NONHALOGENATED ORGANICS USING GC/FID

1.0 SCOPE AND APPLICATION

1.1 Method 8015 is used to determine the concentration of various nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography. The following compounds can be determined quantitatively by this method:

Compound Name	CAS No.[a]	Appropriate Technique: Purge-and-Trap	Direct Injection	Solvent Extraction
Acetone	67-64-1	pp	b,d	I
Acetonitrile	75-05-8	pp	b,d	I
Acrolein	107-02-8	pp	b,d	I
Acrylonitrile	107-13-1	pp	b,d	I
Allyl alcohol	107-18-6	ht	b,d	I
1-Butanol (n-Butyl alcohol)	71-36-3	ht	b,d	I
t-Butyl alcohol	75-65-0	pp	b,d	I
2-Chloroacrylonitrile (I.S.)	920-37-6	NA	d	NA
Crotonaldehyde	123-73-9	pp	b,d	I
Diethyl ether	60-29-7	b	b	I
1,4-Dioxane	123-91-1	pp	b,d	I
Ethanol	64-17-5	I	b,d	I
Ethyl acetate	141-78-6	I	b,d	I
Ethylene glycol	107-21-1	I	b	I
Ethylene oxide	75-21-8	I	b,d	I
Hexafluoro-2-propanol (I.S.)	920-66-1	NA	d	NA
Hexafluoro-2-methyl-2-propanol (I.S.)	515-14-6	NA	d	NA
Isobutyl alcohol	78-83-1	pp	b,d	I
Isopropyl alcohol	67-63-0	pp	b,d	I
Methanol	67-56-1	I	b,d	I
Methyl ethyl ketone (MEK)	78-93-3	pp	b,d	I
Methyl isobutyl ketone (MIBK)	108-10-1	pp	b,d	I
N-Nitroso-di-n-butylamine	924-16-3	pp	b,d	b
Paraldehyde	123-63-7	pp	b,d	I
2-Pentanone	107-87-9	pp	b,d	I
2-Picoline	109-06-8	pp	b,d	I
1-Propanol	71-23-8	pp	b,d	I
Propionitrile	107-12-0	ht	d	I

Compound Name	CAS No.[a]	Appropriate Technique		
		Purge-and-Trap	Direct Injection	Solvent Extraction
Pyridine	110-86-1	I	b,d	b
o-Toluidine	95-53-4	I	b,d	b

[a] Chemical Abstract Services Registry Number.
b Adequate response using this technique
d Amenable to concentration by azeotropic distillation (Method 5031)
ht Method analyte only when purged at 80°C
I Inappropriate technique for this analyte
pp Poor purging efficiency, resulting in high EQLs
NA Not available
I.S. Internal standard appropriate for Method 5031

1.2 This method may also be applicable to the analysis of petroleum hydrocarbons, including gasoline range organics (GROs) and diesel range organics (DROs). GROs correspond to the range of alkanes from C_6 to C_{10} and covering a boiling point range of approximately 60°C - 170°C (Reference 6). DROs correspond to the range of alkanes from C_{10} to C_{28} and covering a boiling point range of approximately 170°C - 430°C (Reference 6). The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present. Methods from other sources may be more appropriate for GROs and DROs, since these hydrocarbons are not regulated under RCRA. Consult State and local regulatory authorities for specific requirements.

1.3 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. In addition, if this method is used for the analysis of petroleum hydrocarbons, it is limited to analysts experienced in the interpretation of hydrocarbon data. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 The method can also be used as a screening tool (for both volatile and semivolatile organics) to obtain semiquantitative data for the prevention of sample overload during quantitative analysis on a GC/MS system. This may be accomplished using an automated (Method 5021) headspace method or by direct injection if a solvent extraction method has been utilized for sample preparation. Single point calibration would be acceptable in this situation. Performance data are not provided for screening.

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile and semivolatile organic compounds.

2.1.1 Samples may be introduced into the GC:

- following solvent extraction (Methods 3510, 3520, 3540, 3541, 3545, 3550, or 3560)

- by direct injection (aqueous samples) including the concentration of analytes by azeotropic distillation (Method 5031)

- by purge-and-trap (Methods 5030 or 5035), or

- by vacuum distillation (Method 5032)

2.1.2 Ground or surface water samples must generally be analyzed in conjunction with Methods 5030, 5031, 5032, 3510, 3520, or other appropriate preparatory methods to obtain the necessary quantitation limits. Method 3535 (solid-phase extraction) may also be applicable to the target analytes, but has not yet been validated by EPA in conjunction with Method 8015.

2.1.3 Diesel range organics (DROs) may be prepared by an appropriate solvent extraction method.

2.1.4 Gasoline range organics (GROs) may be introduced into the GC/FID by purge-and-trap, automated headspace, vacuum distillation, or other appropriate technique.

2.2 An appropriate column and temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.3 The method allows the use of packed or capillary columns for the analysis and confirmation of the non-halogenated individual analytes. Columns and conditions listed have been demonstrated to provide separation of those target analytes. Analysts may change these conditions as long as they demonstrate adequate performance.

2.4 Fused silica capillary columns are necessary for the analysis of petroleum hydrocarbons.

3.0 INTERFERENCES

3.1 When analyzing for volatile organics, samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling must serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample syringe or purging device must be rinsed out between samples with an appropriate solvent. Whenever an unusually concentrated sample is encountered, it should be followed by injection of a solvent blank to check for cross contamination.

3.2.1 Clean purging vessels with a detergent solution, rinse with distilled water, and then dry in a 105°C oven between analyses. Clean syringes or autosamplers by flushing all surfaces that contact samples using appropriate solvents.

3.2.2 All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and organic-free reagent water. Drain the glassware and dry in an oven at 130°C for several hours or rinse with methanol and drain. Store dry glassware in a clean environment.

3.3 The flame ionization detector (FID) is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for solvent injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Recommended GC Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in. ID stainless steel or glass column packed with n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.2.3 Column 3 - 30 m x 0.53 mm ID fused silica capillary column bonded with DB-Wax (or equivalent), 1-µm film thickness.

4.1.2.4 Column 4 - 30 m x 0.53 mm ID fused silica capillary column chemically bonded with 5% methyl silicone (DB-5, SPB-5, RTx, or equivalent), 1.5-µm film thickness.

4.1.2.4.1 Capillary columns are needed for petroleum hydrocarbon analyses. Laboratories may use other capillary columns (e.g. 0.25-0.32 mm ID capillary columns) if they document method performance data (e.g. chromatographic resolution and MDLs) if appropriate for the intended use of the data.

4.1.2.4.2 Wide-bore columns should be installed in 1/4-inch injectors, with deactivated liners designed specifically for use with these columns.

4.1.3 Detector - Flame ionization (FID)

4.2 Sample introduction and preparation apparatus

4.2.1 Refer to the 5000 series sample preparation methods for the appropriate apparatus.

4.2.2 Samples may also be introduced into the GC via injection of solvent extracts or direct injection of aqueous samples.

4.3 Syringes

4.3.1 A 5-mL Luer-Lok glass hypodermic and a 5-mL gas-tight syringe with shutoff valve for volatile analytes.

4.3.2 Microsyringes - 10- and 25-µL with a 0.006 in. ID needle (Hamilton 702N or equivalent) and 100-µL.

4.4 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

4.5 Analytical balance - 0 - 160 g capacity, capable of measuring differences of 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used whenever possible. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 Fuels, e.g., gasoline or diesel. Purchase from a commercial source. Low boiling components in fuel evaporate quickly. If available, obtain fuel from the leaking tank on site.

