
3.36	0.84	37406	42261	39224			
8.39	2.09	92269	112426	106473	105649	1847.6	1.7
8.39	2.09	100311	110729	110032			
8.39	2.09	99963	110090	108552			

METHYL PROPYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.72	0.204	8593	8744	8781	8657	110.5	1.3
0.72	0.204	8857	8689	8522			
0.72	0.204	8594	8653	8478			
2.88	0.818	33363	35311	36422	34232	966.8	2.8
2.88	0.818	33106	35261	33599			
2.88	0.818	32792	34376	33861			
5.76	1.63	66889	63485	65077	64824	789.2	1.2
5.76	1.63	64498	63580	64986			
5.76	1.63	66564	63311	65022			

Table A.2 - Continued.

n-PROPYL ACETATE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.79	0.189	8091	7703	8076	8047	219.1	2.7
0.79	0.189	8267	8178	8344			
0.79	0.189	8053	7828	7880			
3.16	0.756	29495	30475	31913	29897	837.8	2.8
3.16	0.756	28982	30194	29403			
3.16	0.756	28868	30318	29426			
7.9	1.89	74965	73983	74089	73888	568.0	0.8
7.9	1.89	72070	73014	73981			
7.9	1.89	75282	73039	74569			

METHYL ISOBUTYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.71	0.174	9923	11206	9804	9832	950.4	9.7
0.71	0.174	9793	10328	8825			
0.71	0.174	9871	10329	8409			
2.85	0.696	36708	38228	40142	37502	1271.5	3.4
2.85	0.696	37603	37704	36948			
2.85	0.696	37121	36816	36246			
7.1	1.74	94231	95596	92427	93677	973.8	1.0
7.1	1.74	89420	94346	93270			
7.1	1.74	95655	94001	94151			

PERCHLOROETHENE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
1.44	0.213	3929	3568	4825	4261	523.5	12.3
1.44	0.213	3724	4838	4729			
1.44	0.213	3328	5174	4233			
2.85	0.852	19738	20747	22619	20566	775.0	3.8
2.85	0.852	19597	20757	20105			
2.85	0.852	19069	21356	21107			
14.4	2.13	52196	54449	53027	52590	575.4	1.1
14.4	2.13	49332	53288	53239			
14.4	2.13	52270	52707	52800			

Table A.2 - Continued.

CYCLOHEXANOL

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.82	0.201	6549	6023	6340	6076	541.4	8.9
0.82	0.201	5898	5330	6370			
0.82	0.201	5656	5557	6957			
3.28	0.804	31393	39799	31950	35575	3462.8	9.7
3.28	0.804	33416	39750	38830			
3.28	0.804	38787	31990	34263			
8.2	2.01	109124	103534	114204	106632	10223.9	9.6
8.2	2.01	100191	93503	118234			
8.2	2.01	102683	97898	120321			

n-BUTYL ACETATE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.78	0.165	4013	4184	5082	4458	569.3	12.8
0.78	0.165	4128	3990	4998			
0.78	0.165	4599	3854	5278			
3.12	0.66	19418	22090	18384	19963	1298.5	6.5
3.12	0.66	19650	21531	19420			
3.12	0.66	19395	20471	19309			
7.8	1.65	53520	51884	47462	48708	2627.3	5.4
7.8	1.65	46882	49817	46449			
7.8	1.65	48785	49758	43819			

TOLUENE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.77	0.204	11641	9927	13402	12057	1877.5	15.6
0.77	0.204	12525	10214	14070			
0.77	0.204	11497	10779	14458			
3.08	0.816	49919	51400	43698	48069	3281.0	6.8
3.08	0.816	49307	50475	45002			
3.08	0.816	48730	50163	43928			
7.7	2.04	114547	112517	104106	107173	4203.1	3.9
7.7	2.04	105585	105649	99415			
7.7	2.04	110600	109004	103133			

Table A.2 - Continued.

n-OCTANE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.63	0.134	7104	7697	5062	6671	1161.7	17.4
0.63	0.134	7814	7321	5113			
0.63	0.134	8342	6746	4838			
2.5	0.536	32896	38482	32581	33592	2757.9	8.2
2.5	0.536	34996	35979	32002			
2.5	0.536	29909	35245	30242			
6.24	1.34	92193	95291	90190	90783	2534.9	2.8
6.24	1.34	89739	87962	93852			
6.24	1.34	86291	89471	92054			

ETHYL BUTYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.73	0.156	6236	4105	5494	5224	482.5	9.2
0.73	0.156	6421	4304	4947			
0.73	0.156	6329	4294	4886			
2.92	0.623	21786	23256	21850	21407	1136.3	5.3
2.92	0.623	20324	21827	19932			
2.92	0.623	20751	22488	20448			
7.3	1.56	61662	65607	58117	61459	3414.8	5.6
7.3	1.56	61041	65663	58108			
7.3	1.56	64450	60681	57803			

DIISOBUTYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.72	0.124	4466	4107	4316	4287	205.6	4.8
0.72	0.124	4472	4486	4151			
0.72	0.124	4405	4339	3842			
2.88	0.496	16742	17673	21899	18696	1913.6	10.2
2.88	0.496	16345	17206	21807			
2.88	0.496	17840	18308	20444			
7.2	1.24	48845	51591	58235	53026	2488.6	4.7
7.2	1.24	49108	56341	54295			
7.2	1.24	51880	51323	55618			

Table A.2 - Continued.

CHLOROBENZENE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.98	0.214	8170	8376	8873	8547	166.4	1.9
0.98	0.214	8407	8735	8721			
0.98	0.214	8216	8591	8836			
3.92	0.856	42114	44621	48330	43787	2225.9	5.1
3.92	0.856	40434	42248	46546			
3.92	0.856	41482	42269	46036			
9.8	2.14	120480	131100	115179	120918	7584.8	6.3
9.8	2.14	116324	131062	116622			
9.8	2.14	122415	123304	111775			

ISOAMYL ACETATE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.78	0.146	6165	6936	7222	6772	131.3	1.9
0.78	0.146	6078	7098	7171			
0.78	0.146	6019	6963	7298			
3.12	0.584	27103	28290	28226	28146	466.5	1.7
3.12	0.584	26929	29130	27830			
3.12	0.584	28303	29079	28426			
7.77	1.46	72622	79016	74752	74777	1593.8	2.1
7.77	1.46	70736	78198	75301			
7.77	1.46	69932	77071	75364			

m-XYLENE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.77	0.178	9823	11413	11879	10874	382.7	3.5
0.77	0.178	9865	11011	11663			
0.77	0.178	9611	10845	11754			
3.08	0.712	49730	49530	46780	48342	1602.1	3.3
3.08	0.712	48985	49446	45677			
3.08	0.712	49704	49041	46183			
6.16	1.42	85645	94468	90247	88981	2185.3	2.5
6.16	1.42	84283	93710	90475			
6.16	1.42	83620	88152	90225			

Table A.2 - Continued.

METHYL AMYL KETONE

MASS (ng.)	Conc. (ppm)	TRIAL #1	TRIAL #2	TRIAL #3	MEAN	S.D.	% C.V.
0.73	0.156	7442	10089	8686	8540	537.2	6.3
0.73	0.156	7571	9189	8448			
0.73	0.156	7357	9305	8770			
2.92	0.623	32094	33308	33579	33186	484.4	1.5
2.92	0.623	32429	33994	32683			
2.92	0.623	33525	34019	33045			
7.28	1.56	79669	89139	77363	81759	5843.1	7.1
7.28	1.56	81727	88753	76370			
7.28	1.56	79877	86740	76194			

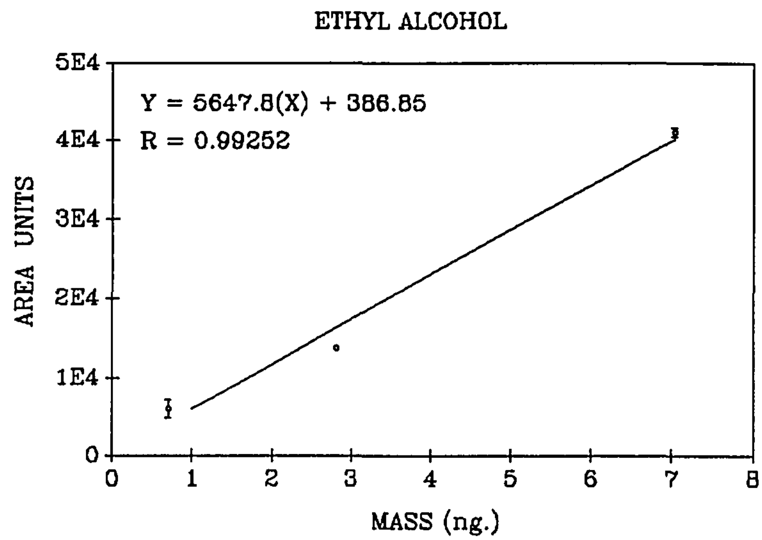


Figure A.1 - Calibration curve for ethyl alcohol using a SP-1000 column at 55 °C and a flow rate of 30 ml/min.

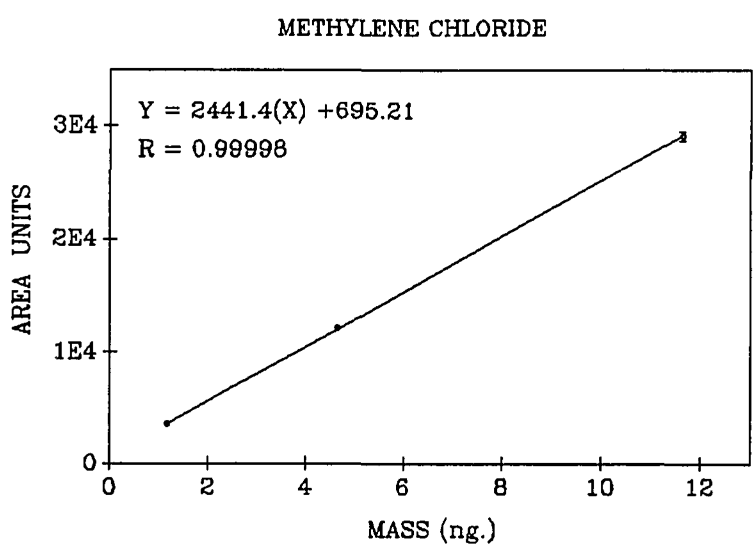


Figure A.2 - Calibration curve for methylene chloride using a SP-1000 column at 55 °C and a flow rate of 30 ml/min.

