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PREFACE
To

"Final Report on Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air" by ENSR Corporation. June 1999

1. The following document is a contractor's report of a single laboratory validation on a new method for the analysis of volatile petroleum hydrocarbons in air (henceforth called Air Phase Petroleum Hydrocarbons, APH). It represents their account of this developmental work. The Massachusetts Department of Environmental Protection (MA DEP) will be taking this procedure and translating it into a detailed MA DEP Standard Operating Procedure (SOP) for its own use and use by the scientific community with interests in air monitoring of petroleum hydrocarbons. Readers are advised that changes to specific aspects of the procedure may yet take place as the method is evaluated during a laboratory round robin evaluation planned for the autumn of 1999. The draft and final MA DEP SOPs should be consulted for the definitive guidance on the methods. These will be made available on the MA DEP homepage. Specific areas where procedural details may change are:

    - specification of marker compounds for the petroleum hydrocarbon ranges;
    - specification of the end marker compound;
    - hydrocarbon range response factors;
    - specific reporting requirements.

2. The contractor's report title identifies this as a method for indoor air. It was developed to meet a programmatic need for characterizing indoor air for health risk assessment purposes. It represents one method which might be used for this purpose. Once this method is available in a SOP for the regulated community to use, the Department hopes to investigate, validate and make available other sampling methods (e.g., adsorbent tubes, passive samplers) for air phase petroleum hydrocarbons. SUMMA™ canisters and GC/MS were chosen as the basis for development of a method because of the existence of a well validated U.S. EPA method for

volatile compounds (TO-14) employing this equipment and because they appeared to offer the capability to meet our needs for sampling, compound separation, identification and quantification. DEP also routinely employs the TO-14 method in its indoor air sampling for volatile hydrocarbons. The method will also be amenable to characterizing volatile petroleum hydrocarbon fractions in ambient air and soil gas.

3. The contractor indicates that the method MDLs are product specific (p. 5-5). MA DEP has taken the position that its MDLs for the Volatile and Extractable Petroleum Hydrocarbon (VPH/EPH) methods are NOT product specific and believes this to be the case for the APH method as well. This issue for the APH will be clarified in the final MA DEP SOP.

4. An additional MDL Run #5 for the hydrocarbon ranges using gasoline vapor was executed at an intermediate spiking level subsequent to the completion of the Final Report. The results of this work are described in an attached Addendum to the Final Report.

ERRATA

Terminology: - this report often refers to the 44 hydrocarbon compounds used in the method validation as "Target Analytes". These "target analytes" and use of the term elsewhere in the report should not be confused by readers who are familiar with the MADEP VPH/EPH analytical procedures with the "Target Analytes" required by the Department in those tests.

p.E-1, 3rd paragraph, 2nd sentence. Change "*Gas*" to "*Gasoline*".

p. 1-2. Last sentence. Change "*is included as Appendix B*" to read *"is contained in Appendix B, bound separately and available on request only from MA DEP's Office and Research and Standards (phone: 617-292-5570).*"

p. 4-2, 1st sentence. Delete second period at end of sentence.

p. 8-10, Fig. 8-8. "*SVE*" in the title stands for "*soil vapor extraction*"

p. 9-3, sec. 9.3, 1st paragraph, 3rd sentence. Add "*passive badge samplers*" to list of additional sampling devices that might be tested.

Massachusetts Department of Environmental Protection
Boston, Massachusetts

Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air

Final Report

ENSR Corporation
June 1999
Document Number 9892-084-000

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EXECUTIVE SUMMARY

ENSR, under contract to the Massachusetts Department of Environmental Protection, has developed a method for the analysis of indoor air samples for petroleum hydrocarbon constituents. This method addresses both the concentrations in air of individual chemicals and the summed concentrations of aliphatic or aromatic hydrocarbons in predefined carbon compound size ranges. It has been designed to provide data for inhalation health risk assessments to complement MADEP's approach for characterizing human health risks from soil and water petroleum hydrocarbon contamination using carbon ranges.

MADEP specified that the method developed be based upon EPA Method TO-14, which employs passivated stainless steel canisters for sample collection followed by gas chromatography/mass spectrometry for the identification and quantitation of analytes. Within this framework, ENSR reviewed available databases for the specific composition of refined petroleum products and developed a comprehensive target analyte list based upon prevalence, volatility and toxicity of the individual chemicals in these products. Subsequent to MADEP's approval of this list, a Quality Assurance Project Plan was written to document the analytical approach and objectives and the QA measures necessary to ensure defensible data.

Over the course of the method development, which included MDL, precision and accuracy determinations for individual compounds and ranges of compounds, instrument operating conditions and practices were optimized. Gas vapor analyses were used for the MDL and precision and accuracy determinations. The method as developed provides detection limits ranging from 0.26 to 1.8 ppbV for a comprehensive list of hydrocarbons. The overall analyte list was reviewed with MADEP to determine those individual chemicals which should be included as target analytes to provide risk data and those which would be required for calibration to accurately measure summed hydrocarbon range concentrations. The final list for the method includes 9 target analytes and 18 additional hydrocarbons for calibration purposes.

This method has been applied to the analyses of air samples collected from several environmental sites where concerns for petroleum hydrocarbon contamination in air exist. These samples include indoor air from residences and commercial establishments as well as some samples of soil gas and groundwater remediation system emissions. Data presented in this report document method performance in measuring individual analyte and range concentrations for these samples; in addition, the method provides fingerprint data that may in some instances prove useful for source confirmation.

Recommendations for additional experimental work are provided. These include tests to more fully characterize air contamination arising from specific petroleum hydrocarbon products as well as method development for alternate sampling and analytical approaches.

1.0 INTRODUCTION

This report presents the procedures and findings of a study completed by ENSR for the Massachusetts Department of Environmental Protection (MADEP) to develop a validated method for the analysis of petroleum hydrocarbons in indoor air samples, the Air Petroleum Hydrocarbon (APH) Method.

1.1 Background and Purpose

The MADEP has an improved method for assessing human non-cancer health risks from exposures to petroleum hydrocarbon mixtures (Hutcheson et al., 1996). The method involves breaking down the full range of Total Petroleum Hydrocarbons (TPH) into aliphatic and aromatic fractions, identifying toxicity values for compounds within select aromatic and aliphatic hydrocarbon ranges, and assigning a representative toxicity value to each range. This improved method has been integrated into the MADEP's regulations for characterizing human health risks associated with petroleum releases to the environment (MADEP, 1997a).

As an initial step, the MADEP developed two analytical procedures to differentiate and quantify the aromatic and aliphatic fractions in soil and groundwater. The final analytical procedures for the Extractable Petroleum Hydrocarbons (EPH) and Volatile Petroleum Hydrocarbons (VPH) methodologies were published in January 1998 (MADEP, 1998a and 1998b). The MADEP has also promulgated soil and groundwater cleanup standards for the aromatic and aliphatic ranges of interest that became effective on October 31, 1997 (MADEP, 1997b).

The purpose of this study was to develop and validate a sampling and analytical procedure for determining the concentrations of petroleum hydrocarbon compounds in indoor air samples. These procedures are to be used to support the improved risk assessment methods recently developed by the MADEP. This report includes a discussion of the equipment and procedures used during the development of this analytical methodology as well as observations and results of the various components of the method development. An SOP for performing the laboratory method has been submitted as a stand alone document.

1.2 Study Components

The study, with the exception of the last component, involved spiking evacuated SUMMA® canisters with known quantities of analytes and then analyzing samples recovered from the containers. The components of the method development program included the following:

- Identifying and selecting the target analytes of interest for air analyses
- Developing a Quality Assurance Project Plan (QAPP)

- Completing a Method Detection Limit (MDL) Study
- Performing a Precision and Accuracy Study
- Quantifying the concentrations of aliphatic and aromatic hydrocarbon ranges
- Evaluating the method with real-world samples

1.3 Report Structure

This report has been designed to discuss the details of each study component and the analytical approach developed for the laboratory validation procedure.

Appendix A list the components of the sample used for the Precision and Accuracy Study. The raw data associated with the MDL Studies and Precision and Accuracy Study is included as Appendix B.

2.0 SELECTION OF TARGET ANALYTES

As an initial step in the method development process, MADEP and ENSR identified the compounds most likely to be present in indoor air from petroleum hydrocarbon products. The purpose of this list was to represent compounds which could be used to help validate the method across the spectrum of petroleum hydrocarbon compounds. After the validation of the method was completed, a final analyte list was identified which would potentially be used by all commercial laboratories in the final version of the method.

2.1 Generating the Initial List

An initial list of 44 target compounds was generated based on three primary factors:

1. Determination of Principal Constituents of selected petroleum products,

2. Ranking of Compounds by Volatility,

3. Ranking of Compounds by Toxicity.

Using a weight of evidence approach, those compounds that ranked the highest overall considering these factors were identified. Finally, several compounds were added or eliminated from the list for various reasons (e.g., commercial availability, MADEP request, etc.). The highlights of each step used in the development of the method development list are presented below. The results of this evaluation were presented to MADEP in a report prepared by ENSR entitled "*Selection of Target Analytes for the Measurement of Petroleum Hydrocarbons in Indoor Air*", dated June 1998. The list of target compounds is provided in Table 2-1.

2.1.1 Determination of Principal Constituents

A database (TPHCWG, 1998) provided by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was used as the primary source in identifying the components of the different petroleum products. Components within the hydrocarbon range of interest (C_5 to C_{12}), with concentrations greater than one percent by weight, were identified for each of the major petroleum product groups (gasoline, kerosene, diesel, fuel oil #2, fuel oil #6, and jet fuel). This established the initial working list of hydrocarbons to be carried through the remainder of the selection process.

2.1.2 Ranking of Compounds by Volatility

In order to evaluate constituent compounds based on their volatility, physical and chemical properties of the compounds were considered. Vapor pressure, Henry's law constant and molecular weight data were input into the initial list of constituents. Because of their low volatility, all of the polynuclear aromatic hydrocarbon (PAH) compounds, except naphthalene, 1- and 2-methylnaphthalenes, and biphenyls were eliminated from further consideration.

2.1.3 Ranking of Compounds by Toxicity

Toxicity data were identified for the remaining compounds on the list. Because the relevant exposure pathway to volatile compounds in indoor air is inhalation, inhalation toxicity values are preferred over oral toxicity values. The potential inhalation toxicity of the compounds was ranked from most toxic to least toxic (higher toxicity was represented by lower risk-specific concentrations or reference concentrations). It should be noted that, when multiple inhalation toxicity values were available for a compound, the lowest of the values was selected in the ranking. Surrogate toxicity values were assigned on the basis of structural similarity for those compounds lacking toxicity data.

Compounds with greater than four carbons that are known or suspected carcinogens (USEPA Class A or B) by the inhalation and oral route of exposures were identified; this consisted only of benzene. Although compounds with four or fewer carbons (e.g., butane) were not originally proposed for inclusion in the method, 1, 3-butadiene (C_4H_6) was included in the list, at the request of the MADEP, because it is a Class B carcinogen and a minor constituent of gasoline.

2.1.4 Selection of Target Analytes

The target analytes most likely to be present in indoor air (based on their weight percent in various products and their volatility), and those that pose the greatest risk (based on toxicity) were selected. When multiple isomers of a compound existed on the list (e.g., dimethylhexanes, dimethylpentanes, methylheptanes, methylhexanes, and trimethylpentanes), it was necessary to limit the method to one representative compound due to potential co-elution problems during the GC/MS analyses. For these cases, with the exception of 2,3-dimethylhexane, the isomer present at the greatest weight percent or with the highest toxicity was retained. Although 2,3-dimethylhexane was present at a higher weight percent than the other dimethylhexane isomers, this analyte was not included due to the lack of a commercially available standard. Therefore, 2,5-dimethylhexane was substituted for this compound.

Several compounds present in petroleum mixtures at less than 1% by weight (according to the composition sources searched by ENSR) were added to the target analyte list at the request of

MADEP. These compounds included isopropyltoluene, isopropylbenzene, n-propylbenzene, and styrene, which are commonly detected in environmental media at petroleum release sites. Undecane, originally eliminated due to lack of toxicity data, was also added to the target analyte list at the request of MADEP due to its frequency in indoor air samples analyzed by MADEP's air toxics laboratory.

1-Methyl-3-propylbenzene, and 1,3,5-trimethylcyclohexane were eliminated from the target compound list because laboratory standards were not commercially available for these compounds. It should be noted that primary toxicity values were not available for either of these compounds; a structural surrogate toxicity value was assigned for 1, 3, 5-trimethylcyclohexane using methylcyclohexane as the surrogate.

The initial list of 44 target analytes for the new analytical methodology is provided in Table 2-1. This list of compounds was used in the determination of MDLs, precision and accuracy, quantification of hydrocarbon ranges, and in the evaluation of real world samples.

2.2 Selection of Final Analyte List

The target compound list utilized for the method validation study was extensive. This extensive list was used in order to determine how appropriate, in general, this method would be for the different structural isomers of aliphatic and aromatic compounds which comprise different petroleum products. It is not considered necessary for laboratories to report such an extensive list in order to meet MADEP objectives. As a result, a final analyte list has been developed which laboratories will be required to utilize in this analysis. This list of compounds is summarized in Table 2-2 and is broken down into four parts. First, compounds which the laboratory will be required to report as "APH Target Analytes" are listed. Second, the hydrocarbon ranges which the laboratories must report are listed. Third, compounds which the laboratory must include in their calibration mixes to define the hydrocarbon ranges are listed. Finally, additional compounds which must be used by the laboratory to generate representative response factors (RFs) for each of the hydrocarbon ranges are listed. These compounds represent various molecular structures within each hydrocarbon range and should therefore yield a representative calibration for each range.

TABLE 2-1
Target Analytes Used in Method Validation Study

C_5-C_8 ALIPHATICS	
n-Pentane	n-Heptane
Isopentane	2-Methylhexane
n-Hexane	Methylcyclohexane
2,3-Dimethylbutane	2,3-Dimethylpentane
2-Methylpentane	n-Octane
3-Methylpentane	2,2,4-Trimethylpentane
Methylcyclopentane	2,5-Dimethylhexane
Cyclohexane	3-Methylheptane
Cyclohexene	
C_9-C_{12} ALIPHATICS	
n-Nonane	n-Dodecane
2,3-Dimethylheptane	Butylcyclohexane
n-Decane	Hexylcyclohexane
n-Undecane	
C_9-C_{10} AROMATICS	
1,2,3-Trimethylbenzene	n-Propylbenzene
1,2,4-Trimethylbenzene	Isopropylbenzene
1,3,5-Trimethylbenzene	p-Isopropyltoluene
1-Methyl-3-ethylbenzene	1,2,3,4-Tetramethylbenzene
Indene	
INDIVIDUAL TARGET ANALYTES	
Benzene	1-Methylnaphthalene
Toluene	2-Methylnaphthalene
Ethylbenzene	1,3-Butadiene
Xylenes	Styrene
1,2,4-Triethylbenzene	Naphthalene
Methyl-t-butyl ether	

Table 2-2

Final Component List

"APH TARGET ANALYTES" **(To Be Reported by Laboratory)**	
Benzene Toluene Ethylbenzene Xylenes Methyl t-butylether	Naphthalene 2-Methylnaphthalene 1-Methylnaphthalene 1,3-Butadiene
HYDROCARBON RANGES **(To Be Reported By Laboratory)**	
C_5-C_8 Aliphatics C_9-C_{12} Aliphatics C_9-C_{10} Aromatics	
RANGE RETENTION TIME COMPOUNDS	
Isopentane 2,3-Dimethylheptane Hexylcyclohexane	o-Xylene[1] Naphthalene[1]
[1] included under APH Target Analytes	
HYDROCARBON RANGE CALIBRATION COMPOUNDS	
n-Hexane Cyclohexane 2,3-Dimethylpentane n-Heptane n-Octane n-Nonane n-Undecane n-Dodecane	Butylcyclohexane Isopropylbenzene m-Ethyltoluene 1,3,5-Trimethylbenzene 1,2,3-Trimethylbenzene p-Isopropyltoluene Indene

3.0 ANALYTICAL APPROACH

SUMMA® Canisters were selected as the sampling container for the method validation study. Cryofocusing/gas chromatography/mass spectrometry (GC/MS) was selected as the analytical approach to this methodology. Both the sampling and analytical methods were chosen due to the overall sensitivity of the method, the ease of sampling using this approach and the existence of validated methods for individual volatile compounds (e.g., US EPA Method TO-14) using SUMMA® canisters and GC/MS.

In general, the analytical approach utilized for the analysis of VPH is similar to US EPA Method TO-14. US EPA Method TO-14, used without modification, looks for individual target analytes and is not meant to identify and quantify hydrocarbon ranges. Table 3-1 highlights the significant similarities and differences between US EPA Method TO-14 and the APH analytical methodology.

3.1 Summary of Analytical Methodology

3.1.1 Cryofocusing Procedure

In order to achieve low detection limits, large volumes of samples must be analyzed. Samples are first preconcentrated using a Graseby Nutech 3550A Cryogenic Concentrator. A Graseby Nutech 3600 Autosampler is used to automate sample analyses. Figure 3-1 provides a schematic of the analytical instrumentation used. Table 3-2 provides the final concentrator parameters which were selected as optimum for the measurement of VPH from SUMMA® canisters. A specified volume of sample is allowed to purge the inlet of the concentrator while the mass flow controller stabilizes to the set sample flow rate. The sample is then pulled through the mass flow controller using a vacuum pump and then through a Nafion® dryer to remove moisture in the sample. The cooled cryotrap is in line with the sample path and the sample loading continues until the target volume is reached. The large volume of sample is then cryogenically concentrated to a volume of less than one mL in a nickel trap filled with nonsilanized glass beads. Next, the internal standard is introduced into a standard 2 mL loop, allowed to come to atmospheric pressure, and then transferred to the cryotrap with helium. The sample and internal standard on the cold cryotrap are flushed with helium to purge out residual air and reduce carbon dioxide levels trapped with the sample.

