2022-S-0005

Standard Test Method for Interpretation of Gas Chromatography-Electron Ionization Mass Spectrometry Data for the Identification of Ignitable Liquid Classes in Fire Debris Analysis

Ignitable Liquids, Explosives, and Gunshot Residue Subcommittee
Chemistry: Trace Evidence Scientific Area Committee
Organization of Scientific Area Committees (OSAC) for Forensic Science

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Prepared by
Ignitable Liquids, Explosives, and Gunshot Residue Subcommittee
Version: 1.0 - OSAC Open Comment
October 2021

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Standard Test Method for

Interpretation of Gas Chromatography-Electron Ionization Mass Spectrometry Data for the Identification of Ignitable Liquid Classes in Fire Debris Analysis

1. Scope

1.1. This test method covers the interpretation of data obtained from ignitable liquids encountered in forensic fire debris analysis and includes requirements for the identification of a class of petroleum and non-petroleum based ignitable liquids.

1.2. This test method is suitable for data obtained from liquid samples and extracts obtained from solid fire debris samples, including those that may contain strong contributions from substrate materials or pyrolysis and combustion products.

1.3. This standard is intended for use in conjunction with E1618 and applies to data obtained in accordance with EXXX (IL GC-MS).

1.4. Identification of a class of ignitable liquid is accomplished through a combination of evaluation of chromatographic patterns, analysis of extracted ions representing specific classes of hydrocarbons, and electron ionization (EI) mass spectral identification of compounds.

1.5. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6. This standard is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (e.g., Practice E2917), and demonstrated proficiency to perform forensic casework.

1.7. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1. *ASTM Standards*

E620 Practice for Reporting Opinions of Scientific or Technical Experts

E1386 Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction

E1388 Practice for Sampling of Headspace Vapors from Fire Debris Samples

E1412 Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal

E1413 Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration onto an adsorbent tube

E1618 Classification for Ignitable Liquids Encountered in Forensic Fire Debris Analysis

E2154 Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME)

E2451 Practice for Preserving Ignitable Liquids and Ignitable Liquid Residue Extracts from Fire Debris Samples

E2881 Test Method for Extraction and Derivatization of Vegetable Oils and Fats from Fire Debris and Liquid Samples with Analysis by Gas Chromatography-Mass Spectrometry

E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs

E2997 Test Method for Analysis of Biodiesel Products by Gas Chromatography-Mass Spectrometry

E3189 Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Static Headspace Concentration onto an Adsorbent Tube

E3197 Terminology Relating to Examination of Fire Debris

E3245 Guide for Systematic Approach to the Extraction, Analysis, and Classification of Ignitable Liquids and Ignitable Liquid Residues in Fire Debris Samples

E3255 Practice for Quality Assurance of Forensic Science Service Providers Performing Forensic Chemical Analysis

WK73482 Practice for Reporting Results and Opinions of Ignitable Liquid Analysis

EXXXX Practice for Validation of Methods for Analysis of Ignitable Liquid(s)/Residues

EYYYY Practice for Gas Chromatography Electron Ionization Mass Spectrometry Analysis of Ignitable Liquids

3. Summary of Test Method

3.1. The sample is analyzed using a gas chromatography-electron ionization mass spectrometry in accordance with EYYYY. Interpretation is based on evaluation of total ion chromatograms (TICs), extracted ion profiles (EIPs) characteristic of the chemical compound types found in ignitable liquids, and mass spectra for the identification of the compounds of interest as needed.

3.2. At a minimum, for petroleum-based ignitable liquids, the TIC and EIP for the alkane, alkylbenzene, cycloalkane, indane, and polynuclear aromatic compound types are evaluated by visual pattern matching against suitable reference ignitable liquids.

3.3. Distinguishing between examples of commercial products within any class could sometimes be possible, but such characterization is outside the scope of this method.

4. Terminology

4.1. Definitions

4.1.1. For definitions of terms that can assist in interpreting this standard refer to Classification E1618, Terminology E1732, Terminology E3197, and Practice E3255.

4.2. Definition of Terms Specific to This Standard

4.2.1. *agreement, adj.*—presence and relative ratio(s) of compounds or key diagnostic features in both the reference ignitable liquid and the unknown sample.

4.2.2. *component, n.*—a compound found in an ignitable liquid.