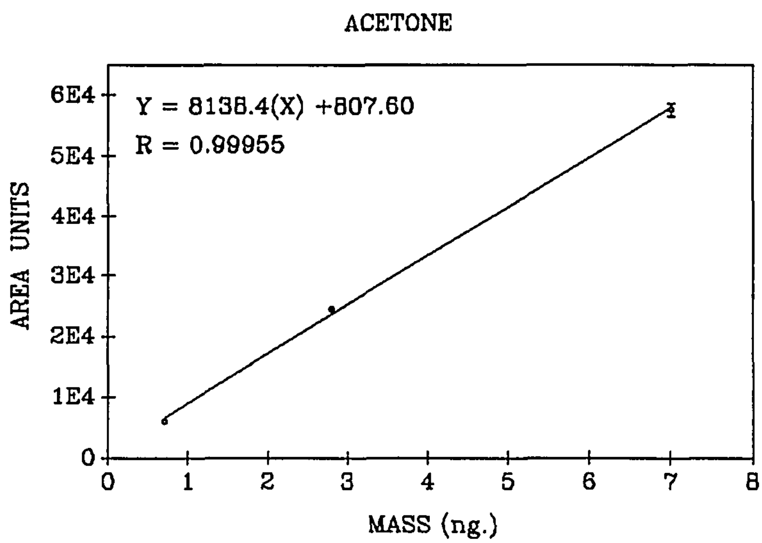


Figure A.3 - Calibration curve for acetone using a SP-1000 column at 55 °C and a flow rate of 30 ml/min.

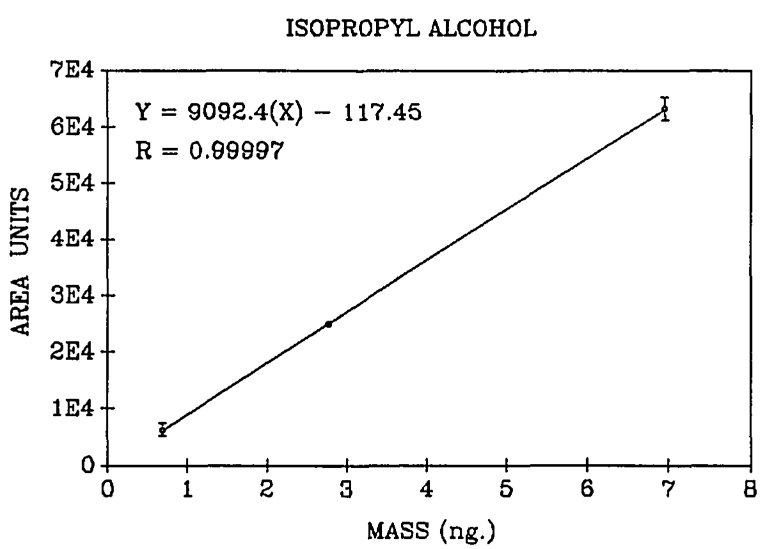


Figure A.4 - Calibration curve for isopropyl alcohol using a SP-1000 column at 55 °C and a flow rate of 30 ml/min.

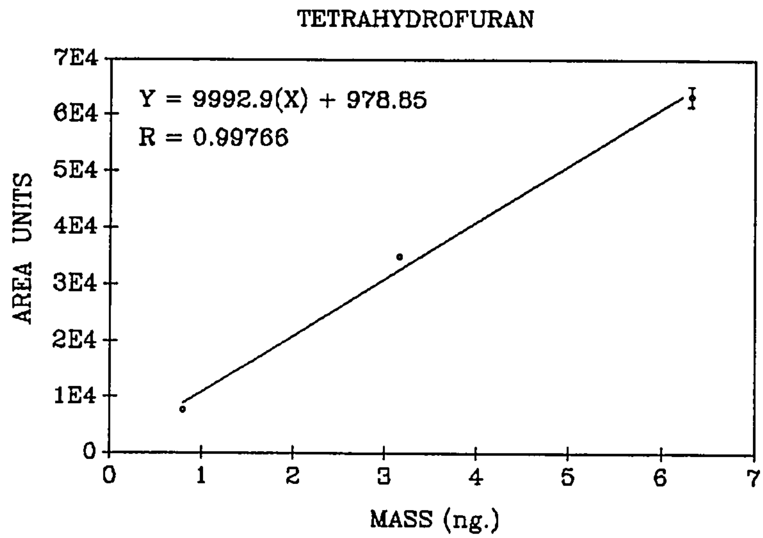


Figure A.5 - Calibration curve for tetrahydrofuran using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

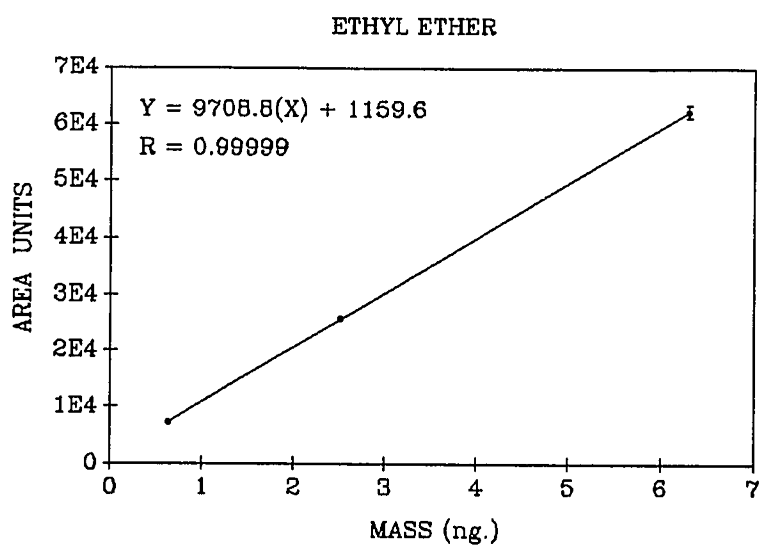


Figure A.6 - Calibration curve for ethyl ether using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

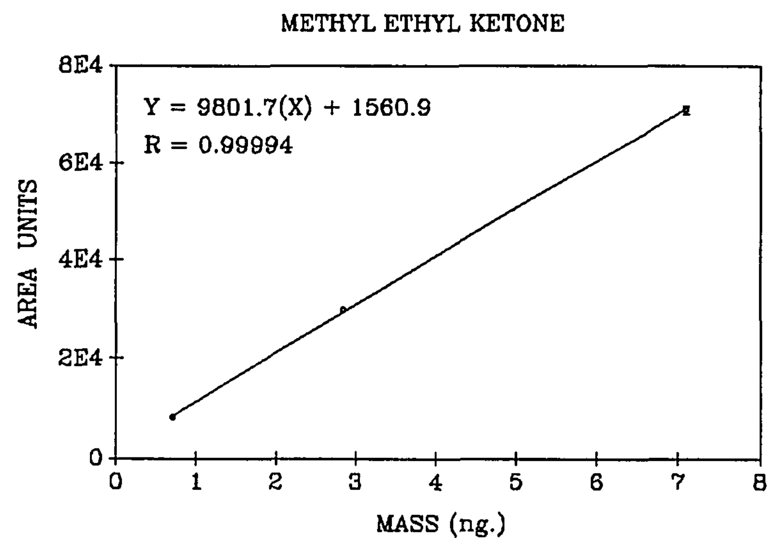


Figure A.7 - Calibration curve for methyl ethyl ketone using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

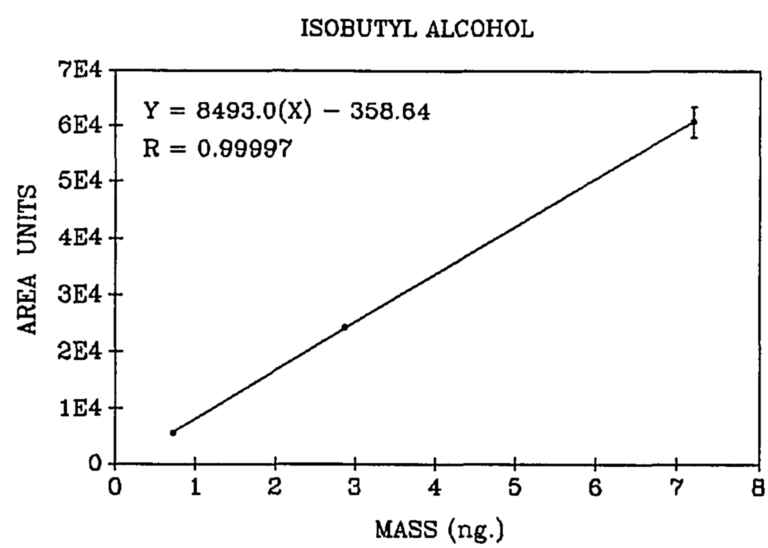


Figure A.8 - Calibration curve for isobutyl alcohol using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

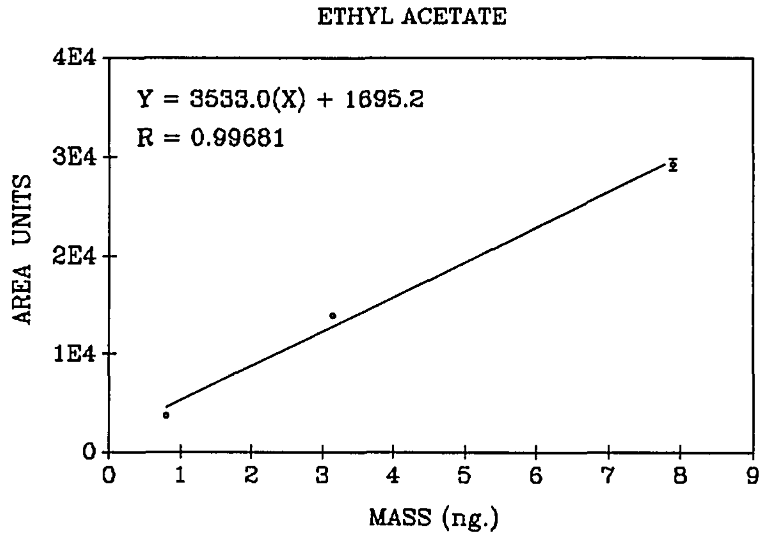


Figure A.9 - Calibration curve for ethyl acetate using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

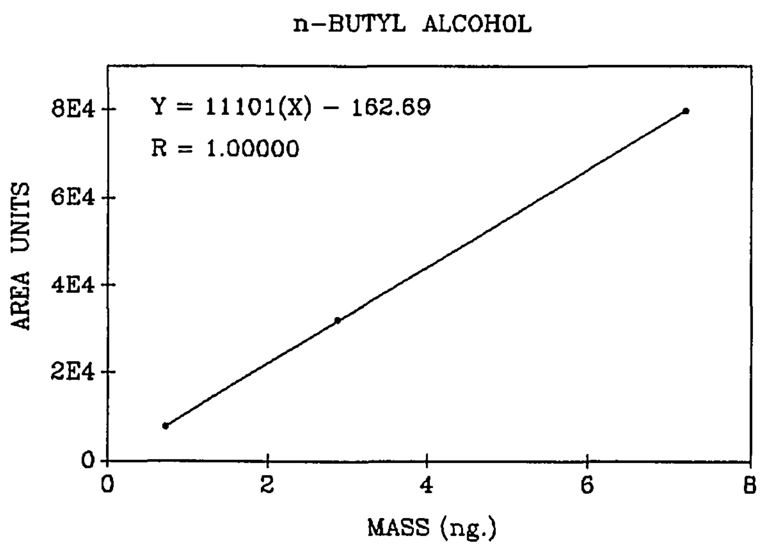


Figure A.10 - Calibration curve for n-butyl alcohol using a SP-1000 column at 120 °C and a flow rate of 30 ml/min.