Following preconcentration, the sample is refocused at the head of the capillary column on the GC using a Graseby Nutech 354A Cryofocusing Accessory. The cryofocus is cooled to the selected setpoint. When the cryofocus reaches its setpoint, the cryotrap is heated and the sample is refocused on the head of the column. This step further reduces the volume to less than one microliter for injection. When the GC is ready, the sample is injected by ballistic heating of the cryofocuser. The cryotrap stays in line with the GC column for an extended transfer of sample and is then switched out of line for bakeout. The sample dryer procedure is then used to dehydrate the Nafion® dryer after sample injection.

3.1.2 GC/MS Procedure

The GC/MS system used during this study was a Hewlett Packard 6890/5973 mass selective detector (MSD) with the EnviroQuant Chem Station data system. However, other MS systems would also be appropriate (e.g., ion trap, quadropole). The sample is injected into the GC, and the temperature program of the GC begins. During this study, it was essential to obtain the best possible resolution of the aliphatic and aromatic analytes and to minimize the occurrence of coelutions. This would allow for a more straightforward as well as accurate calibration of the aliphatic and aromatic hydrocarbon ranges. As a result of the need to minimize the occurrence of coelutions, the temperature program was relatively slow and the analytical run time was therefore approximately one hour. All results were quantitated using an internal standard procedure. Table 3-3 lists the GC and MS parameters. The target analytes are listed in their retention time order in Table 3-4.

The SOP for the analysis of SUMMA® canisters for APH was generated after the completion of the method validation study and includes final instrument parameters and detailed calculations for all aspects of the analysis which were determined to be the most appropriate during this study. The SOP was written using an internal standard procedure. Prior to the onset of the program, it was decided that quantitation using internal standards was generally more accurate for GC/MS analyses. The internal standards also provide a means of monitoring the instrument performance. However, it was noted during this study that the analytical system exhibited extremely good stability and provided reproducible measurements on a consistent basis. Therefore, quantitation using external calibration may also be acceptable.

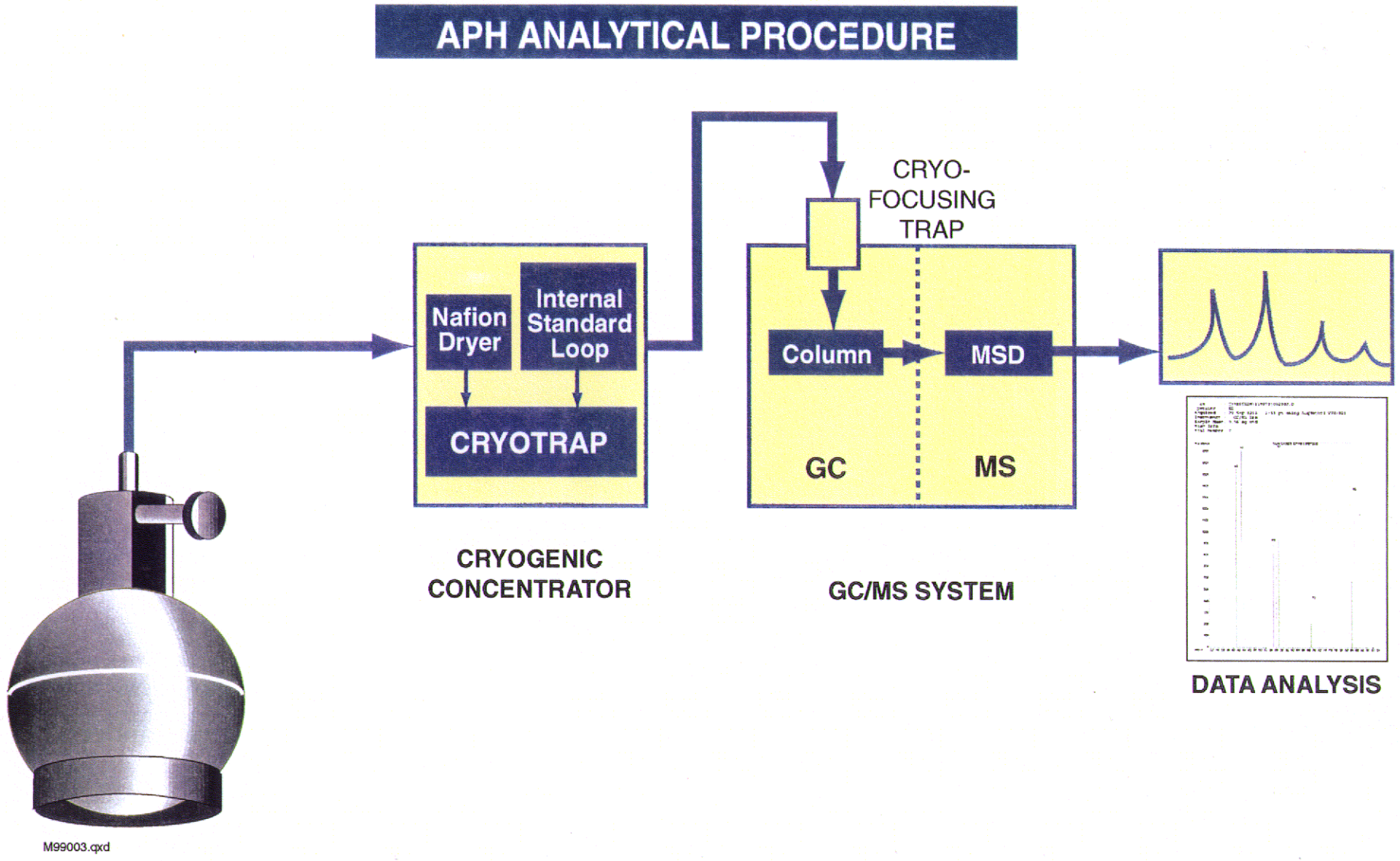

APH ANALYTICAL PROCEDURE
CRYO-
FOCUSING
TRAP
Nafion
Dryer
Internal
Standard
Loop
CRYOTRAP
Column
MSD
GC
MS
CRYOGENIC
CONCENTRATOR
GC/MS SYSTEM
DATA ANALYSIS
M99003.qxd

FIGURE 3-1

TABLE 3-1
Comparison Between EPA Method TO-14 and the APH Method

EPA Method TO-14	APH Method
Sample collection medium: SUMMA® canister	*Sample collection medium*: SUMMA® canister
Analysis performed by *GC/MS or GC/multidetector (e.g., PID/FID/ELCD)*	Analysis performed by *GC/MS only*
Nafionâ dryer is used to remove sample moisture	Same
Sample is transferred to *cryogenically cooled trap*	Same
Capillary column used in GC	Same
Canister cleaning and certification required	Same
Target list: *mainly chlorinated VOCs with a few aromatics*	Target list: *1,3-butadiene, aliphatic and aromatic hydrocarbons*
QC Requirements:	
BFB tune at beginning of each day prior to standards, samples, and blanks	Same
Three point initial calibration	*Five point initial calibration*
No initial calibration acceptance criteria	*%RSD <30 or r >0.99*
Continuing calibration daily prior to samples and blanks	Same
No continuing calibration acceptance criteria	*%D<30 or %R 70-130*
Humid zero air blank	Same
No QC check for precision	*Duplicate analysis required daily*
No QC check for accuracy	*Laboratory control spike* required once per initial calibration
Internal standards not discussed in method	*Internal standards optional*; area must be between 50-200% of internal standards in associated calibration standard

TABLE 3-2
NUTECH 3550A/3600 Operating Parameters

Inlet purge or sample loop purge time	2.0 minutes
Sample loop equilibrium time	10 seconds
Sample loop load time	Volume dependent
Internal standard loop purge time	1.0 minute
Internal standard equilibrium time	10 seconds
Internal standard load time	1.5 minutes
Cryotrap cool setpoint during sample load	-160°C
Cryotrap desorption setpoint	160 °C
Cryofocus cool setpoint during refocusing	-190°C
Cryofocus desorption setpoint (for injection)	160°C
Sample flow setpoint	30 mL/min
Nafion® dryer temperature during sample loading	0°C
Nafion® dryer temperature during cleanup cycle	125°C
Cryotrap/cryofocus transfer time	2.5 minutes
Cryotrap extended transfer time	5.0 minutes
Nafion® dryer purge flow rate (dehydrates Nafion ® membrane)	150 mL/min
Purge gas flow rate (dry purge for low level sample flowpath)	40 mL/min
Autosampler purge flow rate (purges sample flowpaths from autosampler valve)	40 mL/min
Loop gas flow rate (transfers sample loop or standard loop contents to the cryotrap and purges these flowpaths)	20 mL/min
Internal standard flow rate (fills the 2 mL standard loop)	20 mL/min

TABLE 3-3
GC/MS Operating Parameters

GC Column	RTX-1; 60 m; 0.25 mm ID, 1µm df
Injection mode	Splitless
Carrier Gas	Helium
Carrier Gas flow	2 mL/min
GC Temperature Program:	
Initial Temperature	10°C
Initial Time	6.0 minutes
Ramp 1	3°C/min to 135°C
Ramp 2	10°C/min to 180°C
Final Time	6.0 minutes
Mass Spectrometer:	
MS transfer line temperature	240□C
MS quadropole	150°C
MS Source	230°C
Solvent Delay	4.8 minutes
Scanning Parameters	40-250 amu; threshold = 200

TABLE 3-4
Retention Time Order of Target Analytes

CAS Number	Compound	Retention Time
106-99-0	1,3-Butadiene	5.94
78-78-4	Isopentane	8.63
109-66-0	Pentane	9.99
79-29-8	2,3-Dimethylbutane	13.91
107-83-5	2-Methylpentane	14.23
1634-04-4	Methyl t-butylether	14.57
96-14-0	3-Methylpentane	15.21
74-97-5	**Bromochloromethane – IS1**	**16.50**
110-97-5	n-Hexane	16.46
96-37-7	Methylcyclopentane	18.33
71-43-2	Benzene	20.14
110-82-7	Cyclohexane	20.72
540-36-3	**1,4-Difluorobenzene-IS2**	**21.40**
591-76-4	2-Methylhexane	21.43
565-59-3	2,3-Dimethylpentane	21.54
110-83-8	Cyclohexene	21.92
540-84-1	2,2,4-Trimethylpentane	23.01
142-82-5	n-Heptane	23.82
108-87-2	Methylcyclohexane	25.29
592-13-2	2,5-Dimethylhexane	26.13
108-88-2	Toluene	27.83
589-81-1	3-Methylheptane	29.07
111-65-9	n-Octane	30.85
3114-55-4	**Chlorobenzene-d5-IS3**	**32.89**
100-41-4	Ethylbenzene	34.24
3074-71-3	2,3-Dimethylheptane	34.66
108-38-3/106-42-3	m&p-Xylenes	34.85
100-42-5	Styrene	35.96
95-47-6	o-Xylene	36.27
111-84-2	n-Nonane	37.33
98-82-8	Isopropylbenzene	38.31
103-65-1	n-Propylbenzene	40.12
620-14-4	1-Methyl-3-ethylbenzene	40.56
108-67-8	1,3,5-Trimethylbenzene	41.02
95-63-6	1,2,4-Trimethylbenzene	42.54
124-18-5	n-Decane	43.32
526-73-8	1,2,3-Trimethylbenzene	44.20
99-87-6	p-Isopropyltoluene	44.34
95-13-6	Indene	45.30
1678-93-9	Butylcyclohexane	45.34
1120-21-4	n-Undecane	48.76
488-23-3	1,2,3,4-Tetramethylbenzene	50.70
91-20-3	Naphthalene	51.69
112-40-3	n-Dodecane	52.29
877-44-1	1,2,4-Triethylbenzene	53.22
4292-75-5	Hexylcyclohexane	53.52
91-57-6	2-Methylnaphthalene	54.84
90-12-0	1-Methylnaphthalene	55.32

4.0 QAPP DEVELOPMENT

ENSR prepared a QAPP for this method development project prior to the onset of the analytical validation. The QAPP was presented in a document entitled *"Quality Assurance Project Plan for the Method Development and Laboratory Validation of Petroleum Hydrocarbon Analyses in Indoor Air Samples"*, dated May 1998. The QAPP contained the following Sections:

1. Introduction
2. Project Organization and Responsibilities
3. Quality Assurance Objectives for Measurement Data
4. Sample Containers
5. Sample Custody
6. Calibration Procedures
7. Analytical Procedures
8. Internal Quality Control Checks
9. Data Reduction, Validation and Reporting
10. Performance and System Audits
11. Preventive Maintenance
12. Specific and Routine Procedures to Assess Data Precision, Accuracy and Completeness
13. Corrective Action

4.1 Deviations From the QAPP

In general, the QAPP developed for this program was strictly followed. The QAPP goals were not met in one instance; modifications were made in the three other areas during method development.

The QAPP required method blank criterion could not be met despite multiple corrective actions.. The QAPP specified that results for all analytes in the method blank be below the reporting limit. However, as discussed below in Sections 5.0 and 7.0, carryover of several of the heavier molecular weight compounds (C_{12} compounds and naphthalenes) from analysis to analysis could not always be eliminated. Several measures were put into place which minimized the carryover; however, it was never completely eliminated. It should be noted that, in most instances, the levels detected were just slightly above the reporting limit.

Second, the quantitation approach for the hydrocarbon ranges which was proposed in the QAPP was modified and is discussed in more detail in Section 6.0.

Third, the procedure used for the second and third MDL studies was modified based on the results of the first MDL study. This is discussed in more detail in Section 5.0.

Finally, the least significant deviation noted was the procedure used for the analysis of the bromofluorobenzene (BFB) tune. The QAPP stated that 50 ng of BFB would be directly injected into the GC/MS system. However, after the QAPP was written, ENSR purchased a new concentrator system (Nutech 3550A) which eliminated the need for the GC injection port. The new system is connected directly to the GC column through the cryofocusing unit (See Figure 3-1) and direct injection of BFB is therefore not possible with this setup. To compensate for this, BFB was included in the internal standard mix which was connected to the Nutech 3550A concentrator. The BFB was injected at 10 ng and evaluated in the first analysis of each day.

5.0 METHOD DETECTION LIMIT STUDIES

The method detection limit (MDL) is a statistically derived number and is the minimum concentration of an analyte which can be measured and reported with 99% confidence that the concentration is greater than zero. All MDL studies were performed in accordance with 40 CFR Chapter 1, Part 136, Appendix B, *Definition and Procedure for the Determination of the Method Detection Limit*. Four MDL studies were performed for the purposes of this method validation study. The first two MDL studies were performed to obtain MDLs of the 44 individual hydrocarbon analytes listed in Table 2-1. The third and fourth MDL studies were performed to obtain MDLs of each hydrocarbon range (C_5-C_8 aliphatics, C_9-C_{12} aliphatics, and C_9-C_{10} aromatics).

5.1 Preparation of SUMMA® Canisters Used in MDL Studies

Stock standards of the 44 hydrocarbon analytes were purchased as three different liquid solutions in methanol. These liquid standards were purchased from AccuStandard Inc. in New Haven, CT. It should be noted that these liquid standards which were utilized for MDL studies #1 and #2 were custom made by AccuStandard Inc. and are therefore not readily available upon request. Upon receipt at the laboratory, all liquid stock standards were stored at -20°C. Table 5-1 lists the analytes which were contained in each of the three mixes and the concentrations of each, as received from AccuStandard Inc. In addition, a stock standard of regular unleaded gasoline, prepared at 5000 µg/mL in methanol, was purchased from AccuStandard Inc. for the third and fourth MDL studies.

ENSR determined which analytes should be included in each stock standard based on the boiling points and molecular structure of each analyte. In general, analytes which exhibited similar spectra or structure and close boiling points were put into separate mixes. This would allow an easy determination of analyte retention times prior to conducting this study. ENSR requested that AccuStandard Inc. prepare the third stock solution (S-4999C) at a slightly higher concentration than the other two solutions due to the anticipation that the compounds in the third stock solution may be slightly harder to detect using this methodology due to their lower volatility.

Prior to conducting the MDL studies, each of the custom-made liquid stock standards was manually injected onto the GC/MS system in order to determine the spectrum and retention time of each of the 44 hydrocarbon analytes. Table 3-4 lists the retention time order of the target analytes.

5.1.1 SUMMA® Canisters Utilized in MDL Study #1

The SUMMA® Canisters used in the first MDL study contained spikes of all 44 hydrocarbon analytes. Eight SUMMA ® Canisters were prepared at concentrations of 22.2 $\mu g/m^3$ for all analytes with the exception of those analytes which are in the third liquid stock solution (S-4999C:Table 5-1) which were at 41.7 $\mu g/m^3$. The liquid stock solutions which were received from AccuStandard Inc. were injected into precleaned, evacuated six liter SUMMA ® canisters at different volumes, 130 µL of HPLC grade water was added to each canister, and the canisters were pressurized to 30 psig. Table 5-2 outlines the preparation of the SUMMA® canisters used in MDL Study #1.

5.1.2 SUMMA® Canister Utilized in MDL Study #2

The SUMMA® Canister used in the second MDL study also contained spikes of all 44 hydrocarbon analytes. One SUMMA ® Canister was prepared at a concentration of 11.1 $\mu g/m^3$ for all analytes. An intermediate stock standard was prepared at 40 µg/mL in methanol using the liquid stock solutions which were received from AccuStandard Inc. The preparation of this intermediate stock standard is outlined in Table 5-3.

A specified volume of the intermediate stock solution was injected into a precleaned, evacuated six liter SUMMA ® canister, 130 µL of HPLC grade water was added to the canister, and the canister was pressurized to 30 psig. Table 5-4 outlines the preparation of the SUMMA ® canister used in MDL Study #2.

5.1.3 SUMMA® Canister Utilized in MDL Studies #3 and #4

The SUMMA® canister used in the third and fourth MDL studies contained a spike of regular unleaded gasoline. MDL Study #3 was performed using a SUMMA ® canister prepared at a concentration of 122.2 $\mu g/m^3$ of regular unleaded gasoline. An intermediate stock standard was prepared at 100 µg/mL in methanol using a liquid stock solution which was received from AccuStandard Inc. at 5.0 mg/mL The preparation of this intermediate stock standard is outlined in Table 5-5.