5.5 Alkane standard. A standard containing a homologous series of n-alkanes for establishing retention times (e.g., C_{10}-C_{32} for diesel).

5.6 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. When methanol is a target analyte or when using azeotropic distillation for sample preparation, standards should not be prepared in methanol. Standards must be replaced after 6 months or sooner, if comparison with check standards indicates a problem.

5.7 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.8 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.8 Calibration standards - Calibration standards at a minimum of five different concentrations are prepared in water (purge-and-trap or direct injection) or in methylene chloride (solvent injection) from the secondary dilution of the stock standards. One of the standards should be at or below the concentration equivalent to the appropriate quantitation limit for the project. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Sec. 1.1 may be included). Volatile organic standards are prepared in organic-free reagent water. In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

5.8.1 Do not inject more than 20 µL of methanolic standards into 100 mL of water.

5.8.2 Use a 25-µL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.8.3 Rapidly inject the primary standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.8.4 Mix diluted standards by inverting the flask three times only.

5.8.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.8.6 Never use pipets to dilute or transfer samples or aqueous standards when diluting volatile organic standards.

5.8.7 Aqueous standards used for purge-and-trap analyses (Method 5030) are not stable and should be discarded after 1 hour, unless held in sealed vials with zero headspace. If so stored, they may be held for up to 24 hours. Aqueous standards used for azeotropic distillation (Method 5031) may be stored for up to a month in polytetrafluoroethylene (PTFE)-sealed screw-cap bottles with minimal headspace, at 4°C, and protected from light.

5.9 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The following internal standards are recommended when preparing samples by azeotropic distillation: 2-chloroacrylonitrile, hexafluoro-2-propanol and hexafluoro-2-methyl-2-propanol.

5.10 Surrogate standards - Whenever possible, the analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with one or two surrogate compounds which are not affected by method interferences.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Introduction/preparation methods

Various alternate methods are provided for sample introduction. All internal standards, surrogates, and matrix spikes (when applicable) must be added to samples before introduction into the GC/FID system. Follow the introduction method on when to add standards.

7.1.1 Direct injection - This involves direct syringe injection into the GC injection port.

7.1.1.1 Volatile organics (includes gasoline range organics [GROs])

This may involve injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation for nonpurgeable volatile organics); and injection of an organic solvent waste. Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only permitted for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020) to determine if alcohol is present at > 24%.

7.1.1.2 Semivolatile organics (includes diesel range organics [DROs])

This may involve syringe injection of extracts of aqueous samples prepared by Methods 3510 or 3520 or extracts of soil/solids prepared by Methods 3540, 3541, 3545, 3550 or 3560.

WARNING: Ultrasonic extraction (Method 3550) is not as rigorous a method as the other extraction methods for soil/solids. This means it is very critical that the method be followed explicitly to achieve extraction efficiency which approaches that of Soxhlet extraction. Consult Method 3550 for information on the critical aspects of this extraction procedure.

7.1.2 Purge and trap - this includes purge and trap for aqueous samples (Method 5030) and purge and trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of solid and oily waste samples by methanol (and other water miscible solvents) with subsequent purge and trap from an aqueous matrix using Method 5030. Normally purge and trap for aqueous samples is performed at ambient temperatures while soil/solid samples utilize a 40°C purge to improve extraction efficiency. Occasionally, there may be a need to perform a heated purge for aqueous samples to lower detection limits; however, a 25-mL sample should provide the sensitivity needed in most situations.

7.1.3 Vacuum distillation - this is a device for the introduction of volatile organics from aqueous, solid or tissue samples (Method 5032) into the GC/FID system.

7.1.4 Automated static headspace - this is a device for the introduction of volatile organics from solid samples (Method 5021) into the GC/FID system.

7.2 Chromatographic conditions (recommended)

7.2.1 Column 1

Carrier gas (Helium) flow rate:	40 mL/min
Temperature program:	
Initial temperature:	45°C, hold for 3 minutes
Program:	45°C to 220°C at 8°C/min
Final temperature:	220°C, hold for 15 minutes.

7.2.2 Column 2

Carrier gas (Helium) flow rate:	40 mL/min
Temperature program:	
Initial temperature:	50°C, hold for 3 minutes
Program:	50°C to 170°C at 6°C/min
Final temperature:	170°C, hold for 4 minutes.

7.2.3 Column 3

Carrier gas (Helium) flow rate:	15 mL/min
Temperature program:	
Initial temperature:	45°C, hold for 4 minutes
Program:	45°C to 220°C at 12°C/min
Final temperature:	220°C, hold for 3 minutes.

7.2.4 Column 4 (DROs)

Carrier gas (Helium) flow rate:	5-7 mL/minute
Makeup gas (Helium) flow rate:	30 mL/min
Injector temperature:	200°C
Detector temperature:	340°C
Temperature program:	
Initial temperature:	45°C, hold 3 minute
Program:	45°C to 275°C at 12°C/min
Final temperature:	275°C, hold 12 min

7.2.5 Column 4 (GROs)

Carrier gas (Helium) flow rate:	5-7 mL/minute
Makeup gas (Helium) flow rate:	30 mL/min
Injector temperature:	200°C
Detector temperature:	340°C
Temperature program:	
Initial temperature:	45°C, hold 1 minute
Program:	45°C to 100°C at 5°C/min
Final temperature:	100°C to 275°C, at 8°C/min
Final hold:	5 min

7.3 Initial calibration

7.3.1 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each sample introduction mode because of the differences in conditions and equipment. Establish chromatographic operating parameters that provide instrument performance equivalent to that documented in this method. Prepare calibration standards using the procedures described above (Sec. 5.8). The external standard technique is described below. Analysts wishing to use the internal standard technique are referred to Method 8000. Recommended internal standards for the non-purgeable volatiles include hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol, and 2-chloroacrylonitrile.

7.3.2 External standard calibration procedure for single component analytes

7.3.2.1 For each analyte and surrogate of interest, prepare calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration at or below the quantitation limit necessary for the project (based on the concentration in the final volume specified in the preparation method, with no dilutions). The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Introduce each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Tabulate peak height or area responses against the mass injected. Calculate the calibration factor (CF) for each single component analyte as described in Method 8000.

7.3.3 External standard calibration procedure for DROs and GROs

The calibration of DROs and GROs is markedly different from that for single component analytes. In particular, the response used for calibration must represent the entire area of the chromatogram within the retention time range for the fuel type (DROs or GROs), including the unresolved complex mixture that lies below the individual peaks. See Sec. 7.7.2 for information on calculating this area.

7.3.3.1 For each fuel type, prepare calibration standards at a minimum of five different concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration at or below the quantitation limit necessary for the project (based on the concentration in the final volume specified in the preparation method, with no dilutions). The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

NOTE: Whenever possible, the calibration should be performed using the specific fuel that is contaminating the site (e.g., a sample of the fuel remaining in the tank suspected of leaking). Where such samples are not available or not known, use recently purchased commercially-available fuel. A qualitative screening injection and GC run may be performed to identify unknown fuels.