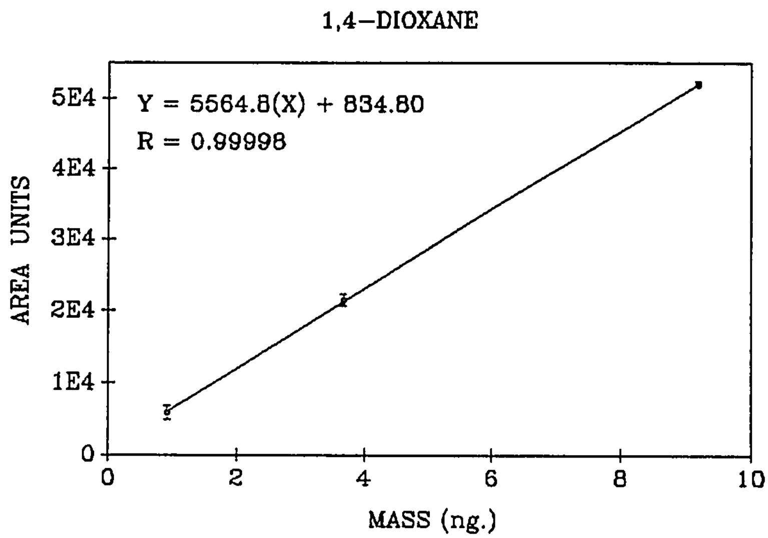


Figure A.11 - Calibration curve for 1,4-dioxane using a SP-1000 column at 150 °C and a flow rate of 30 ml/min.

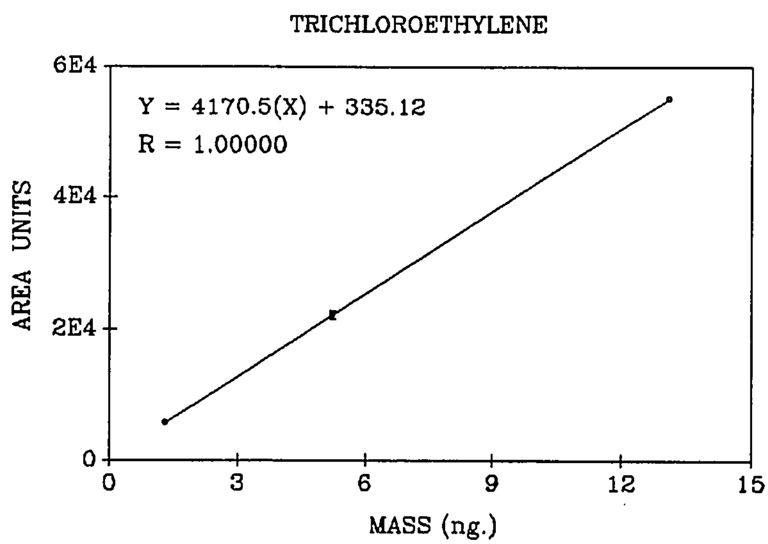


Figure A.12 - Calibration curve for trichloroethylene using a SP-1000 column at 150 °C and a flow rate of 30 ml/min.

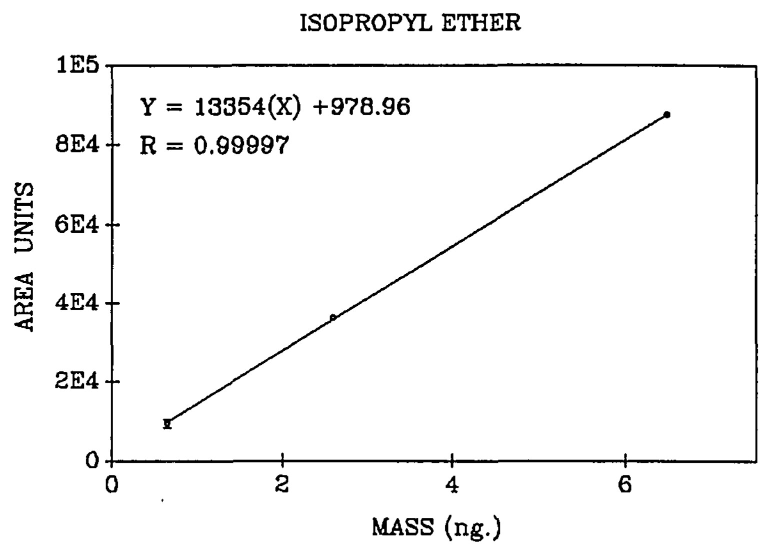


Figure A.13 - Calibration curve for isopropyl ether using a SP-1000 column at 150 °C and a flow rate of 30 ml/min.

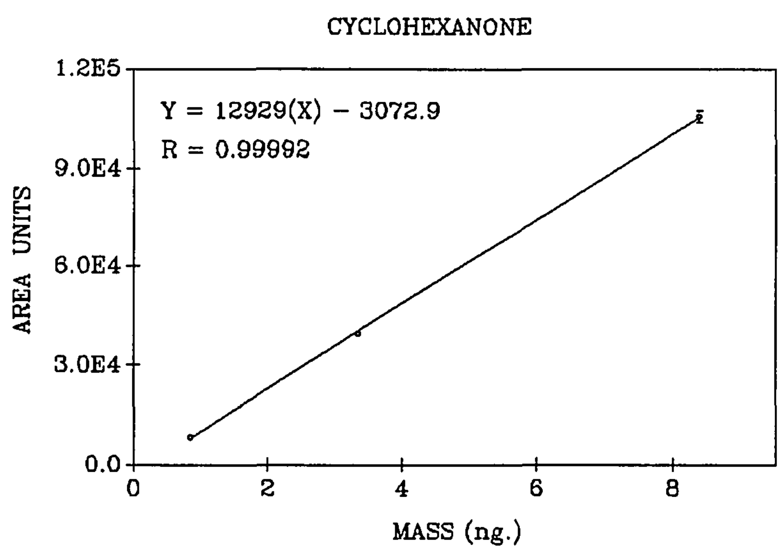


Figure A.14 - Calibration curve for cyclohexanone using a SP-1000 column at 150 °C and a flow rate of 30 ml/min.

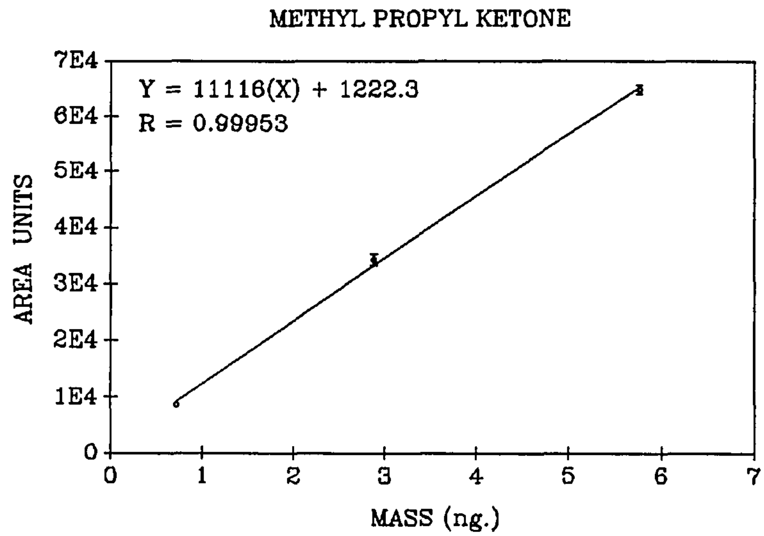


Figure A.15 - Calibration curve for methyl propyl ketone using a SP-1000 column at 180 °C and a flow rate of 30 ml/min.

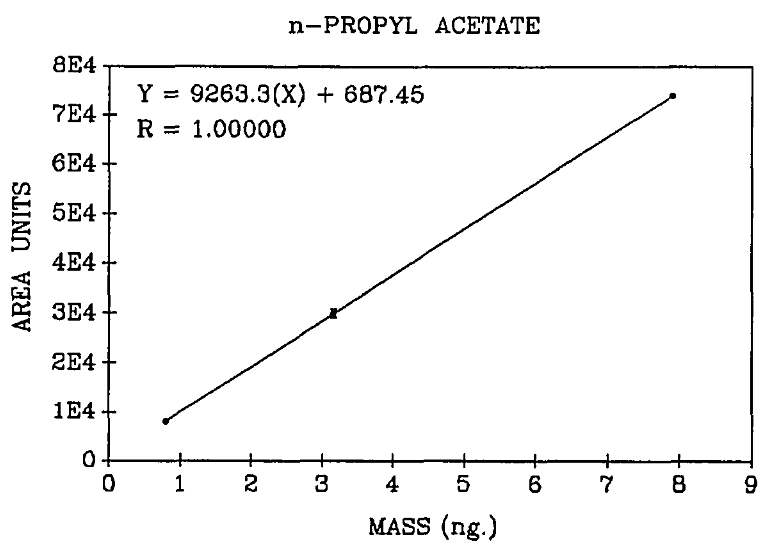


Figure A.16 - Calibration curve for n-propyl acetate using a SP-1000 column at 180 °C and a flow rate of 30 ml/min.