4.2.3. *diagnostic pattern, n.*—pattern representing groups of compounds of interest.

4.2.4. *extracted ion profile* (*EIP*)**,** *n.*—any plot of signal intensity observed at a chosen *m/z* value, or set of values in a series, of mass spectra recorded as a function of time.[1]

4.2.5. *extraneous compounds, n.* – chemicals which are part of the manufacturing process of materials or formed during their thermal decomposition.

4.2.6. *grouping, n.*—an isolated series of chromatographic peaks displayed in a specific pattern or peak ratios comparable to a known reference ignitable liquid.

4.2.7. *identification, n.*—determining or establishing the presence and classification of an ignitable liquid.

4.2.8. *same instrumental chromatographic conditions*—same instrument operating with the same chromatographic parameters in a time period where no instrument maintenance resulting in a retention time shift has occurred.

4.2.9. *suitable reference ignitable liquids*—a known and previously classified ignitable liquid that demonstrates the key diagnostic features which is used for comparison purposes.

4.3. *Abbreviations*

4.3.1. For abbreviations of terms that can assist in interpreting this standard refer to Classification E1618.

5. Significance and Use

5.1. This standard is intended to provide criteria for the evaluation and interpretation of data for the identification of ignitable liquid classes. It is intended to be used in conjunction with approved classification E1618 and analytical processes as outlined in E3245.

5.2. The techniques described here facilitate the identification of ignitable liquid classes by reducing interference from peaks generated from the matrix. When the requirements for identification are not met, due to factors such as overwhelming extraneous peaks, classification is not possible by this method.

Note – It is possible that an ignitable liquid is present in the sample, but it cannot be identified.

5.3. The ignitable liquids described herein are common to the classifications; however each ignitable liquid class contains a range of compositions. It is impractical to provide criteria for every manufactured ignitable liquid. Consider the variability within each ignitable liquid classification during the interpretation process.

5.4. Mixtures of ignitable liquids can be marketed as a single commercial product. This standard cannot differentiate between ignitable liquids that are mixed by a manufacturer for sale or ignitable liquids mixed at the point of use.

6. Apparatus

6.1. *Data System* – Hardware and software capable of performing various data handling functions, including collection and storage of sample data files, generation of extracted ion profiles, performing searches against mass spectral libraries, and qualitative compound analysis.

6.2. *Mass Spectral Libraries* – Software capable of retrieving a specified mass spectrum from a data file and comparing it against a validated library of relevant mass spectra.

6.3. *Data Archival System* – Hardware or software used to save and retain original data files.

6.4. *Reference Ignitable Liquid Data Collection* – Reference files of known ignitable liquids that have been analyzed under the same instrumental method as the questioned samples. This collection should include liquids analyzed as they are marketed and liquids prepared in successive stages of evaporation.[2]

7. General Requirements for Identification

7.1 Identification of the presence of a class of ignitable liquid requires evaluation of the respective KDFs (refer to E1618); comparison with suitable reference ignitable liquids; visual pattern agreement with the reference ignitable liquid and consideration of any dissimilarity.

7.2 Expert human judgement is required at many steps of the interpretation process. Information, such as the matrix and composition of the sample and relevant environmental factors which are required for proper storage should be available. After extraction, analysis, and initial interpretation has occurred additional information such as location, structural composition, or materials known to be in the area can aid in the final interpretation. Transparent documentation should be included when making interpretative judgements. Documentation can include points of similarity and dissimilarity, as well as communication with investigators, in the case record.

7.3 *Comparison with Reference Ignitable Liquids*

7.3.1 At least one reference ignitable liquid, per class identified, used for comparison shall be analyzed at the testing laboratory under the same instrumental chromatographic conditions as the unknown sample.

7.3.1.1 The sole use of externally generated libraries of chromatograms is not sufficient for identification of an ignitable liquid. Such libraries are intended to give guidance for selection of reference ignitable liquids.

7.3.2 Process the data from the reference ignitable liquid using the same instrumental methods as those used for the unknown sample. This includes presentations of the TIC, EIPs and, as appropriate, mass spectral evaluation of major compounds.