7.3.3.2 Introduce each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. Determine the area of the response as described in Sec. 7.7.2. Calculate the calibration factor (CF) for each fuel type as shown below:

$$\text{Calibration Factor} = \frac{\text{Total Area within Retention Time Range}}{\text{Mass injected (in nanograms)}}$$

7.3.4 Calibration linearity

The linearity of the calibration must be assessed. This applies to both the single component analytes and the fuel types.

7.3.4.1 If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

7.3.4.2 If the % RSD is more than 20% over the working range, linearity through the origin cannot be assumed. See Method 8000 for other calibration options that may be employed.

7.4 Retention time windows

Single component target analytes (see Sec. 1.1) are identified on the basis of retention time windows. GROs and DROs are distinguished on the basis of the ranges of retention times for characteristic components in each type of fuel.

7.4.1 Before establishing retention time windows, make sure that the chromatographic system is functioning reliably and that the operating parameters have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Establish the retention time windows for single component target analytes using the procedure described in Sec. 7.0 of Method 8000.

7.4.2 The retention time range for GROs is defined during initial calibration. Two specific gasoline components are used to establish the range, 2-methylpentane and 1,2,4-trimethylbenzene. Use the procedure described in Sec. 7.0 of Method 8000 to establish the retention time windows for these two components. The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

7.4.3 The retention time range for DROs is defined during initial calibration. The range is established from the retention times of the C_{10} and C_{28} alkanes. Use the procedure described in Sec. 7.0 of Method 8000 to establish the retention time windows for these two components. The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

7.5 Calibration verification

7.5.1 The working calibration curve, and retention times must be verified at the beginning of each 12-hour work shift as a minimum requirement. Verification is accomplished by the measurement of one or more calibration standards (normally mid-concentration) that contain all of the target analytes and surrogates when individual target analytes are being analyzed. Verification is accomplished by the measurement of the fuel standard and the hydrocarbon retention time standard when petroleum hydrocarbons are being analyzed. Additional analyses of the verification standard(s) throughout a 12-hour shift are strongly recommended, especially for samples that contain visible concentrations of oily material. See Sec. 7.0 "calibration verification" of Method 8000 for more detailed information.

7.5.2 Calculate the % difference as detailed in Sec. 7.0 of Method 8000. If the response for any analyte is within ±15% of the response obtained during the initial calibration, then the initial calibration is considered still valid, and analyst may continue to use the mean CF or RF values from the initial calibration to quantitate sample results. For analyses employing azeotropic distillation as the sample introduction technique, the % difference may be up to ±20%. If the response for any analyte varies from the predicted response by more

than ±15% (±20% for azeotropic distillation), corrective action must be taken to restore the system or a new calibration curve must be prepared for that compound.

7.5.3 All target analytes and surrogates or n-alkanes in the calibration verification analyses must fall within previously established retention time windows. If the retention time of any analyte does not fall within the ± 3σ window, corrective action must be taken to restore the system or a new calibration curve must be prepared for that compound.

7.5.4 Solvent blanks and any method blanks should be run with calibration verification analyses to confirm that laboratory contamination does not cause false positives.

7.6 Gas chromatographic analysis

7.6.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with calibration verification followed by sample extract analyses. Additional analyses of the verification standard(s) throughout a 12-hour shift are strongly recommended, especially for samples that contain visible concentrations of oily material. A verification standard is also necessary at the end of a set. The sequence ends when the set of samples has been injected or when retention time and/or % difference QC criteria are exceeded.

If the criteria are exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before recalibrating and proceeding with sample analysis. All sample analyses performed using external standard calibration must be bracketed with acceptable data quality analyses (e.g., calibration and retention time criteria). Therefore, all samples must be reanalyzed that fall within the standard that exceeded criteria and the last standard that was acceptable.

7.6.2 Samples are analyzed with the same instrument configuration as is used during calibration. When using Method 5030 for sample introduction, analysts are cautioned that opening a sample vial or drawing an aliquot from a sealed vial (thus creating headspace) will compromise samples analyzed for volatiles. Therefore, it is recommended that analysts prepare two samples for purge-and-trap analysis. The second sample can be stored for 24 hours to ensure that an uncompromised sample is available for analysis or dilution, if the analysis of the first sample is unsuccessful or if results exceed the calibration range of the instrument. Distillates from Method 5031 may be split into two portions and held at 4°C prior to analysis. It is recommended that the distillate be analyzed within 24 hours of distillation. Distillates must be analyzed within 7 days of distillation.

7.6.3 Sample concentrations are calculated by comparing sample response data with the initial calibration of the system (Sec. 7.3). Therefore, if sample response exceeds the limits of the initial calibration range, a dilution of the sample must be analyzed. For volatile organic aqueous samples, the dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use and reanalysis. Extracts should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable as long as calibration limits are not exceeded. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.4 Tentative identification of a single component analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is required on a second column or by GC/MS. Since the flame ionization detector is non-specific, it is highly

recommended that GC/MS confirmation be performed on single component analytes unless historical data are available to support the identification(s).

7.6.5 Second column confirmation is generally not necessary for petroleum hydrocarbon analysis. However, if analytical interferences are indicated, analysis using the second GC column is required. Also, the analyst must ensure that the sample hydrocarbons fall within the retention time range established during the initial calibration.

NOTE: Identification of fuels, especially gasoline, is complicated by their inherent volatility. The early eluting compounds in fuels are obviously the most volatile and the most likely to have weathered unless sampled immediately following a spill. The most highly volatile fraction of gasoline constitutes 50% of the total peak area of a gasoline chromatogram. This fraction is least likely to be present in an environmental sample or present in only very low concentration in relation to the remainder of a gasoline chromatogram.

7.6.6 The performance of the entire analytical system should be checked every 12 hours, using data gathered from analyses of blanks, standards, and replicate samples. Significant peak tailing must be corrected. Tailing problems are generally traceable to active sites on the column, cold spots in a GC, the detector operation, or leaks in the system. See Sec. 7.9 for GC/FID system maintenance. Follow manufacturer's instructions for maintenance of the introduction device.

7.7 Calculations

7.7.1 The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the mean CF or RF from the initial curve.

7.7.2 While both diesel fuel and gasoline contain a large number of compounds that will produce well resolved peaks in a GC/FID chromatogram, both fuels contain many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of these fuels. In addition, although the resolved peaks are important for the identification of the specific fuel type, the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

7.7.2.1 For the analysis of DROs, sum the area of all peaks eluting between C_{10} and C_{28}. This area is generated by projecting a horizontal baseline between the retention times of C_{10} and C_{28}.

7.7.2.2 Because the chromatographic conditions employed for DRO analysis can result in significant column bleed and a resulting rise in the baseline, it is appropriate to perform a subtraction of the column bleed from the area of the DRO chromatogram. In order to accomplish this subtraction, a methylene chloride blank should be analyzed during each 12-hour analytical shift during which samples are analyzed for DROs. The area of this chromatogram is measured in the same fashion as is used for samples (see Sec. 7.7.2.1), by projecting a horizontal baseline across the retention time range for DROs. This area is then subtracted from the area measured for the sample and the difference in areas is used to calculate the DRO concentration, using the equations in Method 8000.

7.7.2.3 For the analysis of GROs, sum the area of all peaks eluting between 2-methylpentane and 1,2,4-trimethyl benzene. This area is used to calculate the GRO concentration, using the equations in Method 8000. Column bleed subtraction is not generally required for GRO analysis.

7.7.3 Refer to Method 8000, Sec. 7.0 for calculation formulae. The formulae cover external and internal standard calibration, aqueous and non-aqueous samples and linear and non-linear calibration curves.