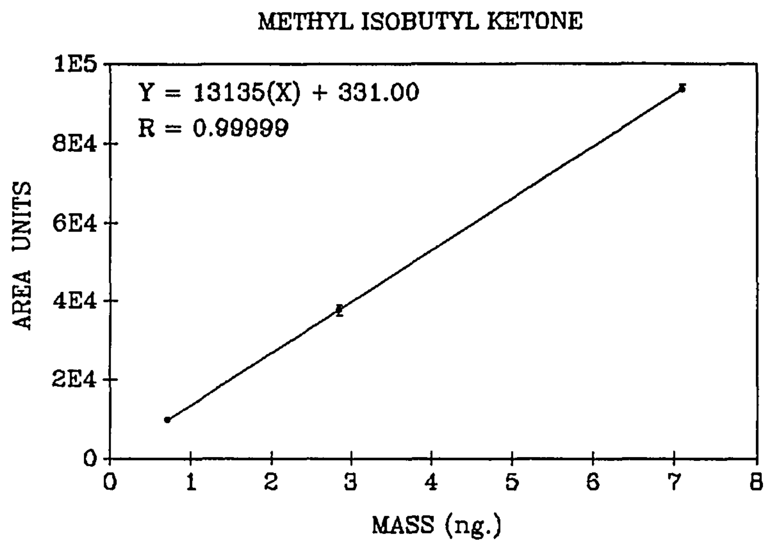


Figure A.17 - Calibration curve for methyl isobutyl ketone using a SP-1000 column at 180 °C and a flow rate of 30 ml/min.

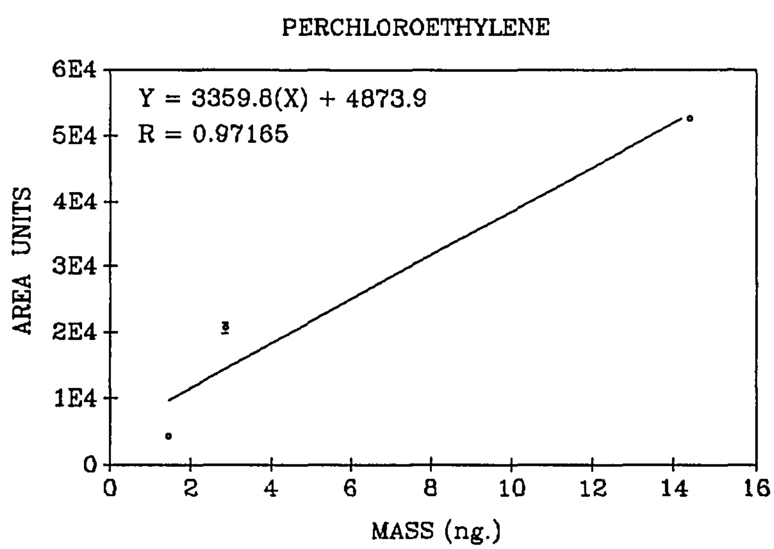


Figure A.18 - Calibration curve for perchloroethylene using a SP-1000 column at 180 °C and a flow rate of 30 ml/min.

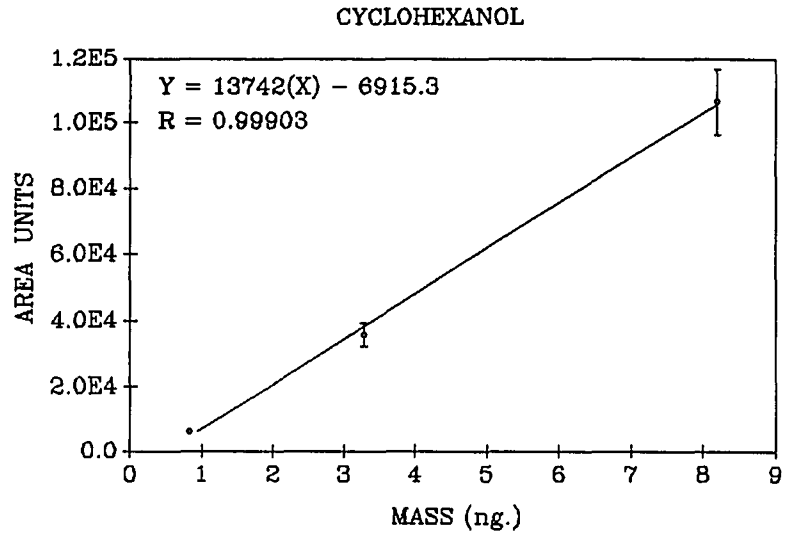


Figure A.19 - Calibration curve for cyclohexanol using a SP-1000 column at 190 °C and a flow rate of 30 ml/min.

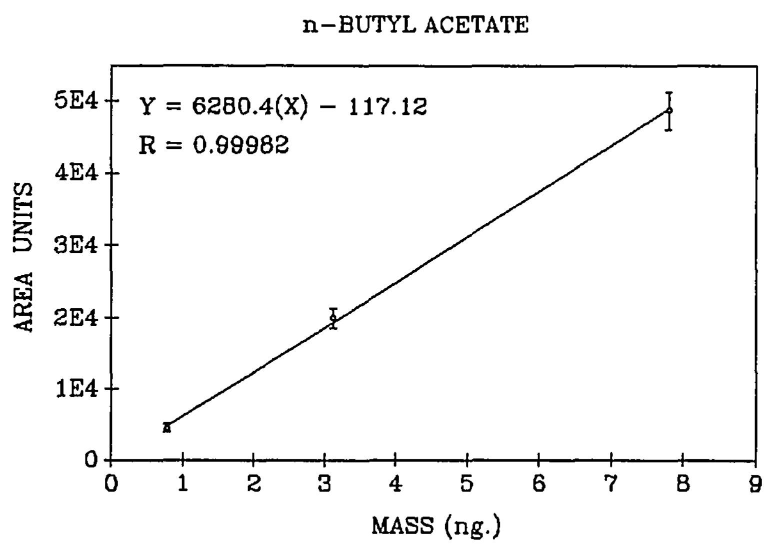


Figure A.20 - Calibration curve for n-butyl acetate using a SP-1000 column at 190 °C and a flow rate of 30 ml/min.

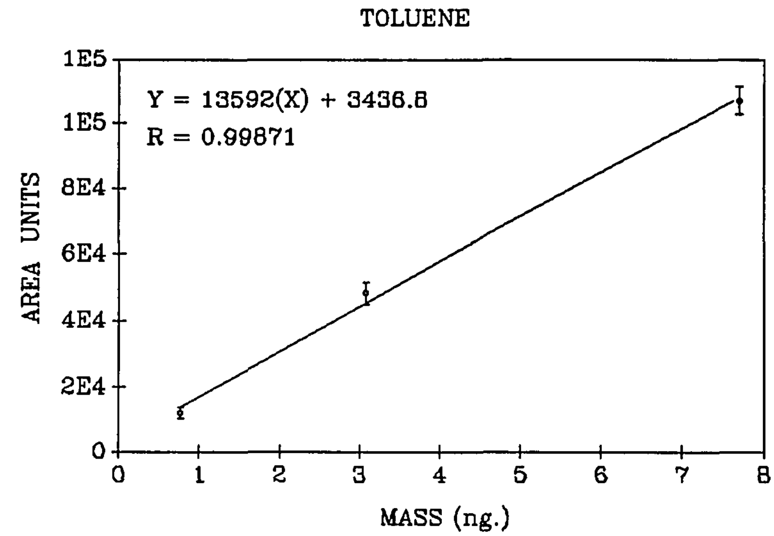


Figure A.21 - Calibration curve for toluene using a SP-1000 column at 190 °C and a flow rate of 30 ml/min.

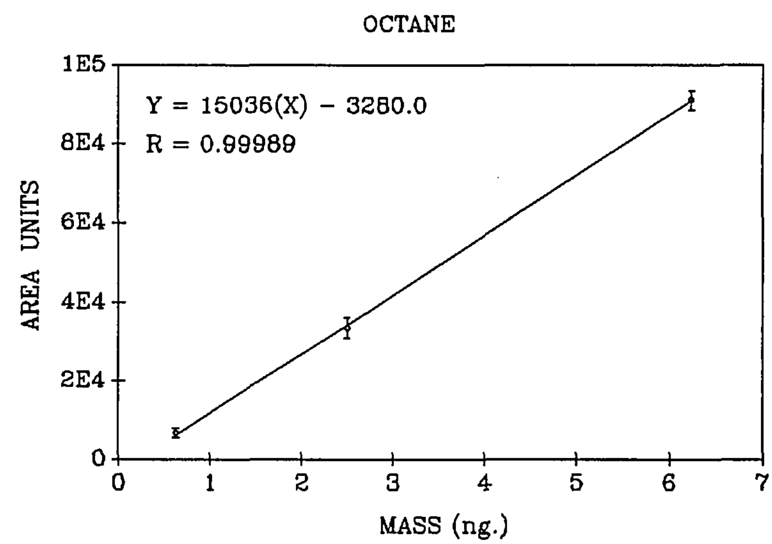


Figure A.22 - Calibration curve for n-octane using a FFAP column at 40 °C and a flow rate of 26 ml/min.

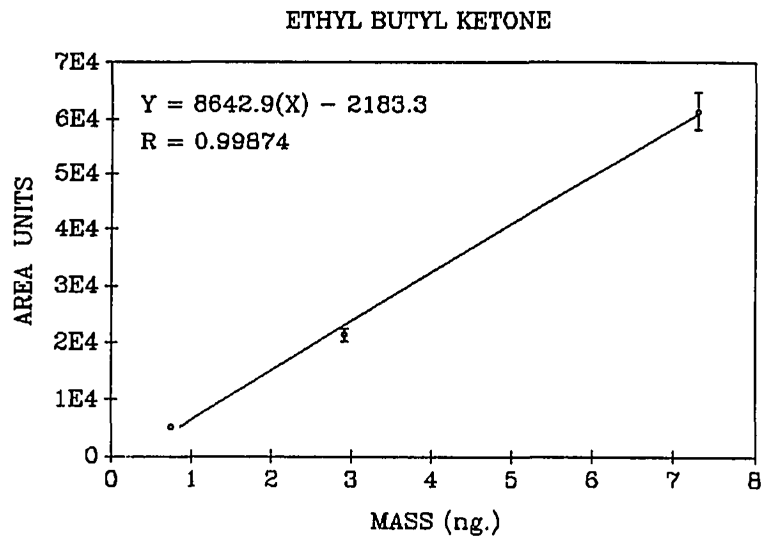


Figure A.23 - Calibration curve for ethyl butyl ketone using a FFAP column at 80 °C and a flow rate of 26 ml/min.