7.3.3 For comparison, evaluate the chromatographic patterns or KDFs of interest (TIC and EIPs) at 50 to 100 % of full scale of the most abundant peak in the pattern or KDFs of interest. Presentation of the data using multiple parameters (abundances and time ranges) can assist in the comparison of targeted chromatographic areas. The chromatogram can be integrated to allow for comparison of retention times with reference ignitable liquids.

7.3.4 Chromatographic pattern comparisons rarely give perfect agreement with reference ignitable liquids. A variety of circumstances can obscure or alter patterns and complicate the analysis including skewing towards less volatile compounds for weathered samples, skewing towards more volatile compounds for incompletely recovered samples, selective loss of classes of compounds as a result of microbiological degradation, and contribution to the pattern from the pyrolysis or combustion of materials from the matrix (refer to section 20). Account for such circumstances when evaluating the data.

7.3.5 The relative intragroup ratios of the isomers of C_2- and C_3-alkylbenzenes do not vary markedly among petroleum products. Therefore, when present as part of an ignitable liquid profile, the relative ratios of these compounds shall be comparable to the ratios found in petroleum-based reference ignitable liquids if they are to be identified.

7.3.5.1 C_2- and C_3-alkylbenzenes can be generated as a result of thermal degradation of synthetic materials. In the presence of styrene at a concentration higher than that of toluene or C_2-alkylbenzenes, the finding of toluene or C_2-alkylbenzenes should not be considered significant.

7.3.6 Distortion due to known or suspected matrix contributions could prevent identification. If any features are skewed or not present, document the justification for accepting the identification in the case record.

Note – Unknown samples can show skewed characteristics specific to the extraction method used or weathering of a potential ignitable liquid that are not observed in the reference ignitable liquid.

7.3.7 The absence of any peaks other than those related to the solvent and an internal standard, if used, can allow for a negative findings with no further evaluation.

7.3.8 Document the interpretation by including the sample chromatograms, reference ignitable liquid chromatograms, and any applicable blanks in the case record. Include data presentations used to formulate findings in the case record.

7.3.9 The appendix in ASTM E1618 provides example images of each classification with KDFs labeled.

8. Requirements for the Identification of Gasoline [9]

8.1 *Requirements for the Identification of Weathered and Unweathered Gasoline*

8.1.1 These criteria are limited to gasoline that is no more than 90% weathered. The identification of highly weathered gasoline is found in Section 8.2.

8.1.1.1 Assess all KDFs and document skewing of intergroup peak patterns (refer to E1618 Figure X1.1).

8.1.1.1.1 KDFs in the C_{10}-C_{13} range have more significance than the C_4-C_{10} range when complex matrix contribution is present.

8.1.1.2 Many compounds found in gasoline are commonly produced in the thermal degradation of synthetic materials. Identification is based on the totality of the pattern and the consistency of inter- and intragroup comparisons of KDFs.

8.1.1.2.1 Identification of gasoline based solely on EIP data is possible, but should be done with caution. At least one of the more abundant KDFs (i.e. C_3 alkylbenzenes) should be distinguishable in the TIC.

8.1.1.2.2 Less substituted alkylbenzenes including toluene, C_2- and C_3-alkylbenzenes can be from gasoline, the matrix, or both.

8.1.1.3 Early eluting compounds in gasoline, notably those that elute prior to ethylbenzene, can be lost to evaporation.

8.1.1.4 The total abundance of the alkylbenzene profile is greater than the alkane profile in C_8-C_{12} range.

8.1.1.5 The alkylbenzene (C_4-alkylbenzenes) and indane (C_1- and C_2-indanes) have the intra- and intergroups ratios similar to a comparable suitable gasoline reference. Skewing of these inter- and intragroup ratios can be an indicator that their source is due to matrix contribution rather than gasoline.

8.1.1.6 C_3-alkylbenzene grouping preceding 1,2,4-TMB is present in ratios represented by a reference gasoline in both the TIC and the alkylbenzene EIP.

8.1.1.7 1,2,4-TMB is at a higher abundance than the second peak of the C_3-alkylbenzene grouping in both the TIC and alkylbenzene EIP.

8.1.1.8 Four peak (double doublet) group comprised of C_4-alkylbenzenes is present with comparative peak heights between each doublet (group 1).

8.1.1.9 Three peak group comprised of C_4-alkylbenzenes, two of which are typically unresolved, preceding the approximate retention time of C_{11} is present with escalating peak heights within the group (group 2).