7.8 Screening

7.8.1 Method 8015 with single-point calibration can also be used for GC/FID screening in order to reduce instrument down-time when highly contaminated samples are analyzed using GC/MS (e.g., Methods 8260 and 8270).

7.8.2 The same configuration of introduction device interfaced to the GC/MS may be utilized for the GC/FID or alternative configurations are acceptable.

7.8.3 Establish that the system response and chromatographic retention times are stable. Analyze the high-point GC/MS calibration standard.

7.8.4 Analyze samples or sample extracts. Compare peak heights in the sample chromatograms with the high-point standard to establish that no compound with the same retention time as a target analyte exceeds the calibration range. However, the FID is much less sensitive to halogenated compounds than the GC/MS system, therefore, the above comparison is not an absolute certainty.

7.8.5 It is recommended that the high-point standard should be run at least every 12 hours to confirm the stability of instrument response and chromatographic retention times. However, there is no QC requirement for screening.

7.9 Instrument Maintenance

7.9.1 Injection of sample extracts from waste sites often leaves a high boiling residue in: the injection port area, splitters when used, and the injection port end of the chromatographic column. This residue effects chromatography in many ways (i.e., peak tailing, retention time shifts, analyte degradation, etc.) and, therefore, instrument maintenance is very important. Residue buildup in a splitter may limit flow through one leg and therefore change the split ratios. If this occurs during an analytical run, the quantitative data may be incorrect. Proper cleanup techniques will minimize the problem and instrument QC will indicate when instrument maintenance is required.

7.9.2 Suggested chromatograph maintenance

Corrective measures may require any one or more of the following remedial actions. Also see Sec. 7.0 in Method 8000 for additional guidance on corrective action for capillary columns and the injection port.

7.9.2.1 Splitter connections - For dual columns which are connected using a press-fit Y-shaped glass splitter or a Y-shaped fused-silica connector, clean and deactivate the splitter or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the

columns and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

7.9.2.2 Column rinsing - The column should be rinsed with several column volumes of an appropriate solvent. Both polar and nonpolar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone; methylene chloride is a satisfactory final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to remain flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen passing through the column.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a

potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Specific method performance information for non-purgeable volatiles prepared using the azeotropic microdistillation technique from Method 5031 is included in Tables 1, 3 and 4 for aqueous matrices and in Tables 2 and 5 for solid matrices.

9.2 Specific method performance information is provided for diesel fuel spiked into soil in Tables 6 and 7.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography", J. Amer. Water Works Assoc., 66(12), pp. 739-744 (1974).

2. Bellar, T.A., and J.J. Lichtenberg. "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.

3. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters: Category 11 - Purgeables and Category 12 - Acrolein, Acrylonitrile, and Dichlorodifluoromethane, Report for EPA Contract 68-03-2635.

4. Bruce, M.L., R.P. Lee, and M.W. Stevens. "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environ. Sci. Technol. 1992, 26, 160-163.

5. Tsang, S.F., N. Chau, P.J. Marsden, and K.R. Carter. "Evaluation of the EnSys PETRO RISc kit for TPH", Report for Ensys, Inc., Research Triangle Park, NC, 27709, 1992.

6. "Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils," API Publication Number 4599, American Petroleum Institute, March 1994.

TABLE 1

METHOD DETECTION LIMITS FOR NON-PURGEABLE VOLATILE COMPOUNDS
IN AQUEOUS MATRICES BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Analyte	MDL (µg/L)[a]		
	Reagent Water	Ground Water	TCLP Leachate
Acetone[b]	48	16	63
Acetonitrile	15	6	14
Acrolein	13	15	7
Acrylonitrile	8	9	14
1-Butanol	14	8	7
t-Butyl alcohol	8	7	17
1,4-Dioxane	12	15	16
Ethanol	18	12	13
Ethyl acetate	9	8	16
Ethylene oxide	8	9	10
Isobutyl alcohol	11	8	4
Isopropyl alcohol	18	17	7
Methanol	21	21	22
Methyl ethyl ketone	4	5	9
Methyl isobutyl ketone	4	2	8
2-Pentanone	2	2	7
1-Propanol	--	7	--
Propionitrile	10	6	13
Pyridine	11	9	21

[a] Produced by analysis of 7 aliquots of water spiked at 25 µg/L, using internal standard calibration.

[b] Problematic due to transient laboratory contamination.

TABLE 2

METHOD DETECTION LIMITS FOR NON-PURGEABLE VOLATILE COMPOUNDS IN SOLID MATRICES BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Analyte	MDL (mg/kg) Incinerator Ash	Kaolin
Acrylonitrile	0.42	0.09
1-Butanol	0.23	0.09
t-Butyl alcohol	0.34	0.13
1,4-Dioxane	0.31	0.16
Ethanol	0.47	0.19
Ethyl acetate	0.18	0.07
Isopropyl alcohol	0.40	0.19
Methanol	0.46	0.31
Methyl ethyl ketone	0.27	0.12
Methyl isobutyl ketone	0.12	0.05
2-Pentanone	0.16	0.07
Pyridine	0.20	0.08

The MDLs calculated for this table were produced by the analysis of 7 replicates spiked at 0.50 mg/kg, using internal standard calibration.

TABLE 3

METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILES IN GROUND WATER BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Compound	Low Conc.[a] Average[d] %Rec	%RSD	Medium Conc.[b] Average[d] %Rec	%RSD	High Conc.[c] Average[d] %Rec	%RSD
Acetone[e]	126	17	N/A	--	N/A	--
Acetonitrile	147	5	105	8	92	9
Acrolein	146	13	120	27	80	20
Acrylonitrile	179	7	143	28	94	21
1-Butanol	127	8	86	8	90	9
t-Butyl alcohol	122	7	N/A	--	N/A	--
1,4-Dioxane	124	16	96	10	99	8
Ethanol	152	10	N/A	--	N/A	--
Ethyl Acetate	142	7	135	33	92	25
Ethylene oxide	114	10	N/A	--	N/A	--
Isobutyl alcohol	122	8	87	13	89	13
Isopropyl alcohol	167	13	N/A	--	N/A	--
Methanol	166	14	94	9	95	7
Methyl ethyl ketone	105	6	N/A	--	N/A	--
Methyl isobutyl ketone	66	4	N/A	--	N/A	--
2-Pentanone	94	3	N/A	--	N/A	--
1-Propanol	N/A	--	91	7	91	7
Propionitrile	135	5	102	14	90	14
Pyridine	92	12	N/A	--	N/A	--

[a] 25 µg/L spikes, using internal calibration.
[b] 100 µg/L spikes, using internal calibration.
[c] 750 µg/L spikes, using internal calibration.
[d] Average of 7 replicates
[e] Problematic due to transient laboratory contamination.