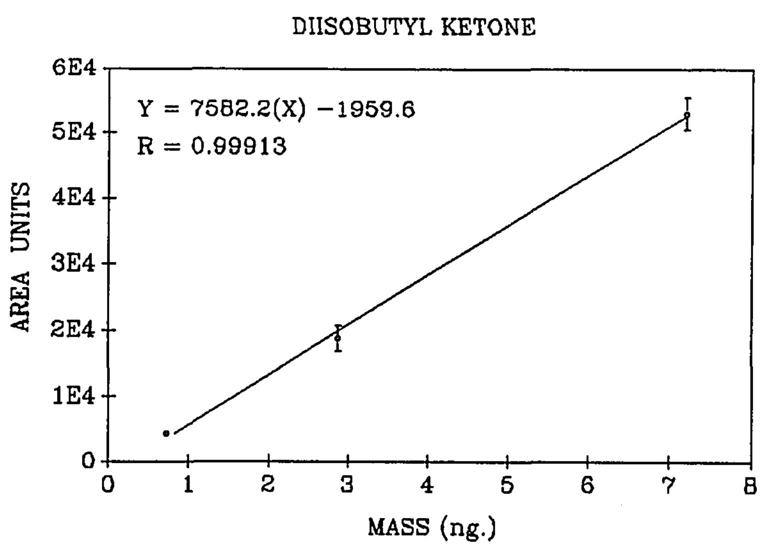


Figure A.24 - Calibration curve for diisobutyl ketone using a FFAP column at 80 °C and a flow rate of 26 ml/min.

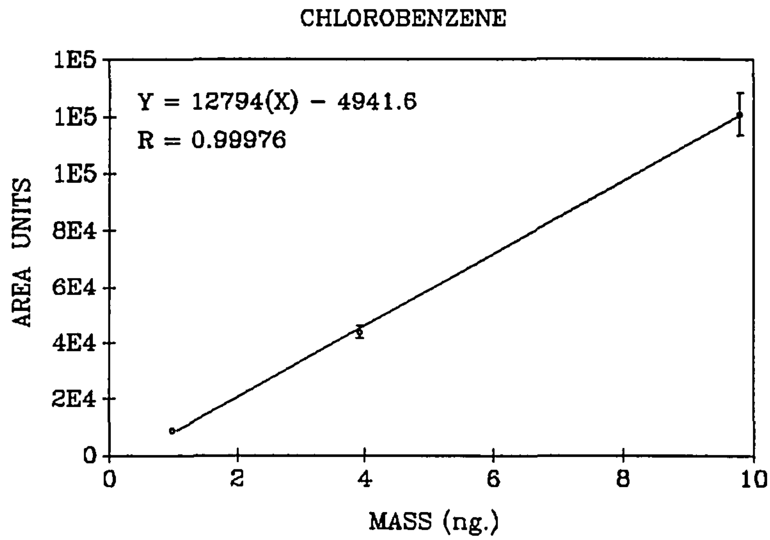


Figure A.25 - Calibration curve for chlorobenzene using a FFAP column at 80 °C and a flow rate of 26 ml/min.

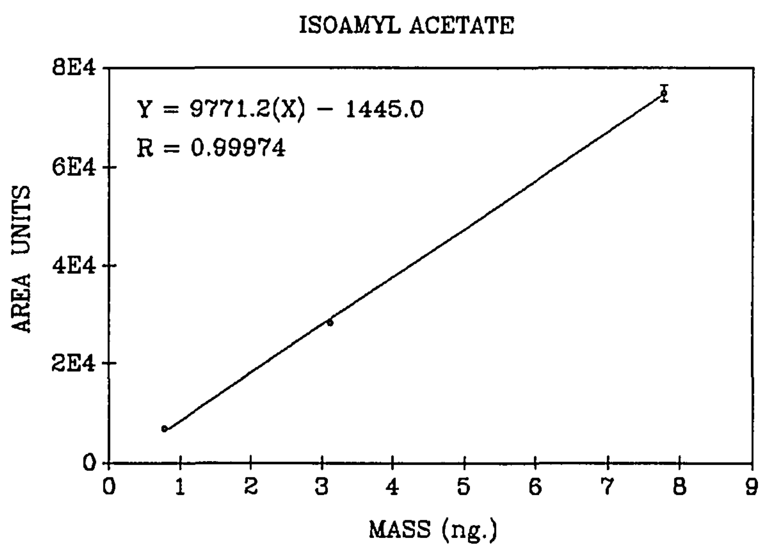


Figure A.26 - Calibration curve for isoamyl acetate using a FFAP column at 100 °C and a flow rate of 26 ml/min.

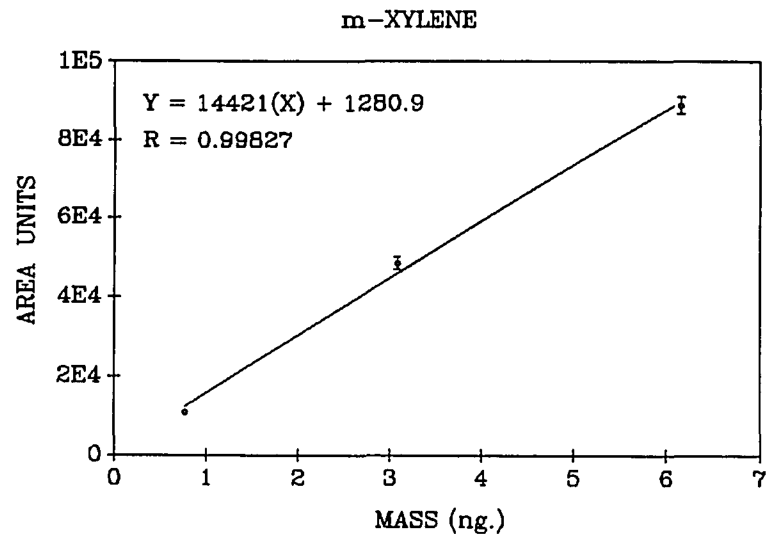


Figure A.27 - Calibration curve for m-xylene using a FFAP column at 100 °C and a flow rate of 26 ml/min.

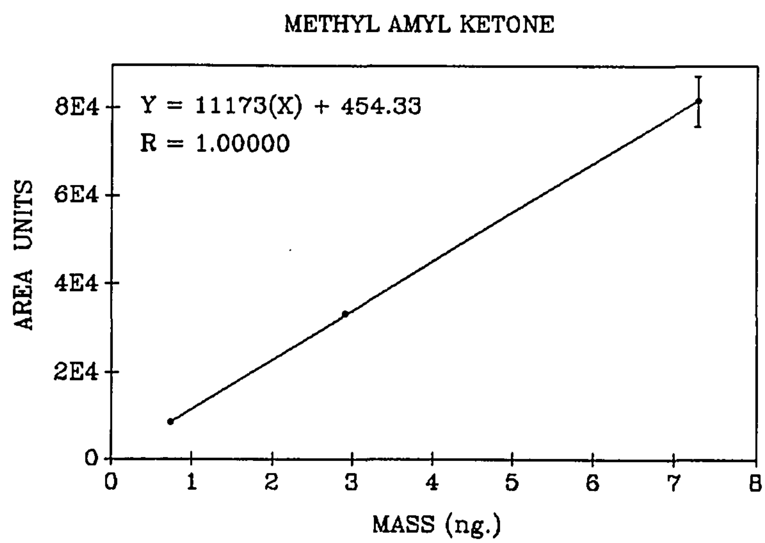


Figure A.28 - Calibration curve for methyl amyl ketone using a FFAP column at 100 °C and a flow rate of 26 ml/min.

APPENDIX B (Precision data)

Table B.1 - Precision data for 28 compounds tested.

RUN #	AMT. INJ. ul.	ETHYL ETHER	MEK	ISOBUTYL ALCOHOL	ETHYL ACETATE	n-BUTYL ALCOHOL	TETRAHYDRO FURAN	ETHYL ALCOHOL
		0.84 ppm	0.97 ppm	0.94 ppm	0.88 ppm	0.95 ppm	1.07 ppm	1.49 ppm
1	1000	26644	30265	21944	14293	31294	35331	14322
2	1000	26443	29629	20815	14963	30679	34991	13901
3	1000	26561	29815	21919	14626	32423	35090	13918
4	1000	25906	29345	21790	14466	32106	34275	13631
5	1000	23500	26182	19843	13009	29506	31032	13001
6	1000	24984	28531	20940	13576	30277	33103	12978
7	1000	26842	29624	22272	14323	31923	34516	12813
8	1000	26339	28828	21806	14175	32252	33993	12645
9	1000	26598	28964	21893	14471	32304	34702	12890
10	1000	25871	28790	21278	14234	31779	34021	13507
SAMPLE MEAN =		25969	28997	21450	14214	31454	34105	13361
SAMPLE S.D. =		1022	1126	734	552	992	1260	571
% C.V. =		3.9	3.9	3.4	3.9	3.2	3.7	4.3

C.V. = Coefficient of Variation

Table B.1 - Continued.

RUN #	AMT. INJ. ul.	ISOPROPYL ALCOHOL 1.13 ppm	1,4-DIOXANE 1.02 ppm	TCE 0.97 ppm	ISOPROPYL ETHER 0.62 ppm	CYCLO HEXANONE 0.84 ppm	METHYL PROPYL KETONE 0.82 ppm	n-PROPYL ACETATE 0.76 ppm
1	1000	25024	20505	20787	35045	37800	33363	29495
2	1000	24464	21035	21020	35582	38224	33106	28982
3	1000	25534	20899	21337	35442	37406	32792	28868
4	1000	25816	21212	21332	36383	40991	32537	28852
5	1000	24535	21286	21411	36101	39876	33024	29044
6	1000	24832	20927	21753	35642	38433	31873	28231
7	1000	24785	21248	20789	35592	37998	32437	28612
8	1000	24986	20890	20906	36378	39428	31910	28347
9	1000	24990	21088	21094	36327	40661	31038	27380
10	1000	24591	20382	20986	35993	37911	31294	27850
SAMPLE MEAN =		24956	20947	21142	35849	38873	32337	28566
SAMPLE S.D. =		432	303	310	456	1274	785	625
% C.V. =		1.7	1.4	1.5	1.3	3.3	2.4	2.2

Table B.1 - Continued.

RUN #	AMT. INJ. ul.	OCTANE	ISOAMYL ACETATE	m-XYLENE	METHYL AMYL KETONE	ETHYL BUTYL KETONE	DIISOBUTYL KETONE	CHLORO BENZENE
		0.54 ppm	0.58 ppm	0.71 ppm	0.62 ppm	0.62 ppm	0.50 ppm	0.86 ppm
1	1000	32896	27103	49730	32094	21786	16742	42114
2	1000	34996	26929	48985	32429	20324	16345	40434
3	1000	29909	28303	49704	33525	20751	17840	41482
4	1000	28974	26496	47188	31315	20231	17670	39771
5	1000	28715	27140	48082	32319	20224	16639	40344
6	1000	30398	28062	49026	33383	19924	16527	39284
7	1000	31312	27668	48508	32817	19723	16604	38190
8	1000	29528	25691	46219	29986	19200	16308	36381
9	1000	28831	27803	48329	32504	18764	15657	36873
10	1000	25412	25894	46157	29942	19110	16691	38592

SAMPLE MEAN =	30097	27109	48193	32031	20004	16702	39347
SAMPLE S.D. =	2592	883	1297	1256	882	637	1868
% C.V. =	8.6	3.3	2.7	3.9	4.4	3.8	4.7

Table B.1 - Continued.