8.1.1.10 Two peak group comprised of C_4-alkylbenzene following the approximate retention time of C_{11} is present with escalating peak heights within the group (group 3).

8.1.1.11 C_5-alkylbenzenes, when visible in the EIP, are in correct proportions to a reference gasoline.

8.1.1.12 Combination of C_2-alkylbenzenes, the C_3-alkyl benzenes, 1, 2, 4-TMB, C_4-alkylbenzenes, C_5-alkylbenzenes, indane, and C_1- and C_2-indanes, are comparable to a reference gasoline in the TIC or EIPs.

8.1.1.13 Alkanes are present as either a petroleum distillate pattern, isoparaffinic product pattern, or a combination of the two.

8.1.1.14 A C_{10}-isoalkane isomer is present in the C_3-alkylbenzene region of the TIC and alkane EIP.

8.2 *Requirements for the Identification of Highly Weathered Gasoline*

8.2.1 These criteria are used to identify gasoline that is over 90% evaporated. Gasoline can be identified up to approximately 99%.

8.2.2 Compare to a highly evaporated gasoline reference for identification.

8.2.2.1 At higher evaporation levels (90-99%), the lighter components up to and including C_3 alkylbenzenes can be lost. C_4 and C_5 alkylbenzenes remain present.

8.2.2.2 The total abundance of the aliphatic, indanes, and the PNAs (when present) become more predominate relative to the alkylbenzenes.

8.2.2.3 Highly weathered gasoline samples which retain the C_4 or C_5 alkylbenzene contribution, indanes, and PNAs, may be further specified as weathered gasoline.

8.2.2.4 Some highly weathered gasoline can appear similar to a distillate with high aromatic content. These samples may be identified as a petroleum product (refer to section 15) or an HPD.

9. Requirements for the Identification of Petroleum Distillates

9.1 *Requirements for the Identification of LPD*

9.1.1 *TIC* – The pattern contains a Gaussian distribution of peaks with a homologous series of spiking normal alkanes or a non-Gaussian distribution containing only one or two *n*-

alkanes having a diagnostic pattern primarily in C_4 to C_9 range (refer to E1618 Figure X1.2).

9.1.2 *Alkanes* – Predominance of alkane and cycloalkane patterns in the diagnostic pattern of interest, excluding known or suspected matrix-produced compounds.

9.1.2.1 The total abundance of the summed alkane EIP attributed to the suspected ignitable liquid pattern greatly exceeds the abundance of the summed alkylbenzene EIP attributed to the suspected ignitable liquid pattern.

9.1.2.2 Isoparaffinic compound groupings are present in the alkane EIP, located between homologous *n*-alkanes, and correspond to peaks and intergroup patterns to a known LPD reference.

9.1.3 *Cycloalkanes* – Cycloalkane EIP contains cycloalkanes within each compound grouping, and there are at least two compound groupings in which corresponding peaks and intergroup patterns compared to a known LPD reference.

9.1.3.1 Methylcyclohexane is present when *n*-C_7 and *n*-C_8 are present [10].

9.1.4 *Alkylbenzenes* – Toluene, C_2, or C_3 alkylbenzenes, when present and exclude known or suspected matrix-produced compounds, are comparable with a known LPD reference.

9.2 *Requirements for the Identification of MPD*

9.2.1 *TIC* – Gaussian distribution of unresolved peaks with predominant spiking *n*-alkanes in the TIC and alkane EIP. Predominance of the diagnostic pattern of interest is in the C_8-C_{13} and excludes known or suspected matrix-produced compounds (refer to E1618 figure X1.3).

9.2.1.1 When the most abundant *n*-alkane peak is approximately less than 1.5 times the major isoalkane/cycloalkane component(s) and is within a comparable carbon range, the product is classified as a naphthenic-paraffinic product rather than a distillate.

9.2.2 *Alkanes* – The total abundance of the summed alkane EIP attributed to the potential ignitable liquid pattern greatly exceeds the abundance of the summed aromatic EIP attributed to the potential ignitable liquid pattern.

9.2.2.1 Isoparaffinic compound groupings are present in the alkane EIP, located between homologous *n*-alkanes, and correspond to peaks and intergroup patterns to a known MPD reference.