A specified volume of the intermediate stock solution was injected into a precleaned, evacuated six liter SUMMA ® canister, 130 µL of HPLC grade water was added to the canister, and the canister was pressurized to 30 psig. Table 5-6 outlines the preparation of the SUMMA ® canister used in MDL Study #3.

MDL Study #4 was performed using a SUMMA ® canister prepared at 555.5 µg/m^3. Table 5-6 also summarizes the preparation of this canister.

5.2 MDL Procedures

In general, each MDL study was conducted using the analytical procedures specified in Section 3.0. However, there were slight differences in the procedures used versus the QAPP requirements.

MDL Study #1 was conducted in accordance with the QAPP requirements. That is, analysis was performed on seven replicate SUMMA ® canister blanks which were spiked with all analytes of interest between 3 to 5 times the expected MDL. The expected MDLs were estimated based on the known MDLs attainable for analytes on the TO-14 list. Eighty mL of each canister were analyzed. This resulted in the on-column injection of all compounds present in stock solutions 1 and 2 (as listed in Table 5-1) at 1.78 ng (m&p-xylenes were at 3.55 ng); the remaining compounds were injected at 3.34 ng on-column.

Based on the results of MDL Study #1, which are discussed below, MDL Study #2 was performed using a slightly different approach. Seven replicate analyses were performed on one SUMMA ® canister which was spiked with all analytes of interest between 3 to 5 times the expected MDL. The use of one canister versus seven canisters was considered to be an acceptable procedure since real-world samples would never undergo any type of preparation procedure prior to analysis. Therefore, the elimination of the replicate preparations was considered to be a valid approach and more consistent with the analysis of real-world samples. All analyses were performed using 150 mL. This resulted in the on-column injection of all compounds at 1.66 ng (m&p-xylenes were at 3.33 ng).

MDL Studies #3 and #4 were not proposed at the onset of this program and therefore were not addressed in the QAPP. However, a procedure similar to that used in MDL study #2 was employed. That is, seven replicate analyses were performed on one SUMMA ® canister. However, these MDL studies were performed without the use of a Nafion ® dryer. Although this is a modification from the procedure used thus far, results were not expected to be significantly affected since the amount of moisture in the SUMMA ® canisters used in the MDL studies was moderate. The SUMMA ® canisters were spiked with regular unleaded gasoline between 3 to 5 times the expected MDL. These MDL studies were used to determine the MDLs of the hydrocarbon ranges (C_5-C_8 aliphatics, C_9-C_{12} aliphatics, and C_9-C_{10} aromatics). Analyses were performed using 250 mL for MDL Study #3 and 200 mL for MDL study #4. This resulted in on-column injections of 30.6 ng for MDL study #3 and 111.1 ng for MDL Study #4.

5.3 MDL Results

The MDL results were evaluated by examining the precision of the seven measurements. The standard deviation of the seven measurements was measured and from this, an MDL was calculated using Equation 5-1.

Equation 5.1: Method Detection Limit

$$MDL = SD_{n-1} * t$$

where
MDL = Method detection limit
SD = standard deviation (n-1 degrees of freedom)
t = student t value at the 99% confidence level (3.14)

In order to be considered acceptable, the MDL was required to be between 1/10 the amount spiked and the amount spiked.

5.3.1 MDL Study #1

The results of MDL Study #1 are presented in Appendix C of the raw data. Only twenty-eight (64%) of the 44 target analytes exhibited MDLs which were within the criteria set forth in the QAPP. MDLs which were acceptable ranged from 2.8 to 35 $\mu g/m^3$ or 0.67 to 6.6 ppbV.

3-Methylpentane, n-hexane, methylcyclopentane, and cyclohexene exhibited MDLs which were outside the QAPP criteria. That is, the MDLs of these compounds were less than 1/10 the spiking level. This indicated that a further MDL study for these compounds would be appropriate at a lower spiking level. These MDLs ranged from 0.22 to 0.55 ppbV.

All compounds which were present in the third liquid stock solution (as in Table 5-1), with the exception of naphthalene, exhibited MDLs which were outside the QAPP criteria. The MDLs of these compounds ranged from 43 to 122 $\mu g/m^3$ or 7.8 to 21 ppbV. These MDLs were too high indicating poorer precision at this spiking level. This also indicated that a further MDL study for these compounds would be appropriate at a higher spiking level. Upon further investigation of these higher MDLs, ENSR felt that spiking at a higher level may not be the solution. It was ENSR's opinion that these compounds were exhibiting carryover from analysis to analysis, thereby resulting in the poor precision. The most likely situation was that these heavier molecular weight compounds were not being fully desorbed from the concentrator unit and therefore exhibited variable results from analysis to analysis.

In order to prevent this or to at least minimize the occurrence of this carryover, the cryotrap extended transfer time was increased from three minutes to five minutes. This allowed more volume to pass through the cryotrap after the injection had occurred, increasing the transfer efficiency of these analytes. Using this modification, a new MDL was proposed (MDL Study #2) with a lower spiking level. Although the precision of these compounds was poor, the sensitivity of these compounds was excellent and therefore ENSR felt that with this instrument modification and a lower spiking level, acceptable MDLs would be attainable.

Methyl-tertbutyl ether (MTBE) also exhibited an MDL which did not meet the QAPP criteria. All samples pass through a Nafion® dryer prior to concentration on the cryotrap. The purpose of the Nafion® dryer is to remove moisture from the sample. Moisture can adversely affect the lifetime of the GC column, the chromatography, and the performance of the mass spectrometer. Therefore, the removal of the moisture is an important part of the analysis. However, the removal of moisture also includes the removal or decreased sensitivity of water-soluble compounds such as MTBE. As a result, MTBE exhibited both poor precision and poor sensitivity and thereby demonstrated a high MDL (approximately 44 $\mu g/m^3$ or 12 ppbV). Based on the instrument parameters used for this study, it was doubtful that a better MDL could be obtained for this compound unless the Nafion ® dryer was taken out of line and not used. Further attempts to improve the MDL of this compound were not made.

5.3.2 MDL Study #2

The results of MDL Study #2 are presented in Table 5-7. Forty-one (93%) of the 44 target analytes exhibited MDLs which were within the criteria set forth in the QAPP. MDLs which were acceptable ranged from 1.2 to 9.5 $\mu g/m^3$ or 0.26 to 1.8 ppbV. Table 5-8 demonstrates the difference in MDL ranges obtained between MDL Study #1 and MDL Study #2. As can be seen in this table, the instrument modifications mentioned above as well as the analysis of lower amounts of each analyte improved MDLs significantly.

In general, as seen in Figure 5-1, the MDLs fell below 1 ppbV with a slight increase starting at undecane (C_{11}). MDLs for C_{11} compounds and higher exhibited slightly higher MDLs. Although the carryover issue had significantly improved from MDL Study #1, the presence of minimal amounts of carryover may still be contributing to this slight increase. Hexylcyclohexane and 1,2,4-triethylbenzene exhibited MDLs which exceeded the QAPP criteria. The MDLs of these compounds were 2.0 ppbV and 2.7 ppbV (or 14 and 18 $\mu g/m^3$), respectively. Although these MDLs were outside the QAPP criteria, these MDLs were considered to be acceptable for the purposes of this program.

MTBE was not detected in any of the analyses performed for MDL Study #2. The low amount spiked and the presence of the Nafion ® dryer both contributed to the lack of

recovery. As stated above, further attempts to obtain a lower MDL for MTBE were not made at this time.

Another potential reason for the lower variability exhibited in this MDL study versus MDL Study #1 may be due to the fact that seven different SUMMA ® canisters were used in MDL Study #1. The preparation of seven different canisters introduces more error into the procedure, and thus the higher variability. Since MDL Study #2 was performed by using seven replicate analyses of one canister, only analytical performance contributed to the variability in the results and thus the lower MDLs.

The results of MDL Study #2 are most representative of the method performance. The remaining MDL study, precision and accuracy study, and the analysis of real world samples were all performed using the same instrument conditions used in MDL Study #2.

5.3.3 MDL Studies #3 and #4

It should be noted that the results from these studies provide MDLs for each hydrocarbon range, but these MDLs are appropriate for gasoline only. The MDLs for the hydrocarbon ranges will be highly dependent on the petroleum product in question and the components of that product which will most likely partition into the indoor air. All components of gasoline are expected to partition into the air and should therefore yield the lowest MDLs. MDLs of some of the heavier petroleum products (e.g., kerosene, diesel fuel) will most likely yield higher MDLs, especially for the lighter hydrocarbon range (C_5-C_8 aliphatics).

The results of MDL Study #3 indicated that the spiking concentration used was too low. In general, poor recoveries of the C_9-C_{12} aliphatics and C_9-C_{10} aromatics were exhibited. These ranges were barely detectable and based on this, it was determined that MDL Study #3 would not be reliable for the determination of MDLs. The raw data associated with MDL Study #3 have not been included in this report but will be retained on file at ENSR.

MDL Study #4 was performed using a concentration which was approximately four times higher than that used for MDL Study #3. Table 5-9 summarizes the results of this study. It should be noted that the calculations of C_5-C_8 aliphatics concentrations were exclusive of target analytes and internal standards which elute in this range. The calculations of C_9-C_{12} aliphatics concentrations were exclusive of target analytes, internal standards, and C_9-C_{10} aromatics which elute in this range. This study yielded low MDLs for each of the hydrocarbon ranges. The amount of gasoline recovered in the SUMMA® canister was calculated based on the amount spiked. When all hydrocarbon ranges (C_5-C_8 aliphatics, C_9-C_{12} aliphatics, and C_9-C_{10} aromatics) and target analytes were totaled, the sum represented approximately 98% of the total amount of gasoline spiked in the SUMMA® canister. Finally, the chromatograms and results from MDL Study #4 indicated that the lack of a Nafion®

dryer in the process still yielded acceptable chromatography and recoveries of target analytes. The sensitivity of the GC/MS system did not change from when the Nafion® dryer was used in the process.

5.4 Reporting Limits

Reporting limits for this method must be based on the lowest calibration standard analyzed under normal operating conditions. The reporting limits must be above the MDL. In general, most compounds included in this study demonstrated reporting limits of 0.28 – 0.55 ng on-column. Heavier molecular weight compounds such as hexylcyclohexane, naphthalene, 1, 2, 4-triethylbenzene, 2-methylnaphthalene, and 1-methylnaphthalene demonstrated reporting limits of approximately 1.11 ng on-column. Based on the analysis of 250 mL sample, these reporting limits correspond to approximately 1.1 – 4.4 $\mu g/m^3$.

Figure 5-1
MDL (ppbV) vs. Molecular Weight
MDL Study #2

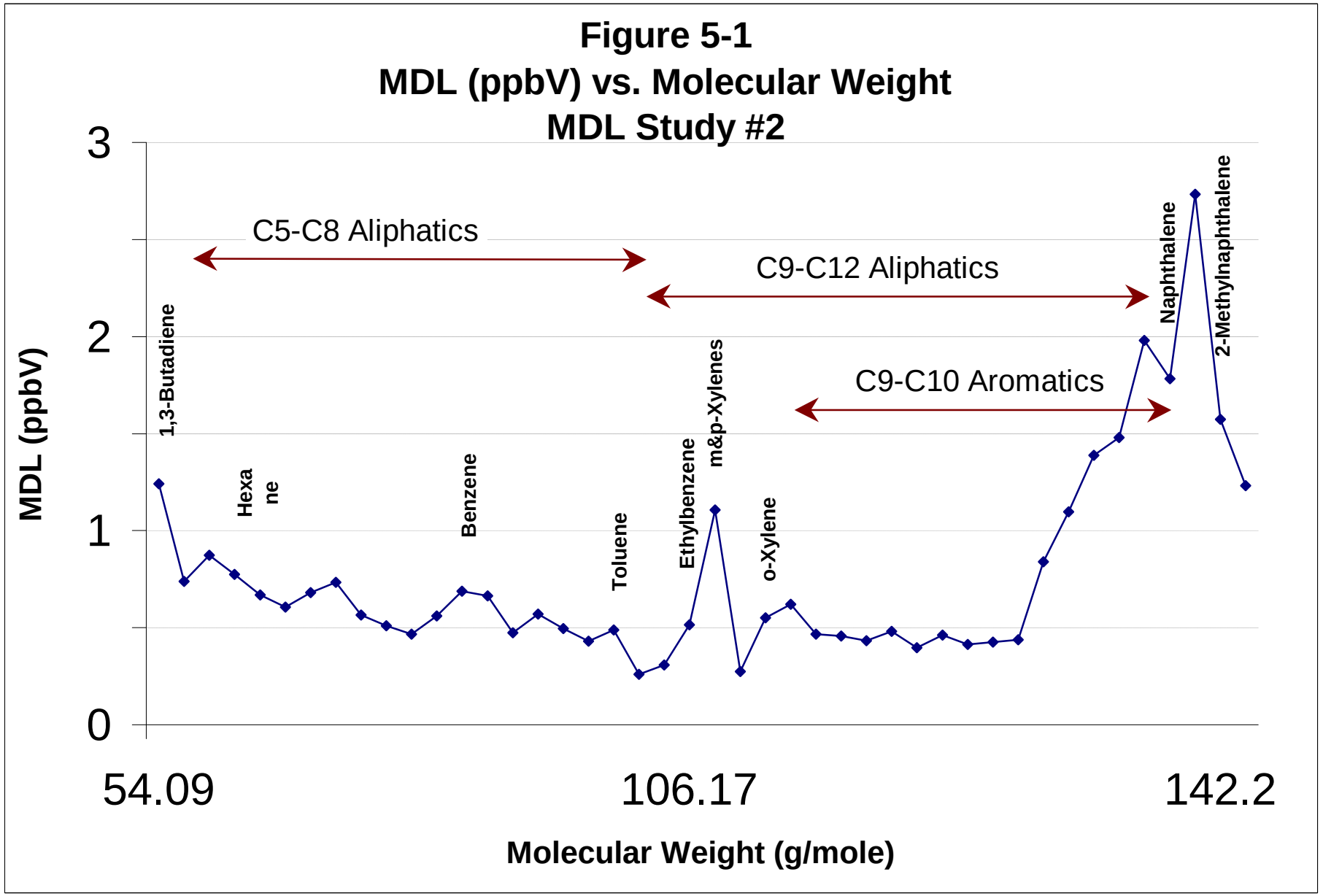


TABLE 5-1
Stock Standards as Purchased From the Vendor

Stock 1 (S-4999A)	Concentration (µg/mL)	Stock 2 (S-4999B)	Concentration (µg/mL)	Stock 3 (S-4999C)	Concentration (µg/ml)
1,3-Butadiene	200	2-Methylbutane [2]	200	n-Decane	500
Benzene	200	Methyl-tert-butylether	200	1,2,3-Trimethylbenzene	500
n-Heptane	200	n-Hexane	200	p-Isopropyltoluene	500
Ethylbenzene	200	Cyclohexane	200	Butylcyclohexane	500
2,3-Dimethylheptane	200	2,3-Dimethylpentane	200	Indene	500
o-Xylene	200	Toluene	200	n-Undecane	500
n-Nonane	200	n-Octane	200	n-Dodecane	500
1-Methyl-3-ethylbenzene [1]	200	m-Xylene	200	Naphthalene	500
		p-Xylene	200	Hexylcyclohexane	500
		Isopropylbenzene	200	2-Methylnaphthalene	500
		1,3,5-Trimethylbenzene	200	1-Methylnaphthalene	500

[1] **m-Ethyltoluene**
[2] **Isopentane**

TABLE 5-2
Preparation of the SUMMA® Canisters Used in MDL Study #1

Stock Standard	Stock Standard Concentration (µg/mL)	Volume of Stock Taken (mL)	Final Volume Canister (L)	Volume HPLC Water Added (mL)	Final Concentration Canisters ($\mu g/m^3$)
(1) S-4999A	200	2	18	130	22.2
(2) S-4999B	200	2	18	130	22.2
(3) S-4999C	500	1.5	18	130	41.7

TABLE 5-3
Preparation of the Intermediate Stock Standard for MDL Study #2

Stock Standard	Stock Standard Concentration (µg/mL)	Volume of Stock Taken (µL)	Final Volume Methanol (mL)	Final Concentration Intermediate Stock (µg/mL)
S-4999A	200	400	2.0	40
S-4999B	200	400	2.0	40
S-4999C	500	160	2.0	40

TABLE 5-4
Preparation of the SUMMA® Canister Used in MDL Study #2

Stock Standard	Stock Standard Concentration (µg/mL)	Volume of Stock Taken (µL)	Final Volume Canister (L)	Volume HPLC Water Added (µL)	Final Concentration Canister (µg/m^3)
Intermediate	40	5	18	130	11.1

TABLE 5-5
Preparation of the Intermediate Stock Standard for MDL Study #3

Stock Standard	Stock Standard Concentration (µg/mL)	Volume of Stock Taken (µL)	Final Volume Methanol (mL)	Final Concentration Intermediate Stock (µg/mL)
Regular Unleaded Gasoline	5000	100	5.0	100

TABLE 5-6
Preparation of the SUMMA® Canisters Used in MDL Studies #3 and #4

Stock Standard	Stock Standard Concentration (µg/mL)	Volume of Stock Taken (µL)	Final Volume Canister (L)	Volume HPLC Water Added (µL)	Final Concentration Canister (µg/m^3)
Intermediate Gasoline Standard	100	22	18	130	122.2 (MDL Study #3)
Regular Unleaded Gasoline	5000	2	18	130	555.5 (MDL Study #4)

TABLE 5-7
METHOD DETECTION LIMIT STUDY #2
PROCEDURE: SEVEN REPLICATE ANALYSES OF ONE SUMMA CANISTER

Amount spiked: 1.66 ng for all compounds (3.33 ng for m&p-Xylenes)