RUN #	AMT. INJ. ul.	TOLUENE	PCE	n-BUTYL ACETATE	METHYLENE CHLORIDE	MIBK	CYCLO HEXANOL	ACETONE
		0.82 ppm	0.85 ppm	0.66 ppm	1.34 ppm	0.70 ppm	0.80 ppm	1.18 ppm
1	1000	49919	19738	19418	11787	36708	31393	24623
2	1000	49307	19597	19650	11611	37603	33416	24100
3	1000	48730	19069	19395	11974	37121	38787	26378
4	1000	49613	18400	18001	11878	36852	34103	25370
5	1000	49236	19074	18421	11299	36949	32483	24056
6	1000	48811	18725	18890	11570	36083	33543	24627
7	1000	50421	18805	18202	11758	36580	35207	24616
8	1000	50146	18474	18371	11232	36340	35312	24060
9	1000	49004	17852	18929	11772	34354	33590	24322
10	1000	49129	18702	17244	11976	34219	31986	25078

SAMPLE MEAN =	49432	18844	18652	11686	36281	33982	24723
SAMPLE S.D. =	574	560	746	259	1131	2107	726
% C.V. =	1.2	3.0	4.0	2.2	3.1	6.2	2.9

APPENDIX C - (Nafion® test data)

Table C.1 - Experimental recovery data compared to historic data.

COMPOUND	% RECOVERY LOW PPM	HIGH PPM	PREVIOUS RESULTS % RECOVERY
Ethyl Alcohol	<3.4	<0.1	-
Isopropyl Alcohol	<3.2	<15.4	-
n-Butyl Alcohol	<2.8	<2.1	<10
Isobutyl Alcohol	<2.4	<2.9	-
Cyclohexanol	10.2	3.9	-
Acetone	3.3	1.0	<10
Methyl Ethyl Ketone	8.7	17.9	-
Methyl Propyl Ketone	11.5	19.1	-
Cyclohexanone	<8.9	<22.1	-
Methyl Isobutyl Ketone	16.1	<11.1	<10
Methyl Amyl Ketone	<25.0	<7.1	-
Ethyl Butyl Ketone	<14.3	<27.7	-
Diisobutyl Ketone	46.1	47.8	-
Ethyl Acetate	81.7	88.5	15
n-Propyl Acetate	27.9	15.7	-
n-Butyl Acetate	6.0	5.3	-
Isoamyl Acetate	37.5	43.0	-
Tetrahydrofuran	<2.6	<6.9	<10
Ethyl Ether	44.7	56.4	>90
1,4-Dioxane	<3.4	<15.4	<10
Isopropyl Ether	<2.1	<11.1	-
Methylene Chloride	99.4	108.7	-
Toluene	102.2	101.2	102
m-Xylene	104.3	117.1	101
Chlorobenzene	102.5	99.0	100
n-Octane	100.0	100.5	100
Trichloroethylene	97.7	100.0	101
Perchloroethylene	100.0	107.3	100

Table C.2 - Dryer data for high and low concentrations.

LOW ppm

TETRAHYDROFURAN

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	59748	<7625
	57972	<7625
	52608	<7625
Average	56776	<7625
Conc. (ppm)	1.89	<0.05
% Recovery	<2.64	

ETHYL ETHER

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	2
Area	63409	54219
	62182	53593
	61827	60431
Average	62473	56081
Conc. (ppm)	2.08	0.93
% Recovery	44.71	

METHYL ETHYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	2
Area	69632	11843
	68047	12852
	66425	14184
Average	68035	12960
Conc. (ppm)	2.30	0.20
% Recovery	8.70	

HIGH ppm

TETRAHYDROFURAN

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	20171	<7625
	19745	<7625
	20445	<7625
Average	20120	<7625
Conc. (ppm)	324.79	<22.55
% Recovery	<6.94	

ETHYL ETHER

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	15217	39018
	14648	40444
	14884	40364
Average	14916	39942
Conc. (ppm)	233.70	131.77
% Recovery	56.38	

METHYL ETHYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	26029	19577
	25565	25920
	26412	24652
Average	26002	23383
Conc. (ppm)	422.80	75.50
% Recovery	17.86	

Table C.2 - Continued.

LOW ppm

CHLOROBENZENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	2	2
Area	43899	45846
	42426	41552
	41246	42289
Average	42524	43229
Conc. (ppm)	0.40	0.41
% Recovery	102.50	

ISOAMYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	5	5
Area	64968	23850
	58819	20727
	62860	21320
Average	62216	21966
Conc. (ppm)	0.24	0.09
% Recovery	37.50	

m-XYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	5	5
Area	72847	74089
	72171	76800
	75231	73819
Average	73416	74903
Conc. (ppm)	0.23	0.24
% Recovery	104.35	

HIGH ppm

CHLOROBENZENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	90562	87900
	89732	90821
	91654	91108
Average	90649	89943
Conc. (ppm)	162.29	161.10
% Recovery	99.02	

ISOAMYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.005	0.005
Area	65596	28544
	66905	26205
	63725	27100
Average	65409	27283
Conc. (ppm)	257.01	110.44
% Recovery	42.97	

m-XYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.005	0.002
Area	77530	37714
	75375	36780
	76780	35120
Average	76562	36538
Conc. (ppm)	240.46	281.54
% Recovery	117.08	

Table C.2 - Continued.

LOW ppm

OCTANE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	1
Area	32886	31033
	30460	28502
	29931	33154
Average	31092	30896
Conc. (ppm)	0.49	0.49
% Recovery	100.00	

ETHYL BUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	2	5
Area	24868	<5224
	17872	<5224
	18886	<5224
Average	20542	<5224
Conc. (ppm)	0.28	<0.04
% Recovery	<14.28	

DIISOBUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	2	5
Area	10969	9968
	9825	9741
	8490	11835
Average	9761	10515
Conc. (ppm)	0.13	0.06
% Recovery	46.15	

HIGH ppm

OCTANE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	49337	51816
	52540	50335
	49469	50062
Average	50449	50738
Conc. (ppm)	76.49	76.90
% Recovery	100.54	

ETHYL BUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	24350	<5224
	25009	<5224
	24959	<5224
Average	24773	<5224
Conc. (ppm)	66.79	<18.35
% Recovery	<27.74	

DIISOBUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.005	0.01
Area	36954	35119
	34298	32617
	35908	34380
Average	35720	34039
Conc. (ppm)	171.13	81.75
% Recovery	47.77	

Table C.2 - Continued.

LOW ppm

CYCLOHEXANOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	69088	32305
	69344	33116
	72808	28955
Average	70413	31459
Conc. (ppm)	1.37	0.14
% Recovery	10.22	

n-BUTYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	28645	5254
	26010	8003
	28408	8666
Average	27688	7308
Conc. (ppm)	0.93	0.05
% Recovery	5.38	

TOLUENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	1
Area	52004	51607
	49435	51231
	49065	51023
Average	50168	51287
Conc. (ppm)	0.91	0.93
% Recovery	102.20	

HIGH ppm

CYCLOHEXANOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.001	0.01
Area	38821	10921
	37810	10104
	38724	11021
Average	38452	10682
Conc. (ppm)	805.89	31.26
% Recovery	3.88	

n-BUTYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.001	0.01
Area	39954	20880
	40098	22021
	40426	21189
Average	40159	21363
Conc. (ppm)	1349.85	71.99
% Recovery	5.33	

TOLUENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	69821	72744
	70148	70427
	71899	71108
Average	70623	71426
Conc. (ppm)	131.18	132.75
% Recovery	101.20	

Table C.2 - Continued.

LOW ppm

n-PROPYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	55636	79362
	55043	71828
	53815	76983
Average	54831	76058
Conc. (ppm)	1.40	0.39
% Recovery	27.86	

METHYL ISOBUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	71398	56305
	68340	53420
	70514	57094
Average	70084	55606
Conc. (ppm)	1.30	0.21
% Recovery	16.15	

PERCHLOROETHYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	5	5
Area	45559	46115
	47235	46382
	47779	47168
Average	46858	46555
Conc. (ppm)	0.37	0.37
% Recovery	100.00	

HIGH ppm

n-PROPYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	68030	11278
	63296	10454
	65321	10939
Average	65549	10890
Conc. (ppm)	167.63	26.37
% Recovery	15.73	

METHYL ISOBUTYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	85078	<9832
	86530	<9832
	85921	<9832
Average	85843	<9832
Conc. (ppm)	158.92	<17.66
% Recovery	<11.11	

PERCHLOROETHYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	20307	21315
	20972	22564
	21091	21981
Average	20790	21953
Conc. (ppm)	69.84	74.94
% Recovery	107.30	

Table C.2 - Continued.

LOW ppm

ISOPROPYL ETHER

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	81536	<9414
	81873	<9414
	81939	<9414
Average	81783	<9414
Conc. (ppm)	1.45	<0.03
% Recovery	<2.07	

CYCLOHEXANONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	20225	<8277
	19569	<8277
	20446	<8277
Average	20080	<8277
Conc. (ppm)	0.45	<0.04
% Recovery	<8.89	

METHYL PROPYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	53482	34015
	52579	25210
	50594	30045
Average	52218	29757
Conc. (ppm)	1.30	0.15
% Recovery	11.54	

HIGH ppm

ISOPROPYL ETHER

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	79158	<9414
	75046	<9414
	77061	<9414
Average	77088	<9414
Conc. (ppm)	136.39	<15.12
% Recovery	<11.08	

CYCLOHEXANONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	46142	<8277
	47244	<8277
	46896	<8277
Average	46761	<8277
Conc. (ppm)	96.03	<21.87
% Recovery	<22.07	

METHYL PROPYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	69714	8993
	65979	10927
	67140	9804
Average	67611	9908
Conc. (ppm)	169.54	22.18
% Recovery	13.08	

Table C.2 - Continued.