N/A Data not available

TABLE 4

METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILES IN TCLP LEACHATE BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

Compound	Low Conc.[a] Average[d] %Rec	%RSD	Medium Conc.[b] Average[d] %Rec	%RSD	High Conc.[c] Average[d] %Rec	%RSD
Acetone[e]	99	91	N/A	--	N/A	--
Acetonitrile	107	17	111	10	95	11
Acrolein	88	10	109	29	87	41
Acrylonitrile	133	13	123	29	103	38
1-Butanol	119	7	89	12	86	8
t-Butyl alcohol	70	31	N/A	--	N/A	--
1,4-Dioxane	103	20	103	16	102	7
Ethanol	122	13	N/A	--	N/A	--
Ethyl Acetate	164	12	119	29	107	41
Ethylene oxide	111	12	N/A	--	N/A	--
Isobutyl alcohol	115	4	86	13	82	13
Isopropyl alcohol	114	8	N/A	--	N/A	--
Methanol	107	10	102	6	N/A	--
Methyl ethyl ketone	87	13	N/A	--	N/A	--
Methyl isobutyl ketone	78	13	N/A	--	N/A	--
2-Pentanone	101	8	N/A	--	N/A	--
1-Propanol	N/A	--	98	10	89	7
Propionitrile	100	16	100	11	90	17
Pyridine	46	59	N/A	--	N/A	--

[a] 25 µg/L spikes, using internal calibration.
[b] 100 µg/L spikes, using internal calibration.
[c] 750 µg/L spikes, using internal calibration.
[d] Average of 7 replicates
[e] Problematic due to transient laboratory contamination.

N/A Data not available

TABLE 5

METHOD PERFORMANCE DATA FOR NON-PURGEABLE VOLATILE COMPOUNDS IN SOLID MATRICES BY AZEOTROPIC MICRODISTILLATION (METHOD 5031)

	Incinerator Ash				Kaolin			
	Low Conc.[a]		High Conc.[b]		Low Conc.[a]		High Conc.[b]	
	Average[c]		Average[c]		Average[c]		Average[c]	
	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD	%Rec	%RSD
Acrylonitrile	50	53	10	31	102	6	12	52
1-Butanol	105	14	61	12	108	5	58	25
t-Butyl alcohol	101	21	60	13	97	9	59	23
1,4-Dioxane	106	19	48	18	105	10	48	25
Ethanol	117	25	52	20	108	11	48	24
Ethyl acetate	62	19	39	12	90	5	41	25
Isopropyl alcohol	119	21	61	15	108	11	58	24
Methanol	55	53	33	28	117	17	37	22
Methyl ethyl ketone	81	21	40	12	91	8	42	20
Methyl isobutyl ketone	68	11	57	14	71	5	55	23
2-Pentanone	79	13	54	10	91	5	54	19
Pyridine	52	24	44	20	50	10	49	31

[a] 0.5 mg/kg spikes, using internal calibration.
[b] 25 mg/kg spikes, using internal calibration.
[c] Average of 7 replicates

TABLE 6

RESULTS FROM ANALYSIS[a] OF LOW AROMATIC DIESEL[b] BY GC/FID
(5 replicates/test)

Spike Concentration	Analysis Results
12.5 ppm	ND
75 ppm	54 ± 7 ppm
105 ppm	90 ± 15 ppm
150 ppm	125 ± 12 ppm
1000 ppm	960 ± 105 ppm

[a] Samples were prepared using 2 g aliquots of sandy loam soil spiked with known amounts of low aromatic diesel. Extractions were accomplished using methylene chloride as a solvent (Method 3550, high concentration option).

[b] Low aromatic diesel is sold in California (Section 2256, CCR). For this study it was purchased at a gas station in San Diego, California.

TABLE 7

RESULTS FROM ANALYSIS[a] OF LOW AROMATIC DIESEL[b] BY GC/FID
(5 replicates/test)

Spike Concentration	Analysis Results
25 ppm	51.2 ± 6.4 ppm
75 ppm	75.9 ± 7.8 ppm
125 ppm	98.9 ± 5.2 ppm
150 ppm	162 ± 10.4 ppm

[a] Samples were prepared using 10 g aliquots of sandy loam soil spiked with known amounts of regular #2 diesel purchased at a gas station in Northern Virginia. Extractions were accomplished using methylene chloride as a solvent (Method 3550).