Compound	#1 (ng)	#2 (ng)	#3 (ng)	#4 (ng)	#5 (ng)	#6 (ng)	#7 (ng)	SD	MDL[1] (ng)	MDL[2] (ug/m3)	MDL[3] (ppbV)		Mol. Wgt (g/mole)
C5-C8 Aliphatics													
Isopentane	1.81	1.65	1.63	1.83	1.84	1.71	1.58	0.1059	0.3325	2.2168	0.7386	*	72.15
Pentane	1.86	1.76	1.74	2.01	2.04	1.84	1.74	0.1251	0.3930	2.6198	0.8729	*	72.15
2,3-Dimethylbutane	1.75	1.65	1.59	1.83	1.93	1.68	1.56	0.1328	0.4168	2.7790	0.7752	*	86.18
2-Methylpentane	1.67	1.52	1.49	1.66	1.77	1.53	1.46	0.1147	0.3602	2.4016	0.6699	*	86.18
3-Methylpentane	1.75	1.60	1.56	1.72	1.82	1.60	1.55	0.1053	0.3307	2.2045	0.6150	*	86.18
n-Hexane	1.77	1.52	1.47	1.61	1.73	1.58	1.49	0.1166	0.3661	2.4408	0.6809	*	86.18
Methylcyclopentane	1.49	1.50	1.53	1.70	1.81	1.59	1.50	0.1227	0.3852	2.5679	0.7335	*	84.16
Cyclohexane	1.69	1.59	1.48	1.64	1.74	1.56	1.51	0.0944	0.2965	1.9764	0.5646	*	84.16
2-Methylhexane	1.38	1.28	1.36	1.38	1.42	1.17	1.18	0.1015	0.3187	2.1245	0.5097	*	100.21
2,3-Dimethylpentane	1.46	1.41	1.33	1.61	1.51	1.49	1.38	0.0927	0.2911	1.9407	0.4656	*	100.21
2,2,4-Trimethylpentane	1.65	1.58	1.52	1.79	1.83	1.75	1.53	0.1270	0.3988	2.6585	0.5595	*	114.23
Cyclohexene	1.65	1.59	1.53	1.80	1.81	1.76	1.64	0.1086	0.3410	2.2730	0.6652	*	82.15
n-Heptane	1.56	1.48	1.46	1.65	1.67	1.68	1.50	0.0946	0.2970	1.9801	0.4750	*	100.21
Methylcyclohexane	1.58	1.49	1.50	1.72	1.72	1.75	1.55	0.1115	0.3501	2.3337	0.5714	*	98.19
2,5-Dimethylhexane	1.57	1.50	1.45	1.74	1.71	1.66	1.51	0.1128	0.3541	2.3604	0.4968	*	114.23
3-Methylheptane	1.59	1.55	1.47	1.68	1.74	1.66	1.51	0.0976	0.3066	2.0439	0.4301	*	114.23
n-Octane	1.39	1.39	1.36	1.49	1.44	1.50	1.36	0.0587	0.1844	1.2291	0.2587	*	114.23
C9-C12 Aliphatics													
2,3-Dimethylheptane	1.44	1.43	1.40	1.60	1.50	1.57	1.56	0.0785	0.2466	1.6439	0.3081	*	128.26
n-Nonane	1.49	1.54	1.43	1.60	1.58	1.64	1.55	0.0702	0.2203	1.4689	0.2753	*	128.26
n-Decane	1.67	1.61	1.67	1.89	1.78	1.90	1.78	0.1125	0.3533	2.3551	0.3979	*	142.29
Butylcyclohexane	1.70	1.75	1.68	1.93	1.89	1.97	1.86	0.1153	0.3621	2.4137	0.4137	*	140.27
Indene	1.98	2.01	1.97	2.31	2.35	2.41	2.30	0.1938	0.6086	4.0573	0.8397	*	116.16
n-Undecane	2.38	2.15	1.32	2.11	2.15	2.22	2.12	0.3410	1.0708	7.1387	1.0979	*	156.31
n-Dodecane	3.36	3.76	2.59	2.47	2.40	2.96	3.09	0.5011	1.5733	10.4888	1.4803	*	170.34
Hexylcyclohexane	3.95	2.72	1.70	3.10	2.97	2.99	2.86	0.6620	2.0787	13.8579	1.9798		168.27
C9-C10 Aromatics													
Isopropylbenzene	1.50	1.51	1.42	1.66	1.64	1.74	1.63	0.1116	0.3505	2.3368	0.4674	*	120.2
n-Propylbenzene	1.54	1.54	1.47	1.73	1.67	1.76	1.67	0.1094	0.3434	2.2895	0.4579	*	120.2
1-Methyl-3-ethylbenzene	1.52	1.55	1.46	1.72	1.64	1.73	1.66	0.1033	0.3245	2.1634	0.4327	*	120.2
1,3,5-Trimethylbenzene	1.58	1.61	1.61	1.84	1.76	1.86	1.74	0.1152	0.3616	2.4107	0.4821	*	120.2
1,2,4-Trimethylbenzene	1.53	1.53	1.52	1.73	1.69	1.79	1.68	0.1105	0.3470	2.3135	0.4627	*	120.2
p-Isopropyltoluene	1.62	1.63	1.59	1.83	1.79	1.88	1.73	0.1137	0.3570	2.3802	0.4263	*	134.22
1,2,3-Trimethylbenzene	1.50	1.51	1.49	1.69	1.63	1.76	1.63	0.1046	0.3285	2.1903	0.4381	*	120.2
1,2,3,4-Tetramethylbenzene	2.72	2.39	1.60	2.47	2.46	2.66	2.47	0.3704	1.1632	7.7546	1.3889	*	134.22
Individual Target Analytes													
1,3-Butadiene	1.69	1.51	1.52	1.78	1.76	1.48	1.49	0.1335	0.4193	2.7951	1.2423	*	54.09
Methyl t-butylether**	4.31	3.26	2.93	3.25	3.57	0.69	3.29	1.1242	3.5301	44.1260	12.0339		88.15
Benzene	1.63	1.62	1.55	1.76	1.86	1.77	1.67	0.1069	0.3357	2.2379	0.6888	*	78.11
Toluene	1.57	1.52	1.50	1.69	1.71	1.70	1.57	0.0893	0.2805	1.8701	0.4879	*	92.14
Ethylbenzene	1.39	1.40	1.35	1.56	1.57	1.63	1.54	0.1088	0.3418	2.2785	0.5159	*	106.17
m&p-Xylenes	3.03	3.02	2.95	3.40	3.33	3.57	3.33	0.2334	0.7330	4.8865	1.1064	*	106.17
o-Xylene	1.48	1.50	1.45	1.68	1.64	1.74	1.68	0.1160	0.3643	2.4288	0.5500	*	106.17
Naphthalene	4.12	3.87	2.81	3.86	3.93	4.15	3.71	0.4537	1.4247	9.4983	1.7815	*	128.17
2-Methylnaphthalene	3.49	4.44	3.38	4.07	3.55	3.66	3.12	0.4447	1.3962	9.3082	1.5736	*	142.2
1-Methylnaphthalene	2.86	3.90	2.98	3.19	2.96	3.31	3.13	0.3483	1.0938	7.2917	1.2327	*	142.2
Other													
Styrene	1.43	1.44	1.39	1.61	1.67	1.71	1.61	0.1286	0.4039	2.6928	0.6216	*	104.15
1,2,4-Triethylbenzene	4.72	2.42	1.85	2.87	2.95	3.12	2.87	0.8815	2.7679	18.4528	2.7336		162.28

* = meets QAPP specifications for an acceptable MDL (between 1/10 amount spiked and amount spiked)

** = MTBE results from MDL Study #2

ppbV and ug/m^3 values based on 150 mL injection

[1] See Equation 5.1 for calculation.

[2] ug/m^3 = MDL (ng)/vol. analyzed (0.150L)

[3] ppbV = MDL (ug/m^3) * $\frac{\text{Molar gas constant (24.04)}}{\text{molecular weight}}$

TABLE 5-8
Summary of Results from MDL Studies #1 and #2

MDL Study	MDLs Which Met QAPP Criteria (µg/m^3)	MDLs Which Met QAPP Criteria (ppbV)
MDL Study #1	2.8 – 35	0.67 – 6.6
MDL Study #2	1.2 – 9.5	0.26 – 1.8

TABLE 5-9
Method Detection Limit Study #4 Results

Compound	#1 (µg/m^3)	#2 (µg/m^3)	#3 (µg/m^3)	#4 (µg/m^3)	#5 (µg/m^3)	#6 (µg/m^3)	#7 (µg/m^3)	SD	MDL (µg/m^3)
Hydrocarbon Ranges									
$C_5 – C_8$ Aliphatics*	326.15	330.95	325.45	325.15	332.55	315.45	323.6	5.5449	17.41
$C_9 – C_{12}$ Aliphatics**	37.9	37.1	37.6	26.75	29.85	32.9	27.15	4.9119	15.42
$C_9 – C_{10}$ Aromatics	61.6	62.85	61.2	61.65	60.35	59.6	60.15	1.1051	3.47
Target Analytes									
Methyl t-butylether	63.5	62.8	61.4	61.7	62.4	63.3	61.1		
Benzene	3.35	3.25	3.20	3.25	3.30	3.40	3.25		
Toluene	18.4	18.5	18.4	18.3	18.2	18.2	18.4		
Ethylbenzene	5.15	5.10	5.15	5.10	5.15	5.20	5.10		
M&p-Xylenes	22.1	22.2	22.0	22.1	21.7	21.7	22.0		
o-Xylene	7.95	7.95	7.90	8.00	7.95	7.85	7.90		
Naphthalene	6.80	6.45	6.35	6.20	6.15	6.10	6.05		
Total µg/m^3 Found	552.9	557.1	548.5	538.2	547.6	533.7	534.6		
Total µg/m^3 Spiked	555.5	555.5	555.5	555.5	555.5	555.5	555.5		
Percent Recovery	99.5	100.3	98.7	96.9	98.6	96.1	96.2		

* C_5-C_8 Aliphatics exclude concentrations of target analytes and internal standards eluting in the range.
** C_9-C_{12} Aliphatics exclude concentrations of target analytes, internal standards, and C_9-C_{10} Aromatics eluting in the range.

6.0 QUANTIFICATION OF HYDROCARBON RANGES APPROACH

The quantification of the individual target analytes described in previous sections was straightforward and similar to other GC/MS methodologies which utilize internal standards. The SOP for this method provides details on these calculations. The quantification of the hydrocarbon ranges was a challenging part of the method validation study. Although the calculations for the hydrocarbon ranges are also discussed in detail in the SOP, these calculations are also worthy of discussion in this report since comparable calculations are not typically performed using other methodologies. This approach to quantitation should be considered the preferred method of quantitation for real world samples based on the acceptable recoveries of these hydrocarbon ranges in the precision and accuracy study described in Section 7.0.

The original quantification procedure proposed in the QAPP was determined to be inappropriate and was therefore modified. It should be noted that the quantification procedures for instrument calibration and sample quantitation differ slightly and are therefore discussed separately below.

6.1.1 Instrument Calibration

Figures 6-1 outlines the steps for the calculation of response factors for each hydrocarbon range. It is important that these steps be followed in the sequence given in order to obtain accurate results. An example spreadsheet from the calculation of response factors is included as Figure 6-2.

Before any calculations can be performed, the retention times of the hydrocarbon ranges must be established. Retention times of each range are established using marker compounds to denote the beginning and end of each range. Table 6-1 shows the beginning and ending marker for each hydrocarbon range.

6.1.1.1 C_5-C_8 Aliphatics Response Factor Calculation

The response factor for C_5-C_8 aliphatics is calculated using total ion integration. All peaks which elute within the appropriate retention time range are summed. It should be noted that prior to summing all peaks over a retention time range, individual peaks which eluted in this range were summed. There was no notable difference between the two summation methods; therefore the easier of the two approaches was utilized. Several aromatic target analytes and all three internal standards elute within this range and must be subtracted from the total area. The total ion integration of MTBE, benzene, toluene, ethylbenzene, and all

internal standards must be subtracted from the original total area. Using the adjusted total area, the response factor is calculated using Equation 6-1.

Equation 6-1: Response Factor for C_5-C_8 Aliphatics

$$RF = [(A_T * C_I)] / [(A_{EI2} * C_T)]$$

where
RF = response factor
A_T = adjusted total ion area count
C_I = amount of internal standard (ng)
A_{EI2} = extracted ion area count of internal standard #2
C_T = summation of the appropriate aliphatic analyte amounts (ng) which elute within this range

6.1.1.2 C_9-C_{12} Aliphatics Response Factor Calculation

The response factor for C_9-C_{12} aliphatics is also calculated using total ion integration. However, not all peaks within the appropriate retention time range are summed due to the overlap with C_9-C_{10} aromatics. Instead, only the total ion integration of the aliphatic hydrocarbon analytes which are known to elute within this range are summed. These include n-nonane, 2,3-dimethylheptane, n-decane, n-undecane, n-dodecane, butylcyclohexane, and hexylcyclohexane. There are two aliphatic analytes in this range which coelute with aromatic analytes and therefore the total areas of these peaks are inclusive of both compounds. The coelutions include 2,3-dimethylheptane/m&p-xylenes and butylcyclohexane/indene. The actual concentrations (C_T) of these peaks used in the equation below include the concentrations of the associated aromatic analytes. Using this total area, the response factor is calculated using Equation 6-2.

Equation 6-2: Response Factor for C_9-C_{12} Aliphatics

$$RF = [(A_T * C_I)] / [(A_{EI3} * C_T)]$$

where
RF = response factor
A_T = adjusted total ion area count
C_I = amount of internal standard (ng)
A_{EI3} = extracted ion area count of internal standard #3
C_T = summation of the appropriate aliphatic analyte amounts (ng) which elute within this range

6.1.1.3 C_9-C_{10} Aromatics Response Factor Calculation

The response factor for C_9-C_{10} aromatics is calculated using extracted ion integration. The use of extracted ions over a retention time range allows for easy segregation of the aliphatic and aromatic compounds which both elute within this range. In order to determine the most appropriate ion or ions to utilize in this quantitation, a search of all substituted C_9 and C_{10} aromatics was performed using the EPA/NIH Mass Spectral Data Base. The search was limited to saturated aromatics due to the higher prevalence of saturated aromatics versus unsaturated aromatics in petroleum products. The results of this search are presented in Table 6-2. Based on the results of this search, extracted ions 120 and 134 were determined to be the most representative of the C_9 and C_{10} aromatics.

Using the extracted ion 120, all peaks which elute within the appropriate retention time range are summed. Using the extracted ion 134, all peaks which elute within the appropriate retention time range are also summed. The area counts obtained using extracted ions 120 and 134 are summed. Using this area, the response factor is calculated using Equation 6-3.

Equation 6-3: Response Factor for C_9-C_{10} Aromatics

$$RF = [(A_T * C_I)] / [(A_{EI3} * C_T)]$$

where
RF = response factor
A_T = summation of area counts using extracted ions 120 and 134
C_I = amount of internal standard (ng)
A_{EI3} = extracted ion area count of internal standard #3
C_T = summation of the appropriate aromatic analyte amounts (ng) which elute within this range

6.1.2 Sample Results Quantitation

The same basic concepts used in the quantitation of response factors also apply for sample results calculations. That is, total ion integration is used for C_5-C_8 aliphatics and C_9-C_{12} aliphatics and extracted ion integration is used for C_9-C_{10} aromatics. Figure 6-3 outlines the steps for the calculation of actual concentrations of the hydrocarbon ranges in samples. It is important that these steps be followed in the sequence given in order to obtain accurate results. An example spreadsheet for the calculation of sample results is included as Figure 6-4.

6.1.2.1 C_5-C_8 Aliphatics Results Calculation

All peaks which elute within the appropriate retention time range are summed. From this sum, the total area of the three internal standards are subtracted. Using the adjusted total area, a preliminary amount (ng) is calculated using Equation 6-4.

Equation 6-4: Hydrocarbon Range Amount (ng)

$$ng = [(A_x * C_{IS})] / [A_{IS} * RF_{avg})]$$

where
A_x = area of appropriate range
C_{IS} = amount of internal standard (ng)
A_{IS} = extracted ion area count of the associated internal standard (same as used in calibration)
RF_{avg} = average response factor for the hydrocarbon range to be measured (determined in calibration)

From the preliminary amount calculated above, the amounts (ng) of MTBE, benzene, toluene, and ethylbenzene must be subtracted. The resulting ng value is then converted to $\mu g/m^3$.

6.1.2.2 C_9-C_{10} Aromatics Results Calculation

It should be noted that the calculation of the C_9-C_{10} aromatics concentration prior to C_9-C_{12} aliphatics concentration is important and purposeful and should therefore be performed in this order. Using the extracted ion 120, all peaks which elute within the appropriate retention time range are summed. Using the extracted ion 134, all peaks which elute within the appropriate retention time range are also summed. The area counts obtained using extracted ions 120 and 134 are summed. Using this area, the amount (ng) is calculated using Equation 6-4. The resulting ng value is then converted to $\mu g/m^3$.

6.1.2.3 C_9-C_{12} Aliphatics Results Calculation

All peaks which elute within the appropriate retention time range are summed. From this sum, the total area of bromofluorobenzene which elutes within this range is subtracted. Using the adjusted total area, a preliminary amount (ng) is calculated using Equation 6-4.

From the preliminary amount calculated above, the amounts (ng) of m&p-xylenes, o-xylene, styrene, naphthalene, 1,2,4-triethylbenzene, and C_9-C_{10} aromatics must be subtracted. The resulting ng value is then converted to $\mu g/m^3$.