LOW ppm

ISOPROPYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	1	5
Area	39080	<6333
	42580	<6333
	42290	<6333
Average	41317	<6333
Conc. (ppm)	1.85	<0.06
% Recovery	<3.24	

1,4-DIOXANE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	1	5
Area	30212	<5838
	30216	<5838
	29322	<5838
Average	29917	<5838
Conc. (ppm)	1.45	<0.05
% Recovery	<3.45	

TRICHLOROETHYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	1	1
Area	30042	28612
	29186	29385
	29773	29231
Average	29667	29076
Conc. (ppm)	1.31	1.28
% Recovery	97.71	

HIGH ppm

ISOPROPYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	0.01	1
Area	74382	<6333
	73577	<6333
	73409	<6333
Average	73789	<6333
Conc. (ppm)	330.74	<0.29
% Recovery	<0.09	

1,4-DIOXANE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	0.01	0.01
Area	33681	<5838
	33423	<5838
	32821	<5838
Average	33308	<5838
Conc. (ppm)	161.95	<24.95
% Recovery	<15.40	

TRICHLOROETHYLENE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	0.01	0.01
Area	31816	29816
	30265	32248
	30982	31008
Average	31021	31024
Conc. (ppm)	136.91	136.92
% Recovery	100	

Table C.2 - Continued.

LOW ppm

ETHYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	38114	<6033
	35720	<6033
	31468	<6033
Average	35101	<6033
Conc. (ppm)	3.26	<0.11
% Recovery	<3.37	

METHYLENE CHLORIDE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	1
Area	28223	27932
	27890	27778
	27417	27312
Average	27843	27674
Conc. (ppm)	3.20	3.18
% Recovery	99.37	

ACETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	47422	7845
	48037	10826
	48960	8234
Average	48140	8968
Conc. (ppm)	2.45	0.08
% Recovery	3.26	

HIGH ppm

ETHYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	1
Area	48756	<6033
	55156	<6033
	55602	<6033
Average	53171	<6033
Conc. (ppm)	496.01	<0.53
% Recovery	<0.11	

METHYLENE CHLORIDE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	0.01
Area	29821	31749
	30215	33147
	29841	32674
Average	29959	32523
Conc. (ppm)	345.03	375.27
% Recovery	108.75	

ACETONE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.01	1
Area	39083	40154
	39263	39852
	39079	39956
Average	39142	39987
Conc. (ppm)	198.29	2.03
% Recovery	1.02	

Table C.2 - Continued.

LOW ppm

ISOBUTYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	55224	<5595
	54500	<5595
	49283	<5595
Average	53002	<5595
Conc. (ppm)	2.07	<0.05
% Recovery	<2.41	

ETHYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	1
Area	28131	23836
	29134	22358
	29204	25415
Average	28823	23870
Conc. (ppm)	2.13	1.74
% Recovery	81.69	

n-BUTYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	1	5
Area	59813	<7759
	60968	<7759
	58600	<7759
Average	59794	<7759
Conc. (ppm)	1.78	<0.05
% Recovery	<2.81	

HIGH ppm

ISOBUTYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	39313	<5595
	41660	<5595
	42792	<5595
Average	41255	<5595
Conc. (ppm)	808.14	<23.12
% Recovery	<2.86	

ETHYL ACETATE

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	18904	78472
	19085	80827
	19330	76731
Average	19106	78677
Conc. (ppm)	683.84	604.71
% Recovery	88.43	

n-BUTYL ALCOHOL

	DRYER IN	DRYER OUT
AMT. INJ. (ml.)	0.002	0.01
Area	74182	<7759
	72846	<7759
	75210	<7759
Average	74079	<7759
Conc. (ppm)	1103.07	<23.54
% Recovery	<2.13	

Table C.2 - Continued.

LOW ppm

METHYL AMYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	5	5
Area	34114	<8540
	29634	<8540
	32001	<8540
Average	31916	<8540
Conc. (ppm)	0.12	<0.03
% Recovery	<25.00	

HIGH ppm

METHYL AMYL KETONE

	DRYER IN	DRYER OUT
AMT. INJ. (mL)	0.002	0.005
Area	45990	<8540
	45691	<8540
	47120	<8540
Average	46267	<8540
Conc. (ppm)	439.01	<30.99
% Recovery	<7.06	

APPENDIX D

Table D.1 - Database used for statistical model.

COMPOUND	H-BOND	DIPOLE MOMENT	WATER SOLUBILITY (g/L)	LOG OF WATER SOLUBILITY	HISTORIC DATA %RECOVERY	EXPERIMENTAL	
						LOW PPM	HIGH PPM
vinyl chloride	1	1.3	2.8	0.447	96		
allyl chloride	2	1.7	0.1	-1.000	>90		
1,2-dichloroethene	1	1.5	0.35	-0.456	100		
chlorobenzene	1	1.5	0.009	-2.046	100	103	99
chloroform	1	1	0.8	-0.097	100		
trichloroethylene	1	1	0.11	-0.959	101	98	100
1,1,1-trichloroethane	1	1.7	4.4	0.643	100		
1,3-dichlorobenzene	1	1.7	0.11	-0.959	100		
1,4-dichlorobenzene	1	1.6	0.08	-1.097	100		
1,2-dichlorobenzene	1	1.4	0.15	-0.824	100		
carbon tetrachloride	1	0	0.16	-0.796	102		
tetrachloroethene	1	1.6	0.015	-1.824	100	100	107
1,2,4-trichlorobenzene	1	1.3	0.038	-1.420	100		
cis-1,3-dichloropropene	1	1.9	0.27	-0.569	105		
1,2-dichloropropane	1	1.5	0.26	-0.585	100		
methylene chloride	1	1.5	2	0.301		99	109
octane	1	0	0.0004	-3.398	100	100	101
decane	1	0	0.00052	-3.284	99		
benzene	1	0.1	0.18	-0.745	100		
toluene	1	0.4	0.53	-0.276	102	102	101
m-xylene	1	0.4	0.17	-0.770	101	104	107
ethyl benzene	1	0.6	0.16	-0.796	103		
decahydronaphthalene	1	1.3	0.03	-1.523	>90		
butyraldehyde	2	1.8	7	0.845	>90		
benzaldehyde	2	2.9	3	0.477	75		
ethylene oxide	2	1.9	870*	2.940	50		
tetrahydrofuran	2	1.7	100	2.000	<10	<2.6	<6.9
ethyl ether	2	1.7	6	0.778	>90	45	56
dioxane	2	0.4	>400	>2.602	<10	<3.4	<15
acetone	2	2.9	788*	2.897	<10	3.3	1
methyl ethyl ketone	2	2.7	26.8	1.428		8.7	17.8
methyl propyl ketone	2	2.7	5.51	0.741		12	19
methyl amyl ketone	2	1.9	0.4	-0.398		<25	<7
methyl isobutyl ketone	2	2.7	10.1	1.004	<10	16	<11
acetonitrile	1	3.5	>400	>2.602	75		
n-butyl amine	3	1.4	733*	2.865	<10		
methanol	3	1.8	791*	2.898	<10		
ethanol	3	1.7	789*	2.897		<3	<0.1
isobutyl alcohol	3	1.7	8	0.903		<2	<3
n-butanol	3	3	810*	2.908	<10	<3	<2
isopropyl alcohol	3	1.6	780*	2.892		<3	<15
n-hexanol	3	1.7	0.6	-0.222	<10		
cyclohexanol	3	1.7	3.4	0.531		10	4
dimethylformamide	2	4.1	944	2.975	<10		
nitropropane	1	3.7	1.4	0.146	>90		
nitrobenzene	1	4.3	1.9	0.279	30		
n-propyl acetate	2	1.9	2	0.301		28	16

* Compounds listed as miscible in water.
Water solubility is based on 100% solubility.

Table D.2 - List of compounds previously tested with a Nafion® dryer.

HALOCARBONS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
vinyl chloride	7.8	-13.37	62.5	0.9016	96	M	1.3
allyl chloride	9.1	45	76.53	0.938	90	M	1.7
carbon tetrafluoride	7.3	-127.8	88.01	1.96	90		0
dichloroethylene	9.8	37	96.95	1.218	102	P	1.3
1,2-dichloroethane	9.6	83.5	98.96	1.2351	100		1.5
cis-1,3-dichloropropene	7.6	108	110.98	0.938	105		1.9
chlorobenzene	9.5	131	112.56	1.107	100	P	
1,2-dichloropropane	9	95	112.99	1.159	100	P	1.5
chloroform	9.3	61.7	119.39	1.4832	100	P	1.2
benzylchloride	9.6	179	126.58	1.1002	100		1
trichloroethylene	9.3	87	131.39	1.4642	101	P	1.8
1,1,1-trichloroethane	9.3	74	133.41	1.339	100	P	1
1,1,2-trichloroethane	9.6	114	133.42	1.4416	100	P	1.7
1,3-dichlorobenzene	9.3	174	147.01	1.2884	100	P	1.6
1,4-dichlorobenzene	11	173	147.01	1.458	100	P	1.4
1,2-dichlorobenzene	10	180	147.01	1.3059	100	P	1.6
carbon tetrachloride	8.6	76	153.82	1.594	102	P	0.8
tetrachloroethene	9.4	121	165.83	1.6227	100	P	
1,2-dibromoethane	11	97	173.86	2.497	107	P	1.3
1,2,3-trichlorobenzene		221	181.46		100	P	
1,2,4-trichlorobenzene	9.3	213	181.46	1.4634	102		
1,3,5-trichlorobenzene		208	181.46	1.288	100	P	0
F-113	7.4	48	187.38	1.5635	100	P	
1,2,4,5-tetrachlorobenzene		243	215.89		100	P	
1,2,3,4-tetrachlorobenzene		254	215.89		100		
pentachlorobenzene	10	277	250.14	1.8342	100		
hexachlorobutadiene		215	260.76	1.5542	104		
hexachlorobenzene	9	325	284.79	1.5691	100	0	0.2

SP - Solubility Parameter
BP - Boiling Point
MW - Molecular Weight

Table D.2 - Continued.

ALIPHATIC HYDROCARBONS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
ethylene		-102.4	28.05		90		
C-7	7.4	98	133.2	0.684	100	P	0
C-8	7.6	125	114.22	0.7028	100	P	
C-9	7.4	150	128.26	0.7176	101	P	
C-10	7.3	174	142.29	0.73	99	P	0
C-11	7.2	196	156.32	0.7402	106	P	
C-12	7	216	170.34	0.7487	102	P	
C-13	7.1	235	184.37	0.7564	99	P	
C-14	7.1	253	198.4	0.7628	100	P	
C-15	7.1	270	212.42	0.7685	93	P	
C-16	7.1	287	226.45	0.7733	70	P	
C-17	7	301	240.48	0.778	70	P	

AROMATIC HYDROCARBONS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
n-decyl benzene					46	P	
n-octyl benzene					94	P	
n-hexyl benzene					103	P	
benzene	9.2	80	78.11	0.8787	100	0	0.1
toluene	8.9	110	92.13	0.8669	102	P	0.4
o-xylene	9	144	106.16	0.8802	101	P	0.4
ethyl benzene	8.8	136	106.16	0.867	103	P	0.6
n-propyl benzene	8.4	159	120.19	0.862	104	P	
n-butyl benzene	8.2	183	134.21	0.8601	100	P	0.5
decahydronaphthalene	8	187	138.24	0.8965	90	P	1.3

Table D.2 - Continued.