FIGURE 1

CHROMATOGRAM OF A 300 PPM GASOLINE STANDARD

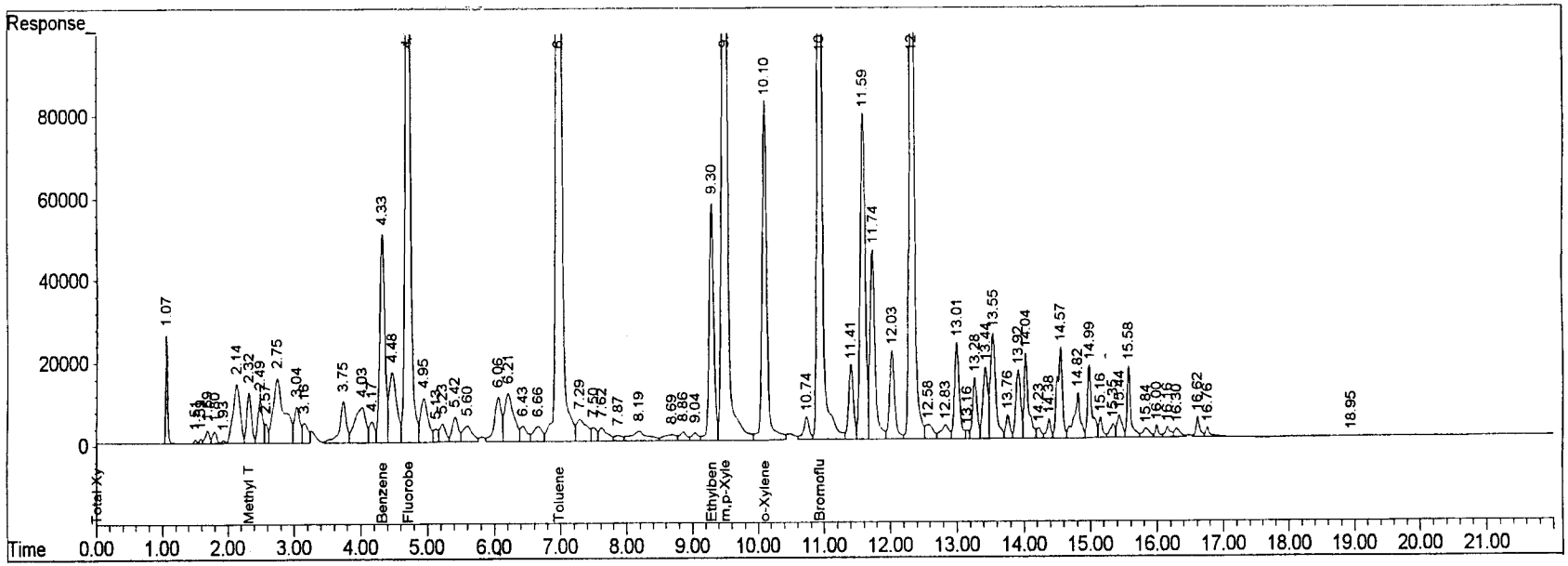


FIGURE 2

CHROMATOGRAM OF A 30 PPM DIESEL STANDARD

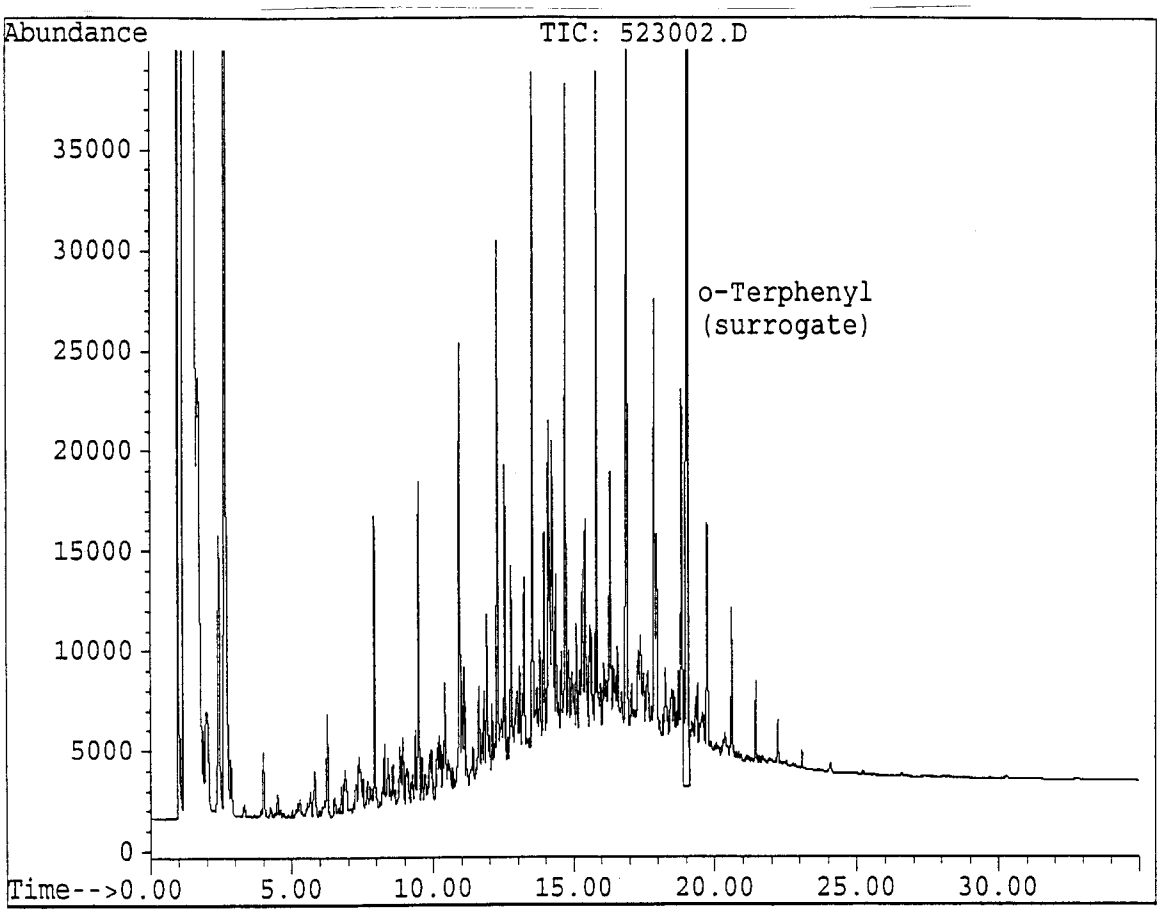


FIGURE 3

CHROMATOGRAM OF A 30 PPM DIESEL STANDARD WITH THE BASELINE PROJECTED BETWEEN C_{10} AND C_{18}

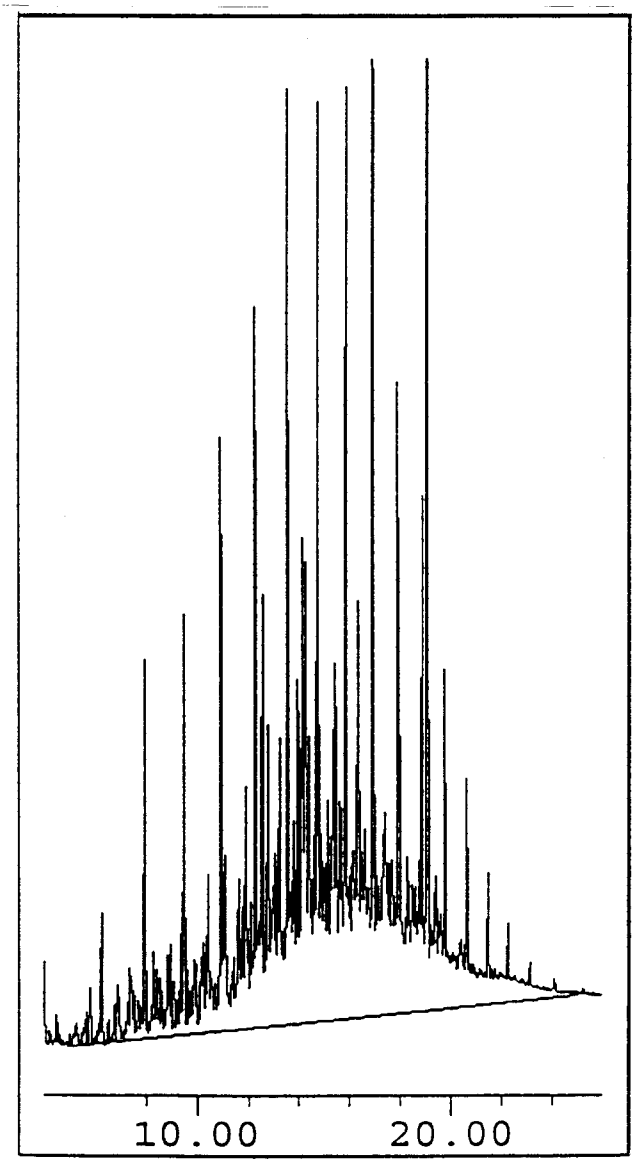
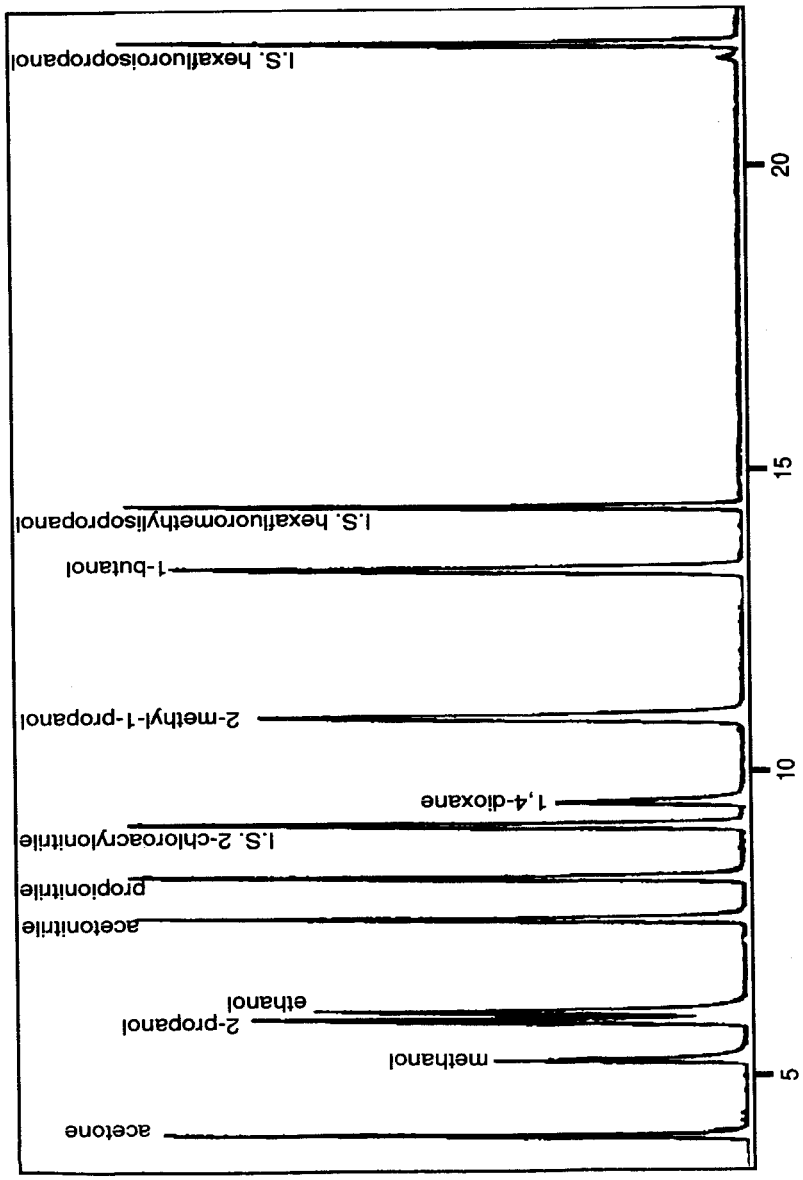