Figure 6-1

Calibration of Hydrocarbon Ranges

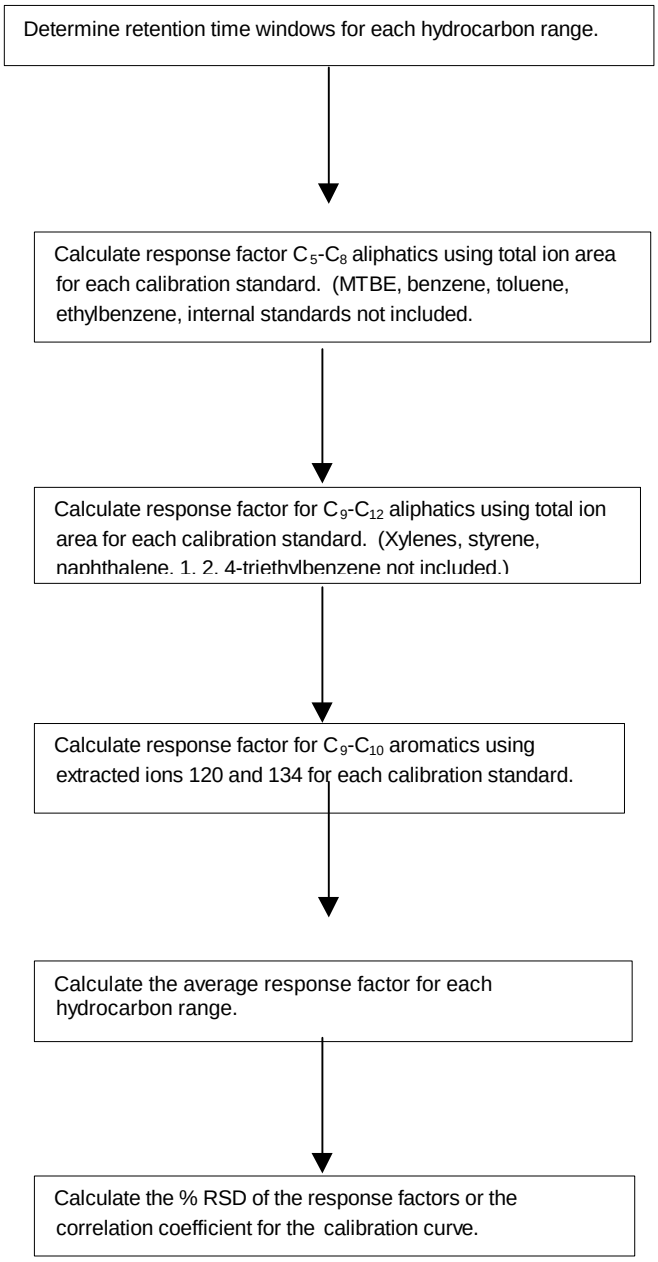


Figure 6-2
Example Calculation of Aliphatic and Aromatic Range Response Factors

I. Retention Time Windows	
C5-C8 Aliphatics	8.55 - 34.6 min
C9-C12 Aliphatics	34.6 - 53.6 min
C9-C10 Aromatics	36.4 - 51.6 min

C5-C8 Aliphatics

File ID	0.28 ng 092901.D
Total Area Range	18390955
MTBE Total Area	0
Benzene Total Area	326311
Toluene Total Area	270028
Ethylbenzene Total Area	231872
IS1 Total Area	2822227
IS2 Total Area	8497263
IS3 Total Area	3282292
Total Area Corrected	2960962
Conc. IS (ng)	10
Area EIC IS 2	2798014
Conc. C5-C8 Aliphatics (ng)	4.76
RF C5-C8 Aliphatics	2.2232
RF C5-C8 Aliphatics	2.2232

C9-C12 Aliphatics

File ID	0.28 ng 092901.D
2,3-Dimethylheptane Total Area	865009
n-Nonane Total Area	249169
n-Decane Total Area	363947
Butylcyclohexane Total Area**	863865
n-Undecane Total Area	435145
n-Dodecane Total Area	0
Hexylcyclohexane Total Area	0
Total Area Sum	2777135
Conc. IS (ng)	10
Area EIC IS 3	1026100
Conc. C9-C12 Aliphatics (ng)	2.52
RF C9-C12 Aliphatics	10.7401
RF C9-C12 Aliphatics	10.7401

+ includes area of m&p-xylenes
** includes area of indene

C9-C10 Aromatics

File ID	0.28 ng 092901.D
Area EIC 120	277647
Area EIC 134	110407
Total Area Sum	388054
Conc. IS (ng)	10
Area EIC IS 3	1026100
Conc. C9-C10 Aromatics (ng)	2.52
RF C9-C10 Aromatics	1.5007
RF C9-C10 Aromatics	1.5007

It should be noted that these data represent one of five calibration standards.

Figure 6-3

Quantitation of Hydrocarbon Ranges

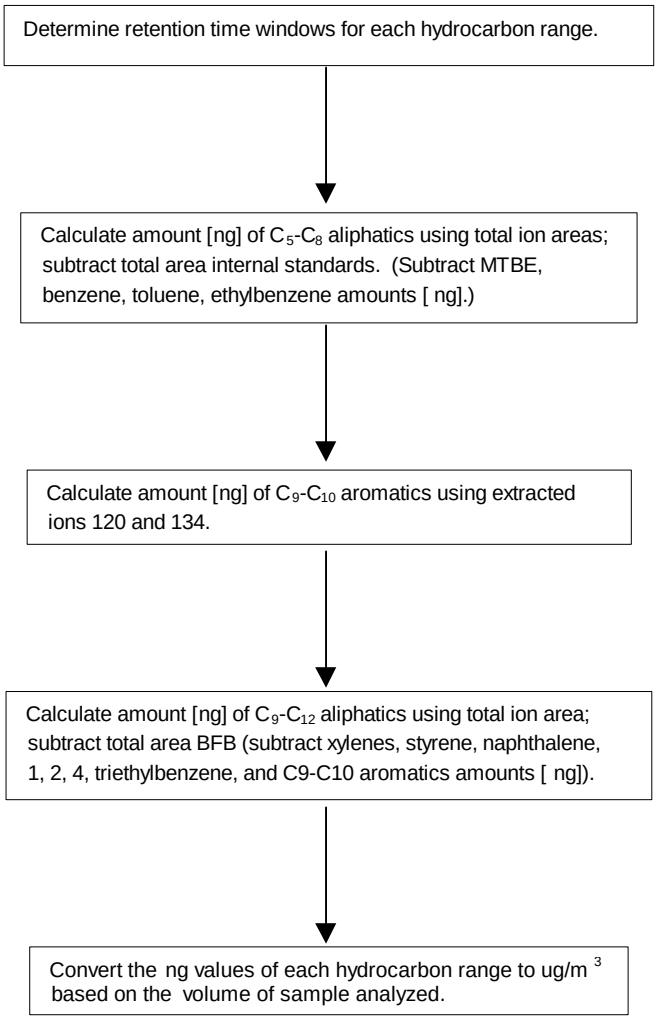


Figure 6-4 SAMPLE CALCULATIONS

I. Retention Time Windows	min
C5-C8 Aliphatics	8.0 - 29.0
C9-C12 Aliphatics	29.0 - 43.6
C9-C10 Aromatics	31.3 - 43.6

C5-C8 Aliphatics

Sample ID	990086-1	
DATE ANALYZED:	06/24/1999	
File ID	062406.d	
Total Area Range	556035289	556035289
IS1 Total Area	3215275	- 3215275
IS2 Total Area	3996316	- 3996316
IS3 Total Area	6961095	6961095
Total Area Corrected	541862603	**541862603 Total Area**
Conc. IS (ng)	10	541862603 x 10 = **2813 ng C5-C8 total hydrocarbons**
Area EIC IS 2	2081477	2081477 0.952
Daily RF C5-C8 Aliphatics	0.9252	
C5-C8 Aliphatics (ng) - prelim	2813.73	**2813 ng total C5-C8 hydrocarbons**
MTBE (ng)	0.3800	- 0.38 ng MTBE
Benzene (ng)	2.2500	- 2.25 ng benzene
Toluene (ng)	0.0000	- 0 ng toluene
Ethylbenzene (ng)	0.8600	- 0.86 ng ethylbenzene
Conc. C5-C8 Aliphatics (ng)	**2810.24**	**2810 C5-C8 ng Aliphatic Hydrocarbons**

C9-C10 Aromatics

Sample ID	990086-1	
DATE ANALYZED:	06/24/1999	
File ID	062406.d	
Area EIC 120	155464	155464
Area EIC 134	64237	64237
Total Area Sum	219701	**219701 Total Area**
Conc. IS (ng)	10	
Area EIC IS 3	1862884	219701 x 10 = **6.24 ng C9-C10 Aromatics**
Daily RF C9-C10 Aromatics	0.1890	1862884 0.1890
Conc. C9-C10 Aromatics (ng)	**6.24**	

C9-C12 Aliphatics

Sample ID	990086-1	
DATE ANALYZED:	01/00/1900	
File ID	062406.d	
C9-C12 Total Area	23389220	23389220
BFB Total Area	15697900	- 15697900
Total Area Sum	7691320	7691320 **Total Area**
Conc. IS (ng)	10	
Area EIC IS 3	1862884	7691320 x 10 = 30.01 Total C9-C12 range hydrocarbons.
Daily RF C9-C12 Aliphatics	1.3759	1862884 1.3759
C9-C12 Aliphatics (ng)-prelim	30.01	**30.01 ng Total C9-C12 Range Hydrocarbons**
m&p-Xylenes (ng)	0.00	- 0 ng m&p xylenes
o-Xylene (ng)	0.00	- 0 ng o-xylene
Styrene (ng)	0.00	- 0 ng sytrene
Naphthalene (ng)	1.98	- 1.98 ng naphthalene
1,2,4-Triethylbenzene (ng)	0.00	- 0 ng 1,2,4-triethyl benzene
C9-C10 Aromatics (ng)	6.24	- 6.24 ng C9-C10 aromatics
Conc. C9-C12 Aliphatics (ng)	**21.79**	**21.79 ng C9-C12 Aliphatic Hydrocarbons**

TABLE 6-1
Hydrocarbon Range Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons	0.1 min before isopentane	0.1 min before 2,3-dimethylheptane
C_9-C_{12} Aliphatic Hydrocarbons	0.1 min before 2,3-dimethylheptane	0.1 min after hexylcyclohexane
C_9-C_{10} Aromatic Hydrocarbons	0.1 min after o-xylene	0.1 min before naphthalene

TABLE 6-2
C_9 and C_{10} Substituted Aromatic Compounds

CAS #	Compound Name	Primary Ion, m/z	Secondary ion, m/z
C_9H_{12} AROMATICS			
95-63-6	1,2,4-Trimethylbenzene	105	120
98-82-8	1-Methylethylbenzene (isopropylbenzene)	105	120,77
103-65-1	Propylbenzene	91	120
108-67-8	1,3,5-Trimethylbenzene	105	120
526-73-8	1,2,3-Trimethylbenzene	105	120
611-14-3	2-Ethyl-1-methylbenzene	105	120
620-14-4	3-Ethyl-1-methylbenzene (3-ethyltoluene)	105	120
622-96-8	4-Ethyl-1-methylbenzene	105	120
$C_{10}H_{14}$ AROMATICS			
95-93-2	1,2,4,5-Tetramethylbenzene	119	134, 120
98-06-6	(1,2-Dimethylethyl)benzene	119	91, 134, 120
99-87-6	1-Methyl-4-(1-methylethyl)benzene	119	134, 120
104-51-8	n-Butylbenzene	91	92, 134
105-05-5	1,4-Diethylbenzene	119	105, 134, 91, 120
135-01-3	1,2-Diethylbenzene	105	134, 119, 91, 120
135-98-8	(1-Methylpropyl)benzene	105	134, 91, 77
141-93-5	1,3-Diethylbenzene	119	105, 134, 120
488-23-3	1,2,3,4-Tetramethylbenzene	119	134, 91, 120
527-53-7	1,2,3,5-Tetramethylbenzene	119	134, 91, 120
527-84-4	1-Methyl-2-(1-methylethyl)benzene	119	134, 91, 120
535-77-3	1-Methyl-3-(1-methylethyl)benzene	119	134, 91, 120
538-93-2	(2-Methylpropyl)benzene	91	92, 134
874-41-9	1-Ethyl-2,4-dimethylbenzene	119	134, 91, 120
933-98-2	1-Ethyl-2,3-dimethylbenzene	119	134, 91, 120
934-74-7	1-Ethyl-3,5-dimethylbenzene	119	134, 91, 120
934-80-5	4-Ethyl-1,2-dimethylbenzene	119	134, 91, 120
1074-17-5	1-Methyl-2-propylbenzene	105	134
1074-43-7	1-Methyl-3-propylbenzene	105	134
1074-55-1	1-Methyl-4-propylbenzene	105	134
1758-88-9	2-Ethyl-1,4-dimethylbenzene	119	134, 91, 120
2870-04-4	2-Ethyl-1,3-dimethylbenzene	119	134, 91, 120

7.0 PRECISION AND ACCURACY STUDY

The precision and accuracy study was performed after the MDL studies were completed and were used for two purposes. One was to evaluate the overall precision and accuracy of the method developed thus far. The quantification procedure developed for the hydrocarbon ranges would be tested using this study. Second, the SUMMA ® canister used in the precision and accuracy study provided an outside verification source for the analytical methodology used thus far from standard preparation through the analytical procedures.

7.1 SUMMAâ Canister Used in Precision and Accuracy Study

The SUMMA® canister used in the precision and accuracy study was provided by the MADEP. This canister contained a known amount of hydrocarbon analytes used in the state Photochemical Assessment Monitoring Stations (PAMS) study at low ppbV concentrations. Not all compounds present in the PAMS study canister were included in the target analyte list utilized in this study (about 30 of the 44 target analytes were present in the PAMS canister). Four replicate analyses of the PAMS canister were performed. A list of compounds included in the PAMS canister and the concentrations of each compound are included in Appendix A.

7.2 Precision and Accuracy Study Results

Table 7-1 demonstrates the precision and accuracy results. The precision results were evaluated by examining the percent relative standard deviation (%RSD) of the four measurements (Equation 7-1). The accuracy was measured by examining the average percent recovery (%R) of the four measurements (Equation 7-2). The %RSDs and %Rs were measured only for the hydrocarbon ranges and for those individual analytes which are present in both the method validation analyte list and in the PAMS study analyte list. However, it should be noted that the hydrocarbon ranges were inclusive of all compounds present in the PAMS study canister in the appropriate ranges and were therefore inclusive of unknown peaks (that is, peaks which were not included in the method validation analyte list).

Equation 7.1: Percent Relative Standard Deviation

$$\%RSD = (SD_{n-1} / Average_x) * 100$$

where
%RSD = percent relative standard deviation
SD = standard deviation (n-1 degrees of freedom)
$Average_x$ = average concentrations measured

Equation 7.2: Percent Recovery

$$\%R = (C_{found} / C_{true}) * 100$$

where
%R = percent recovery
C_{found} = concentration of the analyte or range detected in the sample
C_{true} = true concentration of the analyte in the sample

In order to be considered acceptable, the following goals were set:

- Precision: %RSD: <25
- Accuracy: %R: 70-130

The precision goal was met for all individual target analytes and the hydrocarbon ranges with the exception of C_9-C_{12} aliphatics, which exhibited a %RSD of 31. As with the MDL studies, the variability of this range may be due to the carryover of compounds within this range from analysis to analysis.

The %R of the individual analytes ranged from 58 to 129%. Nineteen of the 30 analytes which were quantitated fell within the accuracy goals of 70-130% with the majority of these analytes from the C_5-C_8 aliphatic range. Although the remaining analytes exhibited lower recoveries, the results were still considered acceptable for the purposes of this program. The lower recoveries of the heavier molecular weight compounds (>C_8) may be due to the fact the PAMS study canister was several months old. The %Rs of the hydrocarbon ranges, C_5-C_8 aliphatics and C_9-C_{10} aromatics, fell within the accuracy goal. The %R of the C_9-C_{12} aliphatics was slightly high at 158%, again most likely due to the carryover effect.

In general, the %Rs and %RSDs of the hydrocarbon ranges provided a good indication that the quantification approach described in Section 6.0 was accurate and appropriate for real world samples.

TABLE 7-1
PRECISION & ACCURACY STUDY
PETROLEUM HYDROCARBONS IN SUMMA CANISTERS
PROCEDURE: FOUR REPLICATE ANALYSES OF PAMS CALIBRATION MIXTURE

Compound	# Carbons	ppbC (true)	ppbV (true)	#1 ppbV found	#2 ppbV found	#3 ppbV found	#4 ppbV found	SD	Avg %R	%RSD
C5-C8 ALIPHATICS										
Isopentane	5	42.73	8.55	8.71	9.47	9.22	9.87	0.4834	109	5.19
Pentane	5	26.04	5.21	6.67	6.36	6.25	7.67	0.6475	129	9.61
2,3-Dimethylbutane	6	50.19	8.37	6.96	7.55	7.46	7.82	0.3584	89	4.81
2-Methylpentane	6	20.54	3.42	2.57	2.94	2.87	3.11	0.2256	84	7.86
3-Methylpentane	6	40.45	6.74	5.27	5.94	5.88	6.10	0.3661	86	6.32
n-Hexane	6	30.42	5.07	4.22	4.93	4.95	5.17	0.4119	95	8.55
Methylcyclopentane	6	25.41	4.24	3.03	3.37	3.37	3.53	0.2096	79	6.30
Cyclohexane	6	40.07	6.68	4.80	5.13	4.94	5.30	0.2170	75	4.31
2-Methylhexane	7	25.39	3.63	1.84	2.45	2.37	2.32	0.2745	62	12.2
2,3-Dimethylpentane	7	51.58	7.37	4.93	5.86	5.20	6.13	0.5584	75	10.1
2,2,4-Trimethylpentane	8	30.34	3.79	2.57	2.84	2.48	2.86	0.1899	71	7.06
n-Heptane	7	25.08	3.58	3.07	2.78	2.54	2.85	0.2172	78	7.72
Methylcyclohexane	7	30.10	4.30	3.35	3.53	3.17	3.64	0.2077	80	6.07
3-Methylheptane	8	25.53	3.19	2.40	2.53	2.25	2.60	0.1542	77	6.31
n-Octane	8	29.89	3.74	2.11	2.18	2.20	2.37	0.1131	59	5.11
C9-C12 ALIPHATICS										
n-Nonane	9	25.12	2.79	1.71	1.81	1.68	1.85	0.0823	63	4.67
n-Decane	10	31.04	3.10	1.96	2.14	1.99	2.20	0.1138	67	5.49
n-Undecane	11	32.61	2.96	1.51	1.96	1.75	1.90	0.2006	60	11.3
n-Dodecane	12	42.99	3.58	1.59	2.28	1.92	2.26	0.3254	56	16.2
C9-C10 AROMATICS										
Isopropylbenzene	9	39.30	4.37	2.98	3.14	2.92	3.22	0.1367	70	4.46
n-Propylbenzene	9	29.57	3.29	2.23	2.43	2.23	2.43	0.1155	71	4.96
1-Methyl-3-ethylbenzene*	9	24.98	2.78	1.79	1.91	1.79	1.91	0.0693	67	3.75
1,3,5-Trimethylbenzene	9	24.62	2.74	1.88	1.95	1.84	2.00	0.0709	70	3.70
1,2,4-Trimethylbenzene	9	39.92	4.44	3.08	3.32	3.03	3.28	0.1451	72	4.56
1,2,3-Trimethylbenzene	9	24.90	2.77	1.51	1.77	1.53	1.63	0.1205	58	7.48
INDIVIDUAL TARGET ANALYTES										
Benzene	6	30.29	5.05	3.84	4.23	3.68	4.25	0.2866	79	7.17
Toluene	7	38.90	5.56	4.23	4.40	3.88	4.47	0.2643	76	6.22
Ethylbenzene	8	24.56	3.07	1.92	2.07	1.90	2.11	0.1064	65	5.32
m&p-Xylenes	8	39.39	4.92	3.04	3.14	2.98	3.17	0.0915	63	2.97
o-Xylene	8	24.75	3.09	1.99	2.08	1.93	2.13	0.0884	66	4.34
Styrene	8	35.54	4.44	2.80	2.99	2.79	3.16	0.1744	66	5.95
TOTAL RANGES			**ug/m3 (true)**	**#1 ug/m3 found**	**#2 ug/m3 found**	**#3 ug/m3 found**	**#4 ug/m3 found**	**SD**	**Avg %R**	**%RSD**
Total C5-C8 Aliphatics			504	425	469	466	486	25.8779	92	5.61
Total C9-C12 Aliphatics			78	90	121	177	104	38.1663	158	31.03
Total C9-C10 Aromatics			176	141	155	140	150	7.2342	83	4.94
							Acceptance Limits:		**70-130**	**25**

ppbV values based on 150 mL injection
* m-ethyltoluene

8.0 ANALYSIS OF REAL-WORLD SAMPLES

The APH method as described in the previous sections of this report has been applied to the analysis of environmental samples collected from a variety of sites. These include indoor air samples from homes and commercial facilities, ambient air samples and soil gas samples. In all instances, there were identified concerns associated with known spills or soil contamination from petroleum hydrocarbon products. The analyses of these samples provided data to characterize the nature of the contamination and potential sources as well as concentrations of specific hydrocarbons and range totals.