9.2.3 *Cycloalkanes* – Cycloalkane EIP contains cycloalkanes within each compound grouping, and there are at least two compound groupings in which corresponding peaks and intergroup patterns compare to a known MPD reference.

9.2.4 *Alkylbenzenes* – Relative content varies. When present and excluding known or suspected matrix-produced compounds, these compounds are comparable to a reference.

9.2.5 *Indanes* – the C_1-indane and C_2-indane groups elute in the range of C_{10}-C_{12}, if present.

9.2.6 *PNAs* – Naphthalene and the C_1-PNA group elute in the range of C_{11}-C_{13}, if present.

9.2.7 Retention times comparable to a known MPD reference or other similar reference ignitable liquid.

9.3 *Requirements for the Identification of HPD*

9.3.1 *TIC* – Gaussian distribution of unresolved peaks with predominant spiking *n*-alkanes in the TIC and alkane EIP. Predominance of the diagnostic pattern of interest occurs after *n*-C_9 and excludes extraneous compounds. These generally contain a minimum of five consecutive normal alkanes and include a subclass of narrow ranged distillates starting above *n*-C_{11} (encompassing fewer than five *n*-alkanes) (refer to E1618 figure X1.4).

9.3.1.1 When the most abundant *n*-alkane peak is approximately less than 1.5 times the major isoalkane/cycloalkane component(s) and is within a comparable carbon range, the product is classified as a naphthenic-paraffinic product rather than a distillate if there are no significant contributions from aromatics, indanes and PNAs.

9.3.2 *Alkanes* – Alkane EIP primarily in the *n*-C_9-*n*-C_{20+} range where the total abundance of the summed alkane EIP attributed to the potential ignitable liquid pattern exceeds the abundance of the summed aromatic EIP attributed to the potential ignitable liquid pattern.

9.3.2.1 Pristane is present following *n*-C_{17} and phytane is present following *n*-C_{18} if the boiling point range includes *n*-C_{17} or *n*-C_{18}.

9.3.2.2 Isoparaffinic compound groupings are present in the alkane EIP, located between homologous *n*-alkanes, and correspond to peaks and intergroup patterns to a known HPD reference.

9.3.3 *Cycloalkanes* – Cycloalkane EIP contains cycloalkanes peak groupings that compare to a known HPD reference ignitable liquid.

9.3.4 *Alkylbenzenes* – When present, they are in the diagnostic pattern associated with their carbon range:

9.3.4.1 Five peak C_3-alkylbenzene group in the range of *n*-C_9-*n*-C_{10}.

9.3.4.2 1,2,4-TMB and 1,2,3-TMB, if the range encompasses *n*-C_9-*n*-C_{10}.

9.3.4.3 C_4-alkylbenzene groups, in the range of *n*-C_{10}-*n*-C_{11}.

9.3.5 *Indanes* – Indane, the C_1-indane group, and the C_2-indane group, if present, elute in the range of *n*-C_{10}-*n*-C_{12}.

9.3.6 *PNAs* – Naphthalene, C_1- PNA, and C_2- PNA groups, if present, elute in the range of *n*-C_{11}-*n*-C_{15}.

10. Requirements for the Identification of Isoparaffinic Products

10.1 *TIC* – Predominance of isoalkanes in the diagnostic pattern of interest, excluding extraneous compounds comparable to a known isoparaffinic product (refer to E1618 figure X1.5).

10.2 *Alkanes* – Alkane EIP is the most abundant and, when discernable in the TIC, will have a similar pattern for the corresponding components.

10.3 *Cycloalkanes* – cycloalkane compounds are not present; however, the associated EIP profile will resemble a diminished alkanes profile.

10.4 No significant contributions from alkylbenzene, polynuclear aromatic and indane EIPs.

11. Requirements for the Identification of Naphthenic-Paraffinic Products

11.1 *TIC* – Predominance of naphthenic and isoalkanes and reduced *n*-alkanes, excluding extraneous compounds comparable to a known naphthenic-paraffinic product (refer to E1618 figure X1.6).

11.1.1 When *n*-alkanes are present, the most abundant *n*-alkane peak is approximately less than 1.5 times the major isoalkane/cycloalkane component(s) and is within a comparable carbon range.