ESTERS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
ethyl acetate	9.1	77	88.1	0.902	15	M	1.6
amyl acetate	8.5	148	130.18	0.879	90	M	1.8

ALDEHYDES

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
acetaldehyde	11	21	44.05	0.788	90	M	
crotonaldehyde		104	70.09	0.853	10		3.4
butyraldehyde	9	75	72.1	0.8016	90	M	1.8
benzaldehyde	10	179	106.12	1.043	75	M	2.9

ETHERS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
ethylene oxide	11	11	44.05	0.8694	50	M	1.9
methyl vinyl ether		12	58		90		1
propylene oxide	9.2	34	58.08	0.859	25	M	1.9
furan		32	68.07	0.9371	90	M	1.8
tetrahydrofuran		66	72.1	0.8892	10	M	1.7
diethyl ether	7.4	35	74.12	0.7134	90	M	1.7
methylal		42	76.09	0.866	10		0.7
dioxane	9.9	101	88.1	1.0329	10	M	0.4
phenyl ether	8.6	259	170.2	1.075	86		1.1

Table D.2 - Continued.

KETONES

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
acetone	10	56	58.08	0.788	10	M	2.9
methyl isobutyl ketone	8.4	117	100.16	0.801	10	M	2.7
ethyl amyl ketone	8.2	160	128.21	0.82	20	M	2.7

NITRILES

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
acetonitrile	12	82	41.05	0.7874	75	P	3.5
benzonitrile	8.4	191	103.12	1.5289	50	P	4.4

AMINES

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
n-butyl amine		78	73.14	0.7327	10	S	1.4

ALCOHOLS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
methanol	15	65	32.04	0.7915	10	S	1.8
n-butanol	11	117	74.12	0.81	10	S	3
n-hexanol	11	157	102.17	0.8153	10	S	1.7

Table D.2 - Continued.

MISCELLANEOUS

COMPOUND	SP	BP	MW	DENSITY	% RECOVERY	Hydrogen Bonding	Dipole Moment
dimethylformamide	12	153	73.09	0.9445	10	M	4.1
nitropropane	11	132	89.09	0.9934	90	P	3.7
phenol	11	182	94.11	1.071	43		2.1
nitrobenzene	10	210	123.11	1.205	30	P	4.3
diphenyl	9.1	254	154.2	1.041	91		
4-ethylbiphenyl			182.57		36		
3-ethylbiphenyl		283	182.57	1.043	44		

Figure D.1 - Plot of % Recovery from Nafion® dryer verses compound water solubility.

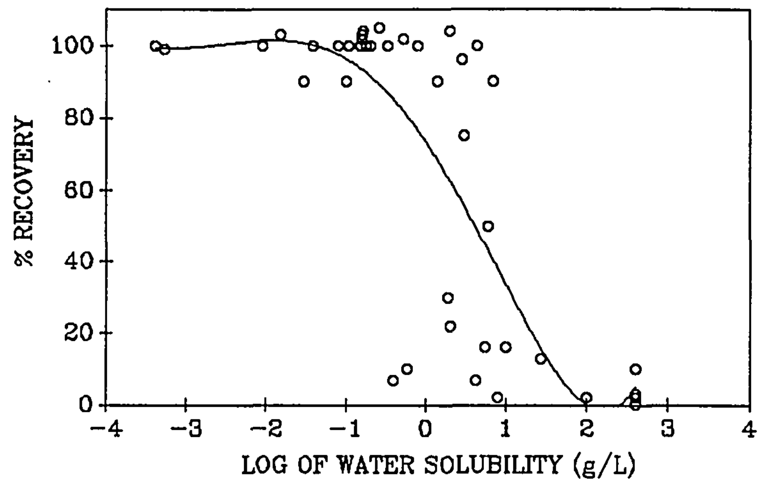


Figure D.2 - Plot of % Recovery from Nafion® dryer verses compound hydrogen bonding capacities.

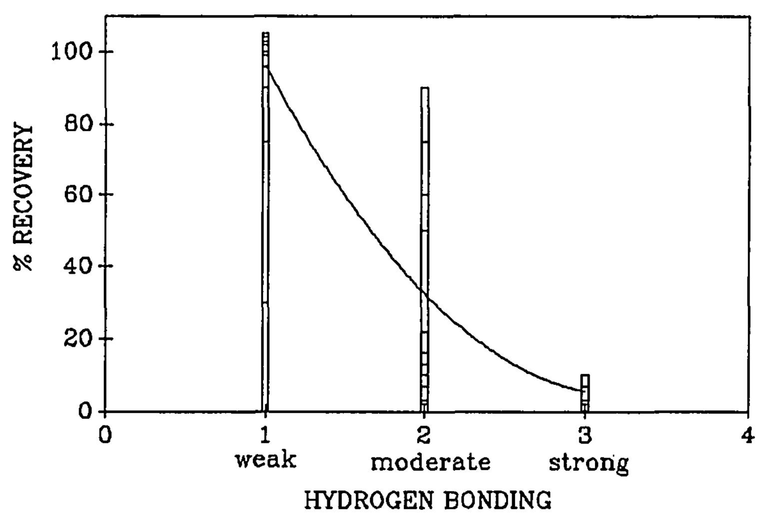


Figure D.3 - Plot of % Recovery from Nafion® dryer verses compound dipole moment.

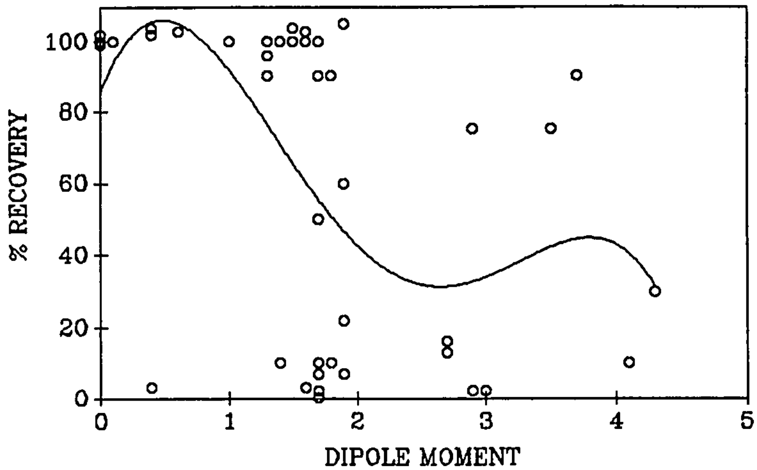


Figure D.4 - Plot of log of water solubility for each compound verses compound dipole moment.

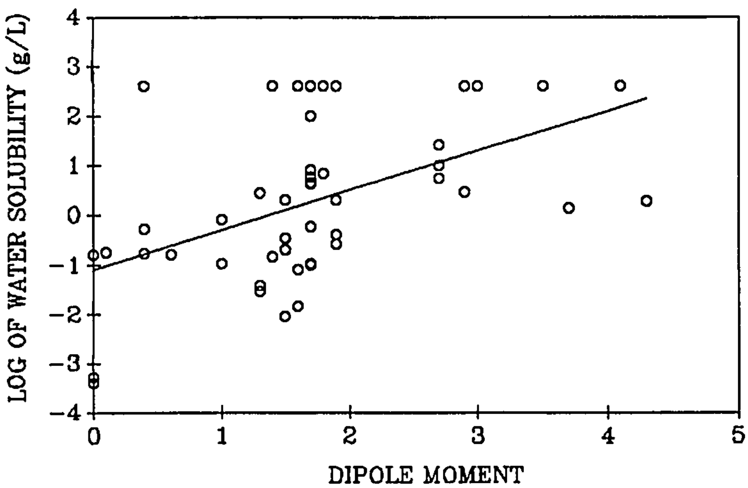


Figure D.5 - Plot of log of water solubility and hydrogen bonding capacity for tested compounds.

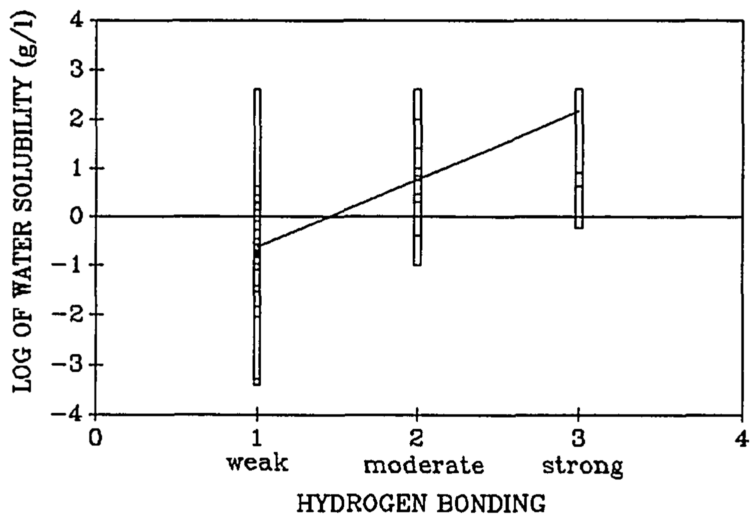
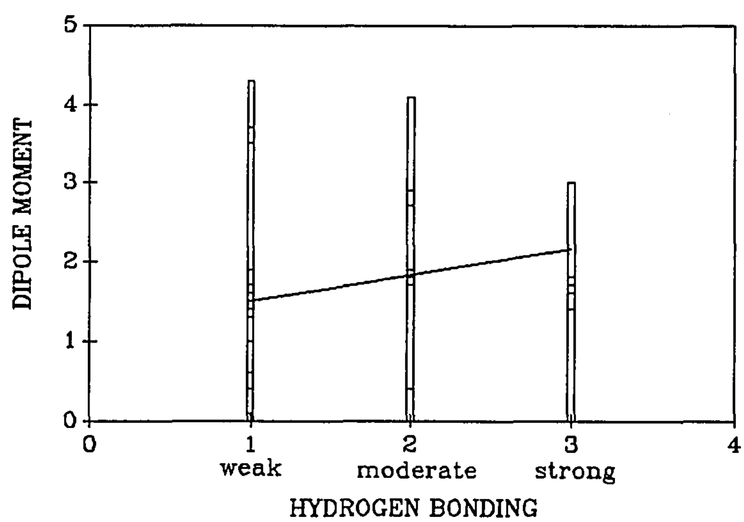


Figure D.6 - Plot of dipole moment and associated hydrogen bonding capacities for tested compounds.



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