Figures 8-1 and 8-2 present the results of analysis of an air sample collected inside a residence where a release of home heating oil had occurred. As noted in the chromatogram (Figure 8-1), the air contains a complex mix of volatile organics in the higher molecular weight/lower volatility range of the method. There is an unresolved complex mixture (UCM) at the right of the chromatogram which is typical for oil samples; this UCM includes many components which cannot be resolved into individual peaks. Individual peaks are noted for the major constituents, which include naphthalene and the methylnaphthalenes and linear alkanes, alkenes, and cycloalkanes in the C_{10}-C_{12} range. The overall pattern of the UCM and individual constituents are characteristic of heating oil; naphthalenes account for approximately 10% by weight of heating oil, the individual C_{10}-C_{12} linear alkanes are also principal constituents. The fingerprint pattern of relative amounts of individual constituents is illustrated by Figure 8-2.

Figures 8-3 and 8-4 present the data for another indoor air sample where concerns for heating fuel contamination had also been raised. Although this air does contain a significant burden of hydrocarbons, the pattern is not indicative of heating oil as the only or even principal source. Light hydrocarbons such as isopentane and pentane are not present at measurable levels in heating fuel. Heating oil constituents, including the naphthalenes and linear alkanes, are present, but the comparatively high concentration of hydrocarbons in the C_5-C_8 range in the air indicates that other, lighter petroleum products are responsible for much of the air burden.

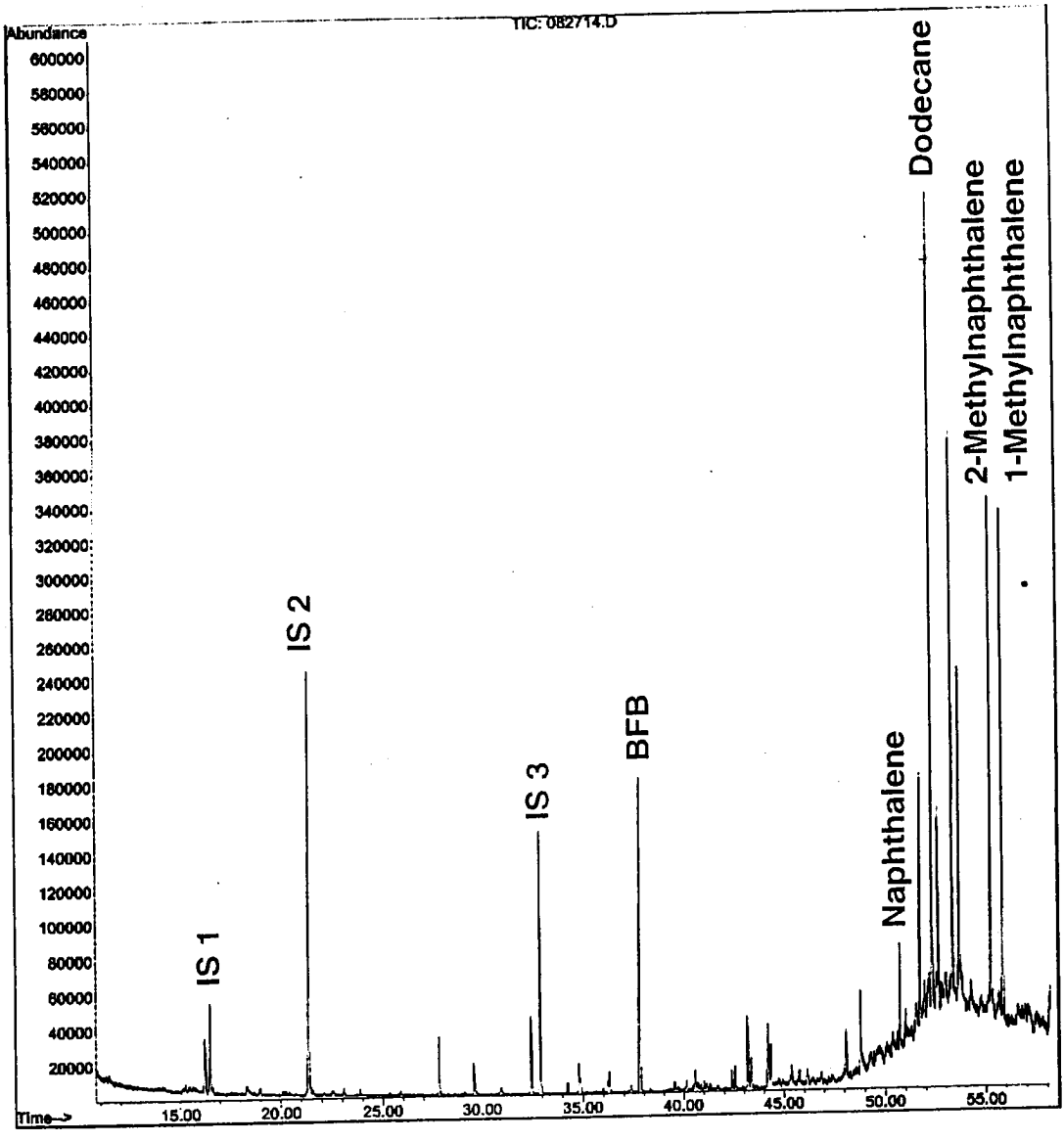
Figures 8-5 and 8-6 present data for the analysis of two different soil gas samples collected at a site where diesel fuel contamination was suspected. The significant levels of lighter hydrocarbons as well as methyl-t-butyl ether (MTBE), a common gasoline additive, indicates that gasoline had been released into the soil either as the primary source or as a thinner for a heavier oil.

Figures 8-7 and 8-8 resulted from the analysis of soil vapor from an area impacted by a kerosene spill. The linear alkanes are principal constituents of kerosene; the individual C_8 - C_{12} n-alkanes account for approximately 17% of the product. This gives kerosene a

fingerprint that is distinctly different from diesel fuel/heating oil or gasoline products and the pattern of air contamination from kerosene sources is accordingly different.

As noted in these illustrations, the APH method provides fingerprint data to complement the measurements of individual target components and totals for ranges. This fingerprint information is potentially useful for source material confirmation. The pattern of constituents in air for most products is not expected to be the same as that for the product as a liquid, but as this method is applied in more cases where source material is definitively known, a better understanding of the opportunities and limitations of the method will be developed.

Indoor Air Impacted by Heating Oil



M99003h.qxd

FIGURE 8-1

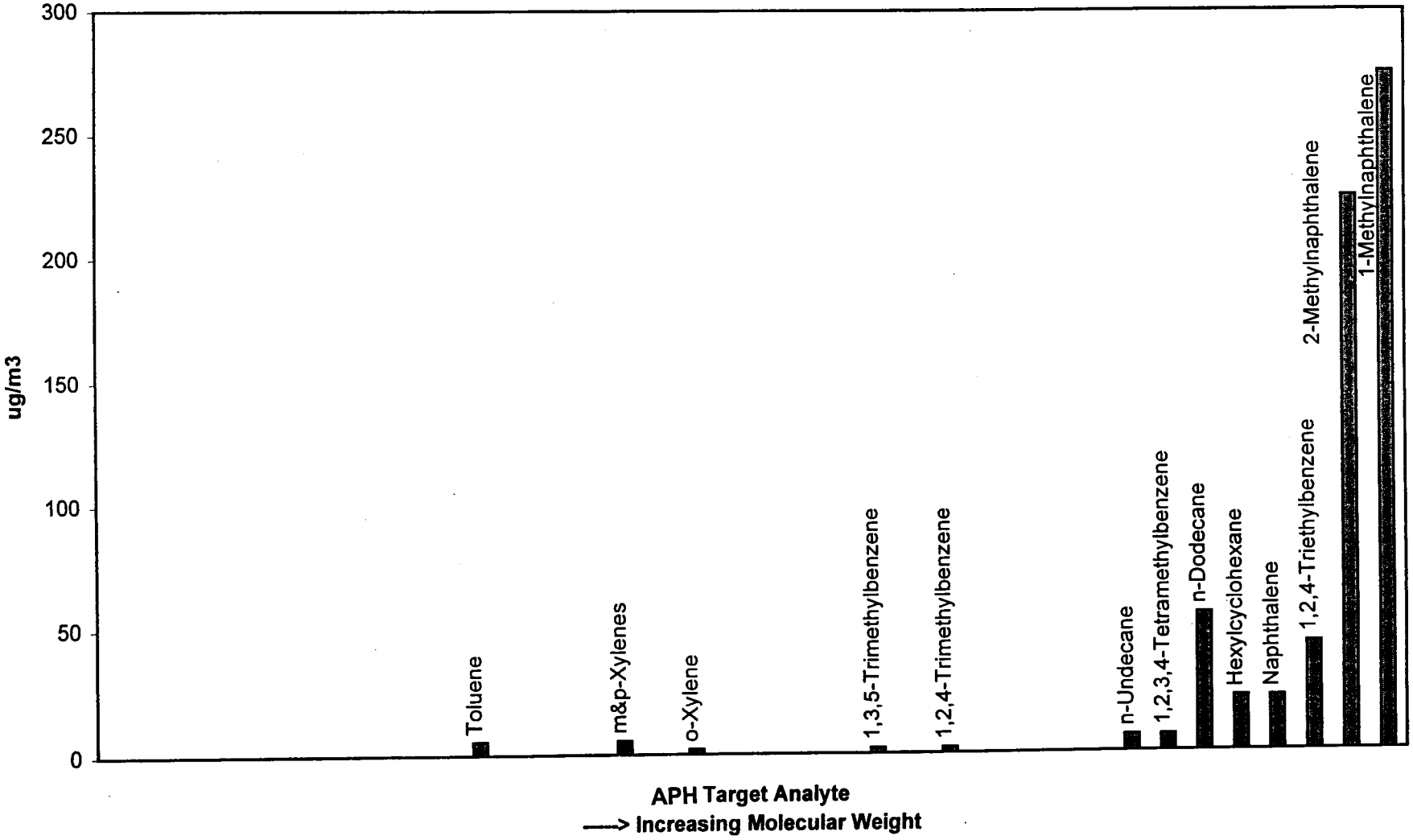
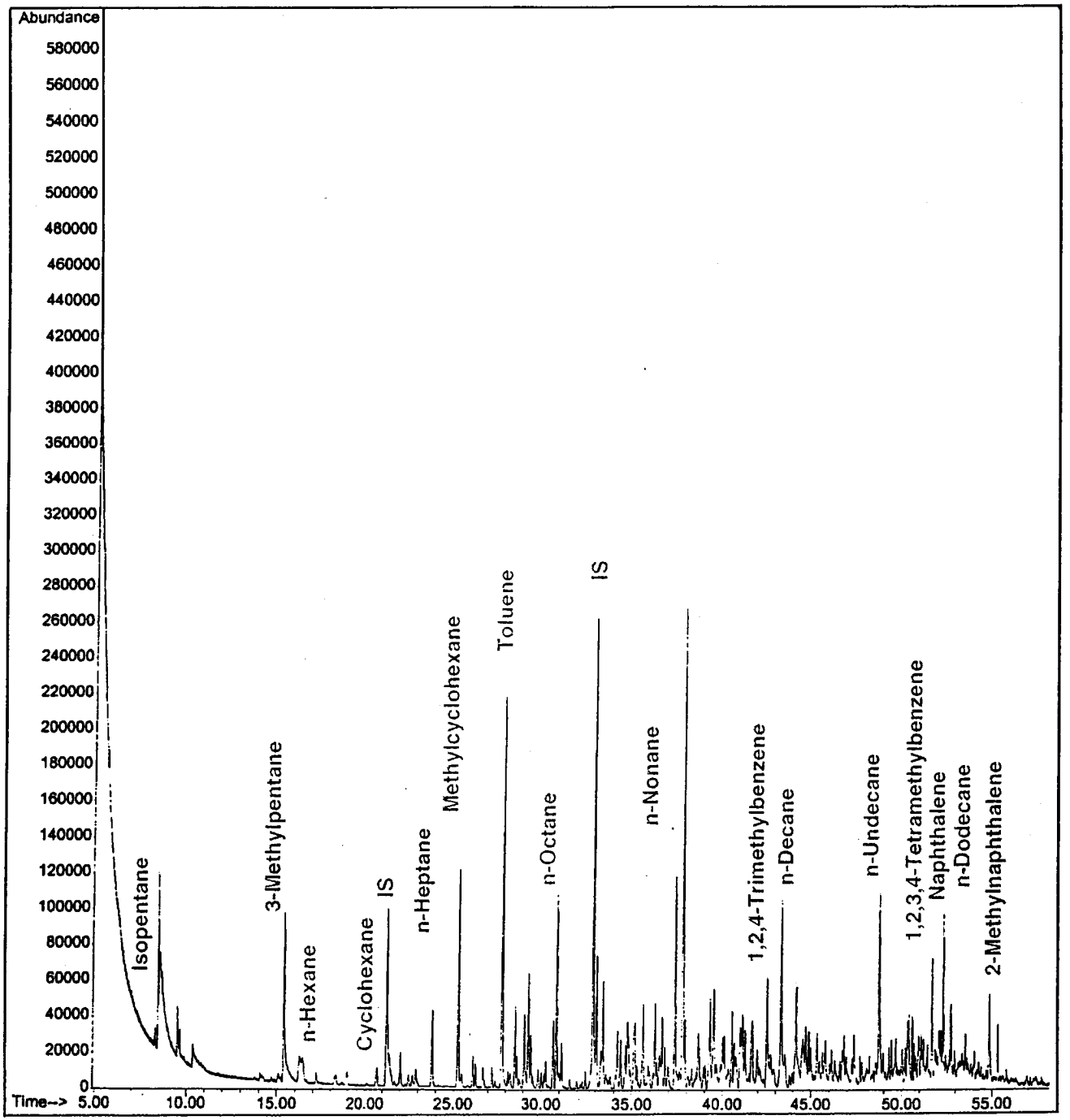

Indoor Air - Residence
Home Heating Oil Spill
300
250
200
150
100
50
0
ug/m3
Toluene
m&p-Xylenes
o-Xylene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
n-Undecane
1,2,3,4-Tetramethylbenzene
n-Dodecane
Hexylcyclohexane
Naphthalene
1,2,4-Triethylbenzene
2-Methylnaphthalene
1-Methylnaphthalene
APH Target Analyte
—> Increasing Molecular Weight