11.2 *Alkanes* – Alkane EIP contains mostly isoparaffinic compounds and *n*-alkanes (when present), where the corresponding peaks and intergroup patterns within the diagnostic pattern of interest are comparable to a known naphthenic-paraffinic reference ignitable liquid.

11.3 *Cycloalkanes* – Cycloalkane EIP contains primarily cycloalkane compounds in between spiking alkylcycloalkanes in Gaussian distribution, where the corresponding peaks and intergroup patterns compare to a known naphthenic-paraffinic reference ignitable liquid.

11.4 No significant contributions from alkylbenzene, polynuclear aromatic and indane EIPs.

12. Requirements for the Identification of Aromatic Products

12.1 *Requirements for Identification of Light Aromatic Products (LAP)*

12.1.1 The chemicals which comprise LAPs are commonly produced in the thermal degradation of synthetic materials. Identification is based on the totality of the pattern and the consistency of the inter- and intragroup comparisons (refer to E1618 figure X1.7).

12.1.2 *TIC* – Light aromatic products typically consist of toluene, C_2-alkylbenzenes, or both.

12.1.2.1 These compounds are identified by both GC retention time and mass spectrum (refer to Section 17).

Note – Benzene is generally removed during the refinery process.

12.1.3 *Alkylbenzenes* – Alkylbenzene EIP is the most abundant profile and, when discernable in the TIC, will have a similar pattern for the corresponding components.

12.2 *Requirements for Identification of Medium Aromatic Products (MAP)*

12.2.1 *TIC* – resembles weathered gasoline pattern within the product's carbon range (refer to E1618 figure X1.8).

12.2.2 *Alkanes* – not present.

12.2.3 *Alkylbenzenes* – Alkylbenzene EIP is the most abundant profile and may contain C_3-, C_4-alkylbenzenes. When discernable in the TIC they will have a similar pattern for the corresponding components.

12.2.4 *Indanes* – Indane EIP may contain C_1-, C_2-indanes, depending on formulation.

12.2.5 *PNAs* – PNA EIP may contain naphthalene or C_1- and C_2-PNAs, depending on formulation.

12.3 *Requirements for Identification of Heavy Aromatic Products (HAP)*

12.3.1. *Indanes* – Indane EIP contains the C_1-, C_2-indanes in aromatic products that encompass *n*-C_{11}-*n*-C_{12} (refer to E1618 figure X1.9).

12.3.2 *PNAs* – the PNA EIP is the most abundant profile and contains naphthalene, C_1-PNAs and C_2-PNAs if the pattern encompasses *n*-C_{11}-*n*-C_{15}. The composition of the C_2-PNA grouping is similar to that of some weathered gasolines.

13. Requirements for the Identification of Normal Alkane Products

13.1 *TIC* – a series of three or more consecutive *n*-alkanes (refer to E1618 figure X1.10).

13.2 *Alkanes* – Alkane EIP and when discernable in the TIC they will have a similar pattern for the corresponding components.

13.3 No significant contributions from cycloalkane, alkylbenzene, polynuclear aromatic, and indane EIPs.

13.4 Normal alkanes are identified by both GC retention time and mass spectrum (refer to section 17).

14. Requirements for the Identification of Oxygenated Products

14.1 Oxygenated compounds are identified by GC retention times and mass spectral characteristics, refer to section 17 for additional guidance (refer to E1618 figure X1.11).

14.1.1 Retention times and mass spectral characteristics for all major chromatographic peaks are comparable to a known oxygenated product or another similar reference ignitable liquid.

14.1.2 When present as a mixture with another ignitable liquid class, the alkanes, cycloalkanes, alkylbenzene, polynuclear aromatic, and indane profiles shall also meet the requirements for the identification for the other classes present. Refer to section 18 for additional guidance.

Note – Mixtures of individual classes are separately identified (e.g., medium petroleum distillate and 2-butoxyethanol) and not identified as an “oxygenated product.”

14.2 Thermal degradation of materials can generate oxygenated compounds, such as alcohols, acetone, or a combination thereof. In addition, these chemicals are used in the manufacture of materials. The mere presence of oxygenated compounds does not indicate a foreign ignitable liquid is present in a debris sample. A large excess of the compound, at least one order of magnitude above the matrix peaks in the chromatogram, should be present before identifying an oxygenated compound in a debris sample [8].