FIGURE 4

CHROMATOGRAM OF SEVERAL NONPURGEABLE VOLATILE COMPOUNDS IN SPIKED REAGENT WATER USING AZEOTROPIC MICRODISTILLATION (METHOD 5031)

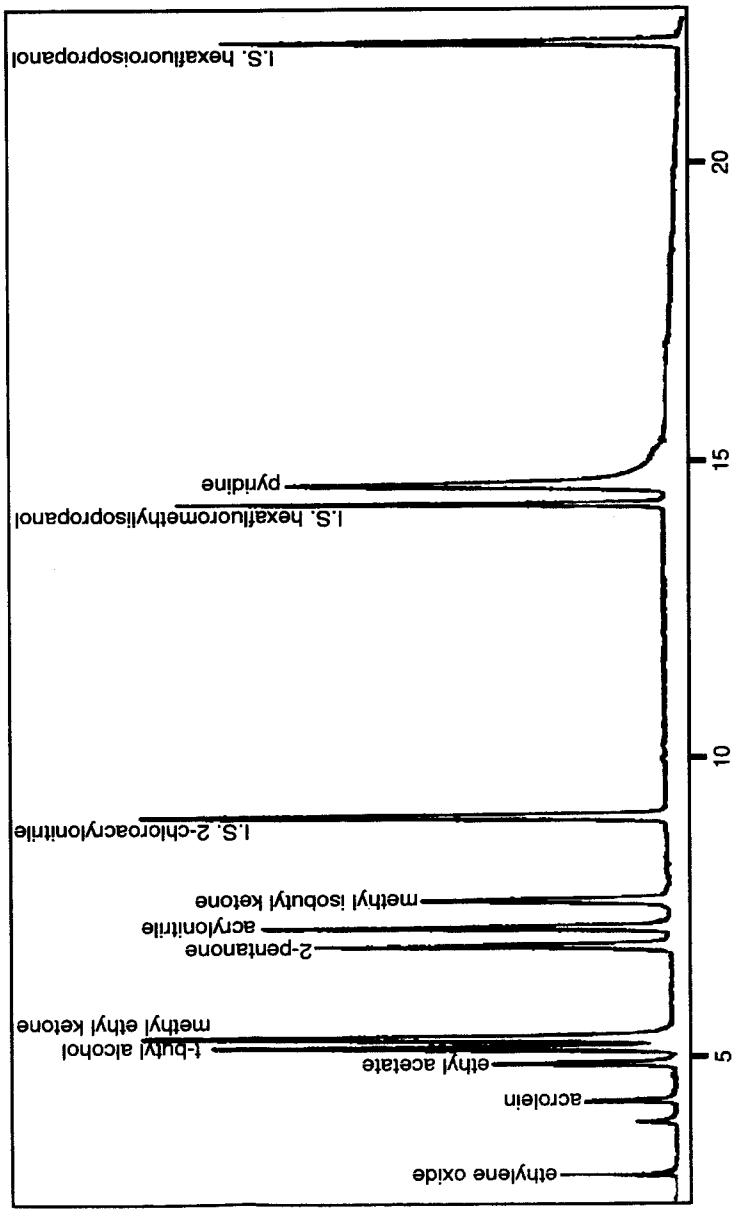


Mix 1: Analytes distilled at 0.25mg/L, Internal Stds. at 2.5 mg/L

Conditions: J&W DB-Wax column with 0.53 ID
Temperature program: 30°C for 2 min.
3°C/min. to 100°C and held for 0 min.
25°C/min. to 200°C and held for 4 min.