FIGURE 8-2

Indoor Air/Suspected Heating Oil Contamination



M99003h.qxd

FIGURE 8-3

Indoor Air - Residence
Suspected Contamination by Heating Oil

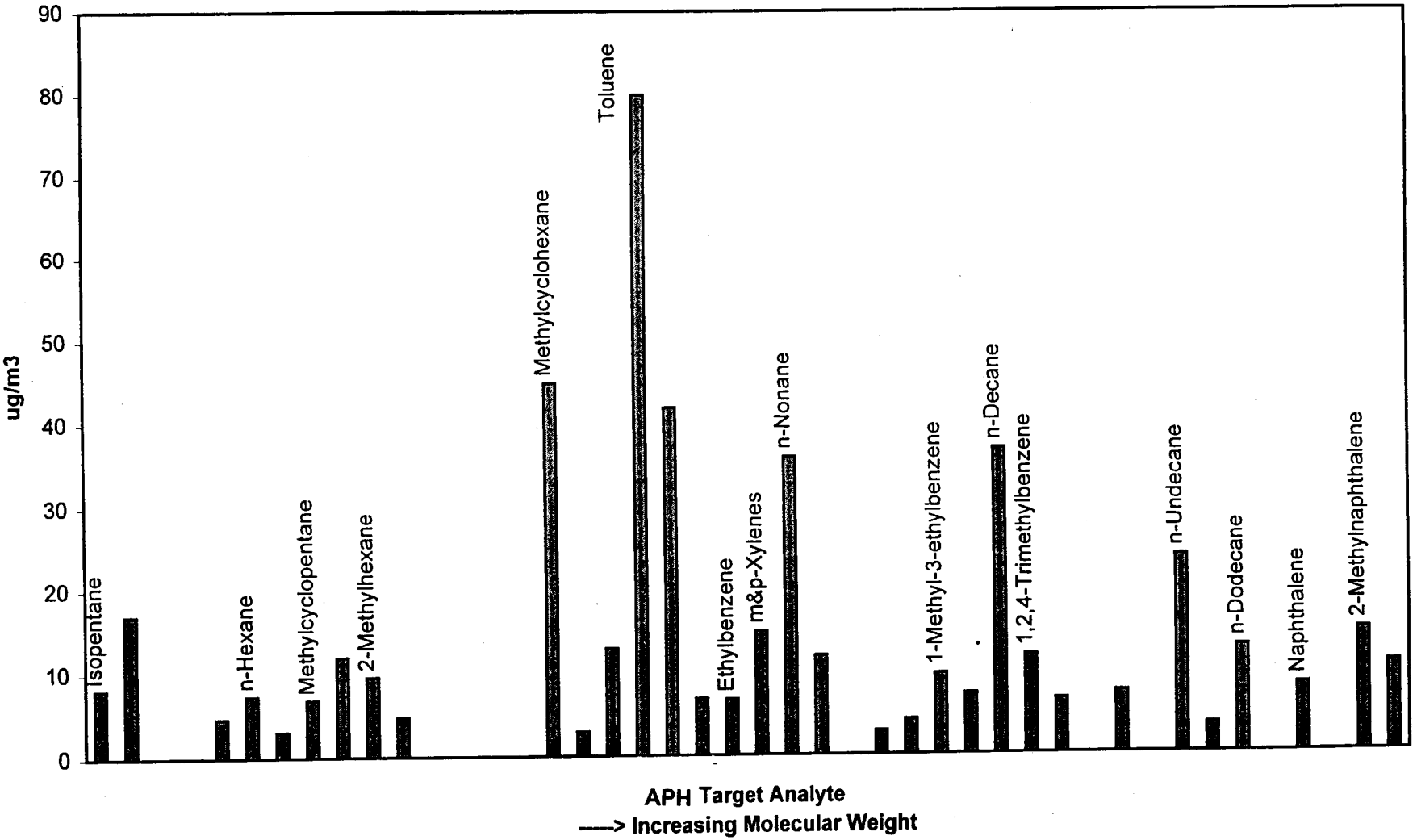
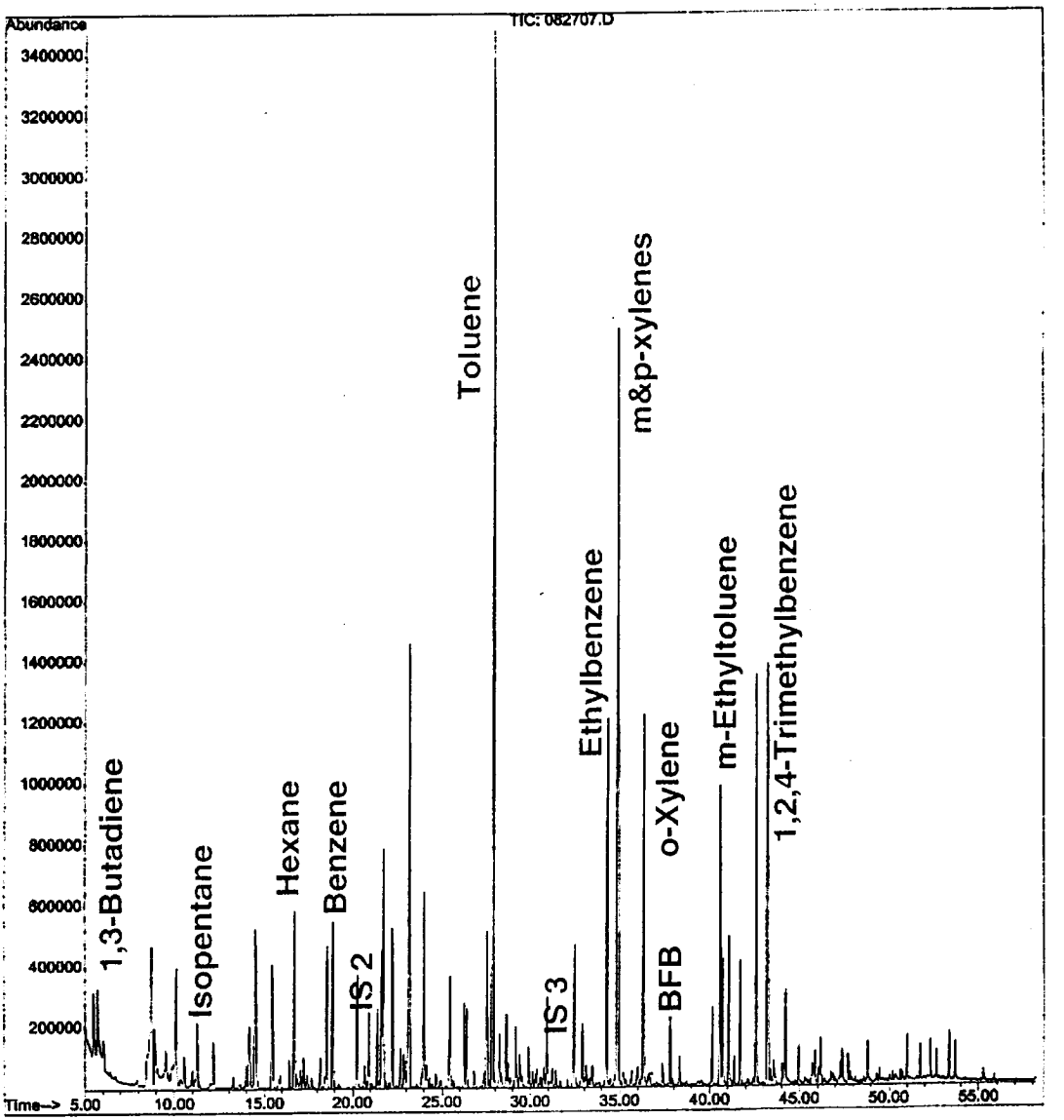


FIGURE 8-4

Soil Gas/Suspected Gasoline Spill



M99003h.qxd

FIGURE 8-5

Soil Vapor Gas
Suspected Gasoline/Diesel Fuel Spill Area

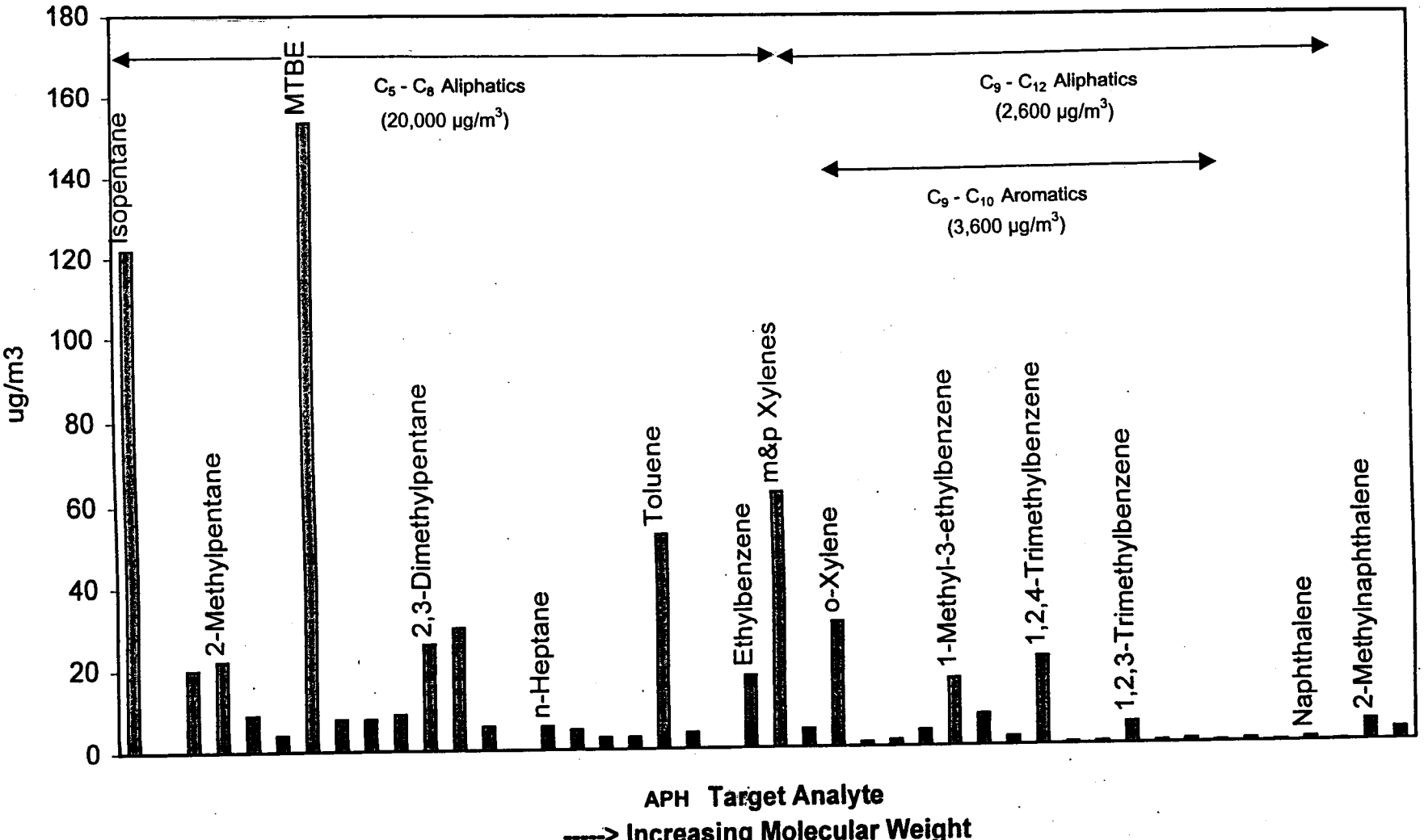
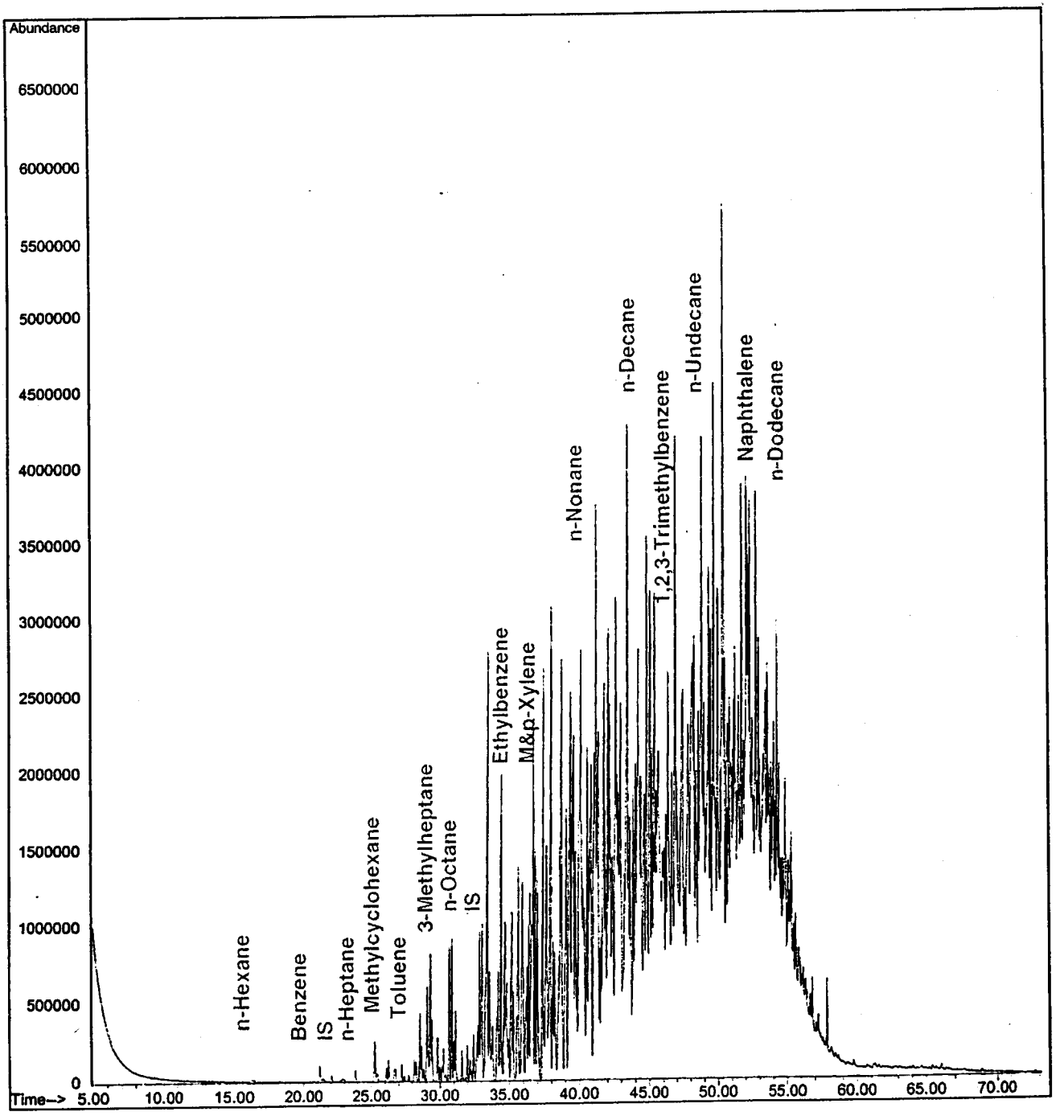


FIGURE 8-6

SVE Treatment Emissions/Kerosene Spill



M99003h.qxd

FIGURE 8-7

SVE Treatment Emissions - Kerosene Spill

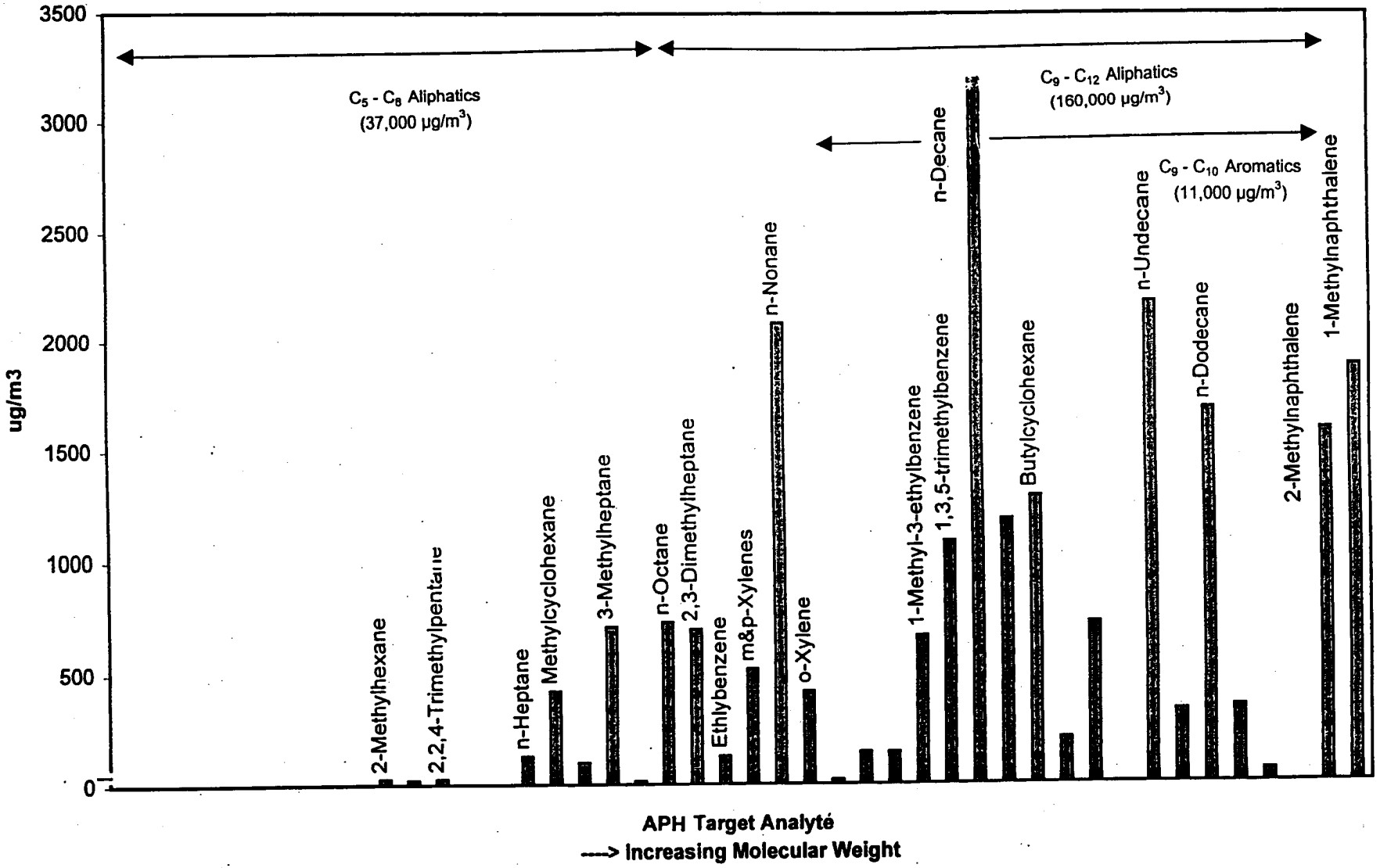


FIGURE 8-8

9.0 CONCLUSIONS

9.1 Advantages of Method

9.1.1 Use of SUMMAâ Canisters

Although not discussed in this report, the use of SUMMA ® canisters allows for a very easy sampling method. Typically, SUMMA ® canisters are collected as time-integrated samples or grab samples. In the collection of time-integrated samples, a pre-calibrated regulator (dependent on the time requirement) is attached to a precleaned, evacuated canister. The canister valve is opened and will fill to 0 psig at the required time. Grab samples are collected by simply opening the canister valve at the required location and allowing it to fill to 0 psig; this process usually takes approximately one minute. Very little field labor or experience is required for either technique.

The use of a SUMMA ® canister allows multiple analyses to be performed on a single sample. That is, the sample contains enough volume to employ screening measures, if necessary. In addition, if dilutions or reanalyses due to quality control nonconformances (e.g., internal standards) are required, sufficient volume exists. Replicate analyses are recommended as a routine QA/QC measure. Other sampling devices such as sorbent tubes cannot be analyzed more than once.

9.1.2 Detection Limits

This method validation study has demonstrated the ability to report sensitive detection limits (0.26 to 1.8 ppbV) using SUMMA ® canisters as the sampling device and GC/MS as the analytical approach. Based on the results of the MDL studies and the precision and accuracy study, this method has demonstrated the ability to yield accurate, precise, reproducible results. In addition, this method is capable of detecting the full range of volatile petroleum hydrocarbons from C_5 to C_{12} as well as a few of the heavier petroleum hydrocarbons, including 2-methylnaphthalene and 1-methylnaphthalene.

9.1.3 Mass Spectrometry

The use of the mass spectrometer allows for unequivocal identifications because of the analyte specific mass spectra. As opposed to GC/FID/PID methods which are typically used for the analyses of petroleum hydrocarbons, GC/MS can discriminate between target analytes and/or nontarget analytes which may coelute. Examples of non-target analytes which may be present in indoor air samples include VOCs which may be derived from solvents and household cleaning products. Since GC/FID/PID techniques rely solely on

retention times for the identification of target compounds, non-petroleum interferences are automatically assumed to be present as part of a hydrocarbon range since there is no other means to disprove that it should not be included. The use of GC/MS eliminates the need to report these non-petroleum interferences as included in the collective ranges of aliphatic and/or aromatic hydrocarbons and therefore eliminates the greater likelihood of over quantitation of these ranges. The possibility of false positives is thus dramatically reduced with GC/MS due to the higher degree of positive identification attainable.

The use of GC/MS also provides a more accurate quantitation of marker compounds (MTBE, BTEX, etc.). These compounds can be used as potential marker compounds in source discrimination. Since petroleum hydrocarbons typically result in the presence of many compounds, GC/MS is the preferred technique for a target analyte analysis. Resolution and confirmed identifications of these compounds would be much more difficult with a PID/FID.

9.2 Disadvantages of Method

9.2.1 Custom-Made Standards

In the proposal for this project, ENSR proposed to possibly utilize the PIANO (paraffin, isoparaffin, aromatics, naphthenes, olefins) analysis standards or the PAMS study canister for calibration standards. However, after the development of the target analyte list for this study, it was realized that neither one of these standards would be appropriate. Since this method is not yet published and routinely utilized by commercial laboratories, calibration standards containing the analytes of interest are not readily available, in liquid or the air matrix. As a result, this method now requires the use of custom-made standards. This practice is not only expensive, but also time-consuming. Once this method is published, it is possible that vendors will eventually supply standards as they have done for the soil and water EPH/VPH methods.

9.2.2 Matrix Interferences

Samples which contain high methane and/or carbon dioxide may have elevated reporting limits. All samples are concentrated prior to analysis in a cryotrap. High levels of moisture or other gases which condense in the trap may limit the volume of air that can be successfully concentrated. As stated earlier, high levels of moisture and other gases can adversely affect the lifetime of the analytical system as well as the chromatography. As a result, dilutions are required and reporting limits are therefore elevated. On the other hand, it is not expected that indoor air samples will typically contain high levels of methane, which is a product of biodegradation, or carbon dioxide, which is a product of combustion sources.

However, it is noted that indoor air problems due to poor ventilation or over crowding can yield high carbon dioxide levels (≥0.5%). These levels are typically not high enough to cause analytical problems. The potential for their effect, however, needs to be acknowledged, especially as the method is applied to non-ambient air samples such as soil gas.

9.2.3 System Carryover

As discussed throughout this report, the carryover of heavier molecular weight compounds (C_{12} and naphthalenes) can and will most likely occur. The lab analyses must include precautions which may include the analysis of more than one blank after standards, the analysis of blanks after samples which are highly contaminated, and occasional humidification of sample lines on the concentrator unit. These compounds have been present in blanks has been at levels just slightly above the reporting limits. The final method should consider raising the required reporting limits for these compounds.

9.2.4 Calibration of Heavier Molecular Weight Compounds

Acceptable calibrations may not always be attainable for some of the heavier molecular weight compounds. The final method may want to consider reducing the acceptance criteria for these compounds (specifically, C_{12} aliphatics and methylnaphthalene isomers).

9.2.5 Quantification of Hydrocarbon Ranges

The quantification procedure for the hydrocarbon ranges is relatively straightforward if followed in the sequence outlined in Section 6.0. However, this procedure is not easy and cannot necessarily be performed at a low cost. At this point, it is doubtful whether GC/MS manufacturers' data systems will be able to automate such a procedure. Presently, the procedure requires a high degree of manual manipulation of data and thus must be performed by an experienced GC/MS analyst. Alternative data reduction procedures which may require less labor are inherently less accurate.

9.3 Future Activities

This method should be considered as one possible means for the analysis of gaseous petroleum hydrocarbons in indoor air. Future activities should include the validation with different sampling methods as well as analytical approaches. Additional sampling devices to be tested might include sorbent tubes and tedlar bags. As mentioned earlier, sorbent tubes have the disadvantage of only being able to be analyzed once. As a result, dilutions and reanalyses cannot be performed. In addition, there is the potential for breakthrough of some of the lighter molecular weight compounds (e.g., 1,3-butadiene, isopentane, pentane)

with sorbent tubes. However, there are advantages to using sorbent tubes as well which include the possibility of lower reporting limits. Also, sorbent tubes do not retain methane or carbon dioxide which, as discussed previously, can potentially interfere with the analysis from SUMMA® canisters. The cost of sampling and analysis with sorbent tubes is expected to be comparable to SUMMA ® canisters. Sampling using sorbent tubes is comparable to SUMMA® canisters in terms of ease.

The use of tedlar bags will most likely yield similar detection limits as SUMMA ® canisters for the C_5–C_8 range compounds and the same interferences (e.g., methane and carbon dioxide) may also be present. The cost of sampling and analysis with tedlar bags is typically less expensive than SUMMA ® canisters. Sampling using tedlar bags is also an easy procedure. There are two main disadvantages to the use of tedlar bags versus SUMMA ® canisters. One is the short holding time required for tedlar bags. Typically, tedlar bags should be analyzed within 24 to 48 hours while SUMMA ® canisters can be held for 14 days from sample collection until analysis. The short holding time can potentially be a problem with commercial laboratories. Second is the adsorption of the heavier molecular weight compounds on the walls of the tedlar bags. This could be alleviated by heating the tedlar bag during the sample loading procedure. However, this process cannot be automated and would require the presence of an analyst during all sample analyses, which may also not always be possible in the commercial laboratories.

Validation could also be performed using FID/PID techniques. However, as mentioned earlier, GC/MS is most likely the preferred technique. In addition, most laboratories currently performing SUMMA® canister analyses typically utilize a GC/MS setup as opposed to FID/PID.

Some other activities which also may be performed include the following:

- Additional testing of real world samples
- Circulation of the final method to commercial laboratories and a round robin program initiated
- Study of background concentrations of petroleum hydrocarbons in indoor air
- Development of fingerprints showing how the components of the different petroleum products enter the air matrix
- Uncertainty introduced into results with the use of simpler data reduction procedures conducted for the hydrocarbon ranges
- Incorporation of the final method into the guidance document currently under preparation at the MADEP

10.0 REFERENCES

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. US EPA 1987. EPA-600/4-84-041. Research Triangle Park, NC.

Hutcheson, M.S., D. Pederson, N.D. Anastas, J. Fitzgerald, and D. Silverman. 1996. Beyond TPH: Health-Based Evaluation of Petroleum Hydrocarbon Exposures, Reg. Tox. Pharm. 24, 85-101.

MADEP. 1997a. Characterizing Risks Posed by Petroleum Contaminated Sites, Implementation of the MADEP VPH/EPH Approach – Public Comment Draft, September 25, 1997.

MADEP. 1997b. 310CMR 40.0000 The Massachusetts Contingency Plan – as updated through October 31, 1997.

MADEP. 1998a. Method for the Determination of Volatile Petroleum Hydrocarbons (VPH) – January 1998.

MADEP. 1998b. Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) – January 1998.

TPHCWG. 1998. Access Database, provided by Wade Weisman, U.S. Air Force Armstrong Lab, Wright Patterson Air Force Base.

APPENDIX A

PAMS Study Canister Components

PAMS Study Canister Components

Compound	ppbC	ppbV
Ethylene	23.97	11.99
Acetylene	49.68	24.84
Ethane	28.37	14.19
Propylene	24.21	8.070
Propane	44.05	14.68
Isobutane	28.03	7.008
Isobutylene	33.23	8.308
n-Butane	44.20	11.05
t-Butene-2	27.22	6.805
c-Butene-2	38.77	9.693
Isopentane	42.73	8.546
Pentene-1	24.93	4.986
n-Pentane	26.04	5.208
Isoprene	39.50	7.900
trans-2-Pentene	35.06	7.012
cis-2-Pentene	24.82	4.964
2,2-Dimethylbutane	40.94	6.823
Cyclopentane	20.46	4.092
2,3-Dimethylbutane	50.19	8.365
2-Methylpentane	20.54	3.423
3-Methylpentane	40.45	6.742
Hexene-1	59.31	9.885
n-Hexane	30.42	5.070
Methylcyclopentane	25.41	4.235
2,4-Dimethylpentane	40.11	5.730
Benzene	30.29	5.048
Cyclohexane	40.07	6.678
2-Methylhexane	25.39	3.627

Compound	ppbC	ppbV
2,3-Dimethylpentane	51.58	7.369
3-Methylhexane	25.18	3.597
2,2,4-Trimethylpentane	30.34	3.793
n-Heptane	25.08	3.583
Methylcyclohexane	30.10	4.300
2,3,4-Trimethylpentane	24.55	3.069
Toluene	38.90	5.557
2-Methylheptane	24.81	3.101
3-Methylheptane	25.53	3.191
n-Octane	29.89	3.736
Ethylbenzene	24.56	3.070
m-& p-Xylene	39.39	4.924
Styrene	35.54	4.443
o-Xylene	24.75	3.094
Nonane	25.12	2.791
Isopropylbenzene	39.30	4.367
n-Propylbenzene	29.57	3.286
m-Ethyltoluene	24.98	2.776
p-Ethyltoluene	39.11	4.346
1,3,5-Trimethylbenzene	24.62	2.736
o-Ethyltoluene	29.84	3.316
1,2,4-Trimethylbenzene	39.92	4.436
n-Decane	31.04	3.104
1,2,3-Trimethylbenzene	24.90	2.767
m-Diethylbenzene	39.99	3.999
p-Diethylbenzene	25.35	2.535
n-Undecane	32.61	2.965
n-Dodecane	42.99	3.583

APPENDIX B

Supporting Analytical Data for MDL Studies, and the Precision and Accuracy Study

(Bound Separately)

Massachusetts Department of Environmental Protection
Boston, Massachusetts

Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air

Addendum
Gasoline Detection Study

ENSR Corporation
June 1999
Document Number 9892-084-000

1.0 EXECUTIVE SUMMARY

This report presents the results of a Method Detection Limit Study conducted on gasoline vapor in air. This study was completed by ENSR for the Massachusetts Department of Environmental Protection to complement the previous work reported in ENSR report 9892-084-000, "Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air", May, 1999. Two types of method detection limit (MDL) studies were included in that report; the first addressed the method sensitivity for the selected target analytes and the second type was designed to determine detection limits for the hydrocarbon ranges using gasoline vapor in air.

Results of the gasoline detection limit study reported in May, 1999 were evaluated and the determination was made that the spiking level, 555 ug/m^3 gasoline in the air, was too high to accurately determine the detection limit for the C5-C8 aliphatic hydrocarbons and the C9-C10 aromatic hydrocarbons. The precision of the replicate analyses was very high, leading to statistical detection limits which were less than 1/10th the concentration of the ranges measured in the samples. The calculated detection limit for the C9-C12 aliphatic hydrocarbons, which are present as minor constituents in gasoline, fell within the guidance range.

The MDL study was therefore repeated with a lower spiking concentration of gasoline. Final detection limits established through these studies are presented below:

Hydrocarbon Range	MDL, ug/m^3
C5-C8 Aliphatic Hydrocarbons	57
C9-C12 Aliphatic Hydrocarbons	15
C9-C10 Aromatic Hydrocarbons	5.3

2.0 METHOD DETECTION LIMIT STUDY 5

MDL Study #5 was conducted following procedures as discussed in Section 5.2 of the referenced report. Briefly, the SUMMA canister was prepared by the addition of the gasoline stock standard (prepared from AccuStandard unleaded gasoline standard) into a precleaned, evacuated 6 liter SUMMA canister. The canister was prepared at a concentration of 333 ng/liter. Water was added to result in a humidified sample and the canister was pressurized to 30 psig.

Analyses were conducted using 300 ml aliquots of the prepared spike with the concentrator and instrument conditions as provided in the method.

The canister was analyzed a total of ten (10) times for the MDL study, rather than the seven times specified in the QAPP for the target analyte MDL study. All analyses were used for the MDL determination.

Data were reduced for the aliphatic and aromatic hydrocarbon ranges in accordance with method requirements as detailed in Section 6 of the referenced report.

3.0 RESULTS

Results for the MDL study are summarized below in Table 3-1, with the results for MDL 4 presented for comparison. Full data are presented in Table 3-2 for all MDL 5 measurements. MDLs were calculated for this study using all 10 analyses conducted and the appropriate t-statistic for 10 data points for each.

MDLs as established with a sample concentration of 333 ug/m^3 are somewhat higher for the C5-C8 aliphatic hydrocarbons and the C9-C10 aromatic hydrocarbons than calculated from the 555 ug/m^3 spikes. These new values do, however, fall within the range of greater than 1/10^{th} the level measured in the spiked sample and are therefore considered acceptable.

Table 3-1: Summary of Detection Limit Studies, Gasoline in Air

Range	MDL, Study 4 Total Spiking Level 555 ug/m3	MDL Study 5 Total Spiking Level 333 ug/m3
C5 – C8 Aliphatic Hydrocarbons	17 ug/m3	57 ug/m3
C9-C12 Hydrocarbons	15 ug/m3	NA
C9-C10 Aromatic Hydrocarbons	3.5 ug/m3	5.3 ug/m3

NA = Not acceptable

Results for the C9-C12 aliphatic hydrocarbons from the earlier MDL study met the guidance that the spiking level for the MDL study should be within 3 to 5 times the anticipated MDL and that the calculated MDL be within 1/10^{th} of the spiking level. Results for the C9-C12 aliphatic hydrocarbons from MDL Study 5 demonstrated a high degree of variability, likely the result of the measured concentration falling below the calculated MDL from Study 4. The first runs may have been affected by instrument carryover, elevating the calculated content of the sample and increasing the variability. However, the levels of individual constituents in the gasoline standard of hydrocarbons in this range are low, and appear to fall below the instrument's ability to reproducibly detect and reliably quantify.

Results for this MDL Study 5 are therefore considered acceptable for the C5-C8 aliphatic hydrocarbons and C9-C10 aromatic hydrocarbons. The MDL for C9-C12 aliphatic hydrocarbons from gasoline are valid from MDL4.

It should be noted that at the concentration used for this study (333 ug/m^3), the average total mass measured by the analysis was within 10% of the total injected into the instrument. At the 555 ug/m3

concentration, the total for the ranges measured averaged 98% of the material present. At the 333 ug/m3 concentration, the recoveries averaged 108%, over a range of 91 to 126%. The higher recoveries were noted for samples potentially affected by minor carryover in the C9-C12 range.

Table 3-2 Method Detection Limit Study # 5 Results

	#1 ug/m3	#2 ug/m3	#3 ug/m3	#4 ug/m3	#5 ug/m3	#6 ug/m3	#7 ug/m3	#8 ug/m3	#9 ug/m3	#10 ug/m3	Standard Deviation	MDL ug/m3
Hydrocarbon Ranges												
C5-C8 Aliphatics*	214	191	234	238	189	213	204	177	225	195	20	57
C9-C12 Aliphatics**	81	36	37	29	1.6	18	24	3.5	8.1	5.2	24	67
C9-C10 Aromatics	22	18	23	17	20	23	21	22	21	21	1.9	5.3
Target Analytes												
MTBE	60	59	64	61	60	62	64	59	63	64		
Benzene	1.0	0.8	3.0	2.5	1.6	1.7	1.7	0.0	1.6	1.5		
Toluene	13	12	17	16	12	13	12	12	12	13		
Ethylbenzene	4.7	4.9	4.9	4.9	4.5	4.7	4.5	4.7	4.5	4.7		
m&p-Xylenes (ng)	17.5	18.5	18.5	18.2	16.9	18.0	17.3	17.9	17.5	17.8		
o-Xylene (ng)	6.0	5.9	6.6	5.7	5.9	6.4	6.1	6.1	6.0	6.1		
Styrene (ng)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Naphthalene (ng)	1.9	1.9	1.7	1.8	1.4	1.4	1.4	1.3	1.3	1.4		
Total ug/m3 measured	421	348	409	394	312	361	356	304	361	329		
Total ug/m3 spiked	333	333	333	333	333	333	333	333	333	333		Average
Percent recovery	126%	105%	123%	118%	94%	108%	107%	91%	108%	99%		108%

*C5-C8 Aliphatics exclude concentrations of target analytes and internal standards eluting in the range

**C9-C12 Aliphatics exclude concentrations of target analytes, internal standards and C9-C10 aromatics eluting in the range.