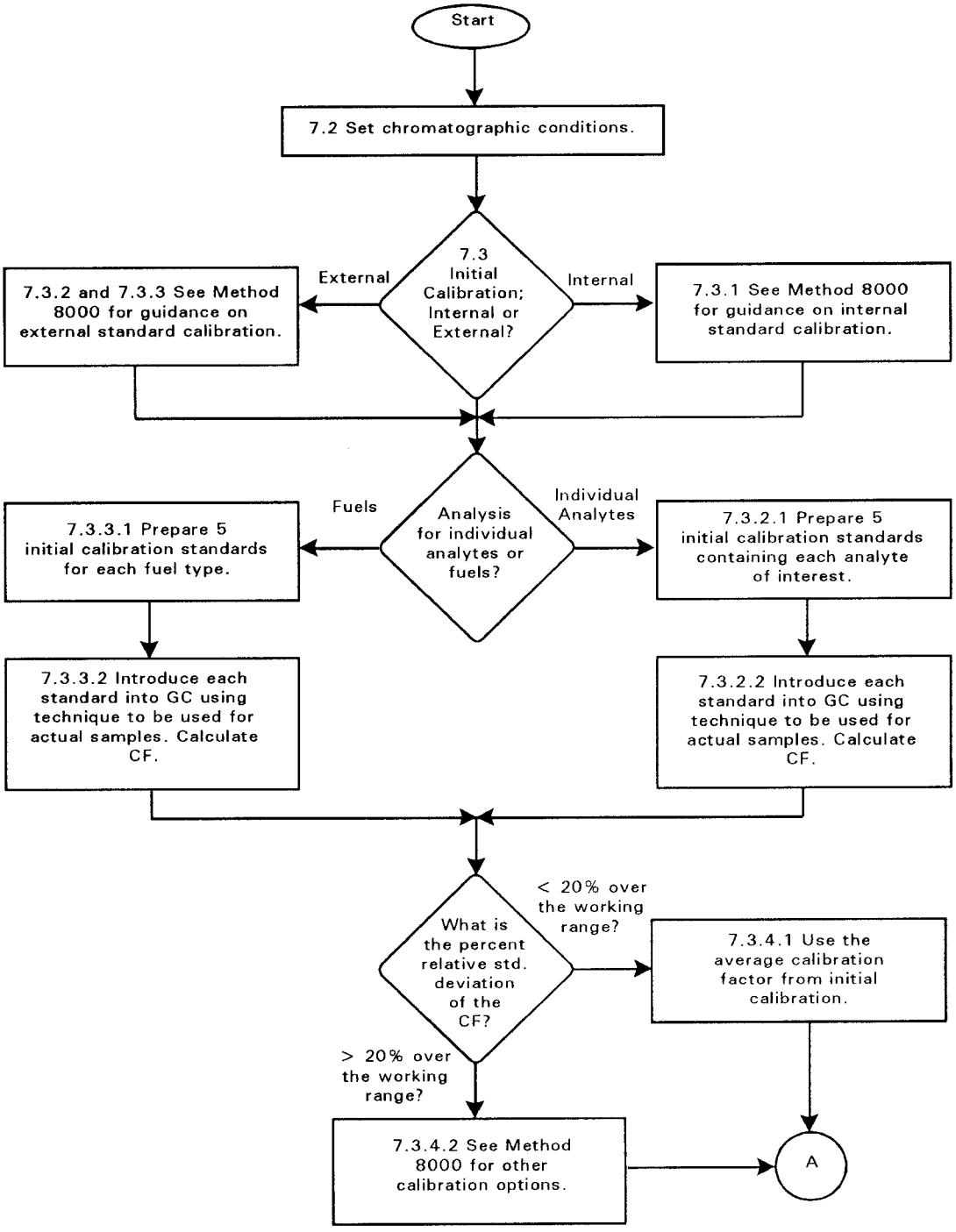
FIGURE 5

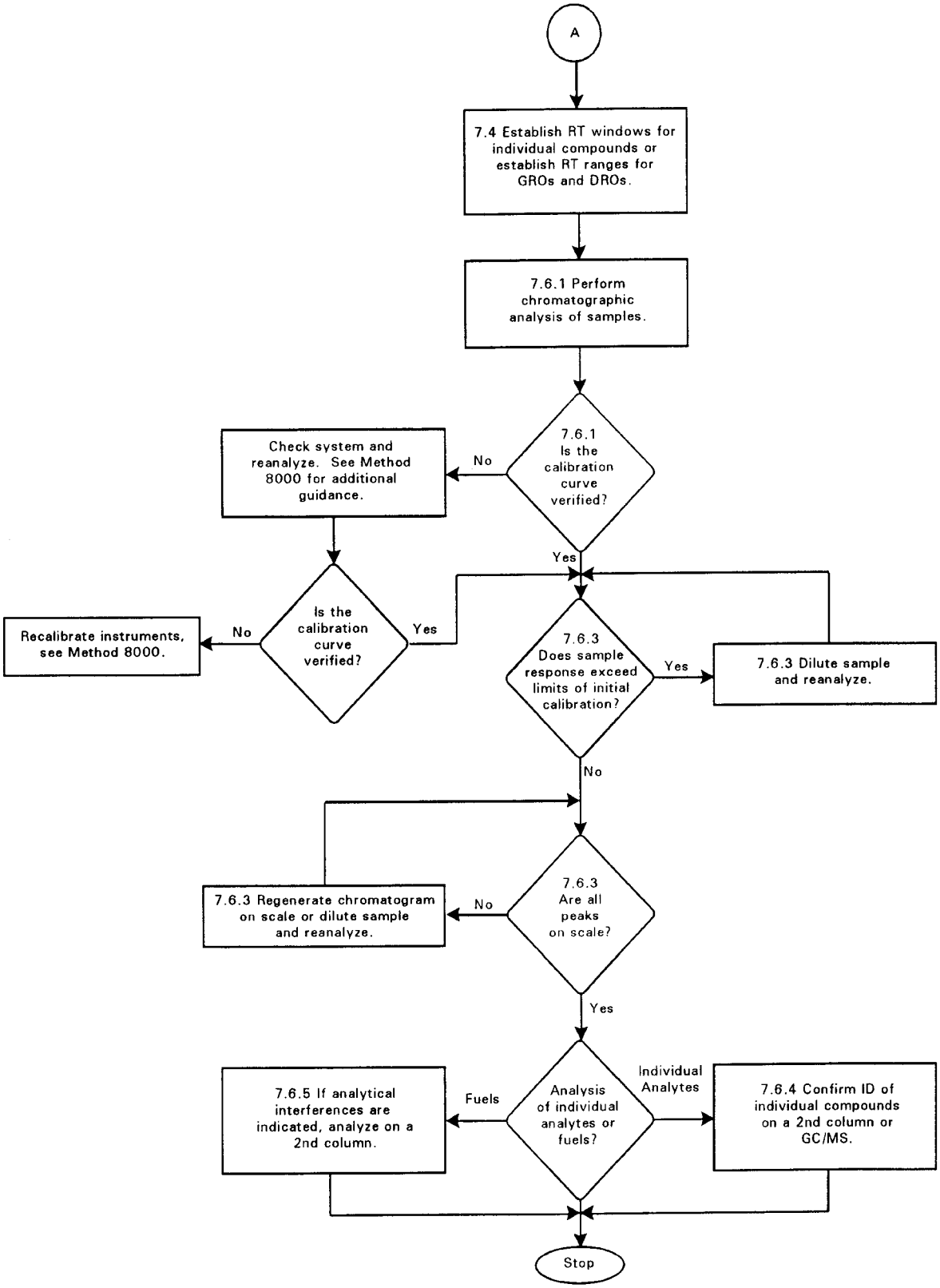
CHROMATOGRAM OF SEVERAL NONPURGEABLE VOLATILE COMPOUNDS IN SPIKED REAGENT WATER USING AZEOTROPIC MICRODISTILLATION (METHOD 5031)



Mix 2: Analytes distilled at 0.25mg/L, Internal Stds. at 2.5 mg/L

Conditions: J&W DB-Wax column with 0.53 ID
Temperature program: 30°C for 2 min.
3°C/min. to 100°C and held for 0 min.
25°C/min. to 200°C and held for 4 min.


Start
7.2 Set chromatographic conditions.
7.3 Initial Calibration; Internal or External?
External
Internal
7.3.2 and 7.3.3 See Method 8000 for guidance on external standard calibration.
7.3.1 See Method 8000 for guidance on internal standard calibration.
Analysis for individual analytes or fuels?
Fuels
Individual Analytes
7.3.3.1 Prepare 5 initial calibration standards for each fuel type.
7.3.2.1 Prepare 5 initial calibration standards containing each analyte of interest.
7.3.3.2 Introduce each standard into GC using technique to be used for actual samples. Calculate CF.
7.3.2.2 Introduce each standard into GC using technique to be used for actual samples. Calculate CF.
What is the percent relative std. deviation of the CF?
< 20% over the working range?
> 20% over the working range?
7.3.4.1 Use the average calibration factor from initial calibration.
7.3.4.2 See Method 8000 for other calibration options.
A


A
7.4 Establish RT windows for individual compounds or establish RT ranges for GROs and DROs.
7.6.1 Perform chromatographic analysis of samples.
7.6.1 Is the calibration curve verified?
No
Check system and reanalyze. See Method 8000 for additional guidance.
Yes
Is the calibration curve verified?
No
Recalibrate instruments, see Method 8000.
Yes
7.6.3 Does sample response exceed limits of initial calibration?
Yes
7.6.3 Dilute sample and reanalyze.
No
7.6.3 Are all peaks on scale?
No
7.6.3 Regenerate chromatogram on scale or dilute sample and reanalyze.
Yes
Analysis of individual analytes or fuels?
Fuels
7.6.5 If analytical interferences are indicated, analyze on a 2nd column.
Individual Analytes
7.6.4 Confirm ID of individual compounds on a 2nd column or GC/MS.
Stop