15. Requirements for the Identification of Petroleum Products

15.1 *TIC* – indicates potentially two or more classes but there is insufficient delineation between the patterns to warrant identifying each classification separately (refer to E1618 figure X1.12).

15.2 All major chromatographic peaks attributed to a petroleum product are comparable to at least one similar reference ignitable liquid.

16. Requirements for the Identification of Vegetable Oil-Based Products

16.1 *TIC* – FAMEs, whether present as FAMEs or derivatized fatty acids (refer to E2881), are identified by GC retention times and mass spectral characteristics (refer to E1618 figure X1.13).

16.1.1 Example esters include: 9,12-octadecadienoic acid, methyl ester; 9-octadecadecenoic acid, methyl ester.

16.2 *EIPs* - When comprised exclusively of FAMEs (e.g. B100 and derivatized vegetable oils), the alkanes, cycloalkanes, alkylbenzenes, indanes, and polynuclear aromatics profiles will not be present.

16.3 When present as a mixture of FAMEs or fatty acids and another ignitable liquid class, the alkanes, cycloalkanes, alkylbenzenes, indanes, and polynuclear aromatics profiles also meet the requirements for the identification for the other class(es) present and are comparable to a known product reference.

Note – Mixtures of individual classes are separately identified (e.g. medium petroleum distillate and a vegetable oil; butanol and a FAME-based product) and not identified as a "vegetable oil-based product." Refer to E2881 and E2997 and section 18 for further information.

17. Requirements for the Identification of Single Compounds

17.1 It is sometimes necessary to identify single compounds present in chromatograms. Some classes of ignitable liquids contain one or few compounds of interest. The associated lack of pattern does not allow for identification by chromatographic pattern comparison alone.

17.2 In situations where the identity of a compound is to be reported, compare the chromatographic retention time and mass spectra to those of a reference ignitable liquid.

17.3 The chromatographic retention time of an unknown compound is, at most, within 1% or 0.1 minutes (whichever is greater) of the retention time of the reference ignitable liquid. [3]

17.4 The relative abundances of ions in the mass spectra of the unknown sample and the reference ignitable liquid will generally agree across the majority of the ions. The unknown and known samples have the same base peak and the same molecular ion, when the molecular ion is present. Isotopic ions present in the reference spectrum is present in similar proportions in the unknown sample spectrum; low abundance ions (less than 5% of the total spectral abundance) may be absent without precluding an identification. Background subtraction may be necessary to remove any background contribution to the sample. There are no unexplainable extraneous ions.

17.5 The mere presence of a compound, such as ethanol, toluene, or acetone, does not indicate a foreign ignitable liquid is present in a debris sample. A large excess of the compound, at least one order of magnitude above the matrix peaks in the chromatogram, should be present before identifying a compound in debris samples.

18. Requirements for the Identification of Mixtures

18.1 More than one ignitable liquid class or subclass may be identified in a single sample.

18.1.1 For each identified class or subclass, the requirements for identification is met (refer to E1618 figures X1.14 – X1 and X1.15).

Note – Mixtures of ignitable liquid classifications can be the result of a single commercial product or a mixture of products. This standard cannot differentiate between ignitable liquids that are mixed by a manufacturer for sale or ignitable liquids mixed at the point of use.

19. Other Ignitable Liquid Products - Numerous commercial and industrial products are ignitable and do not fall into any of the defined ignitable liquid classifications. Many of these are synthetic mixtures consisting of only a few compounds, rather than distillation fractions, such as terpenes. When these products are found in unknown samples, they are identified by describing composition and not classed as a "miscellaneous" or other product.

20. Considerations [7, 11]

20.1 The appendix contains images of various circumstances that can obscure or alter patterns and complicate the analysis.

20.2 Ratios of compounds within an ignitable liquid classification can vary. Additionally, contributions can occur from the matrix.

20.3 The extraction technique used, evaporation of the liquid, or degradation can cause alterations of a sample pattern when compared to a reference ignitable liquid. Exercise caution when identifying mixtures of overlapping ignitable liquids present in an unknown sample.

20.4 *Weathering* – Exposure of an ignitable liquid to heat, light, and other environmental conditions typically results in a shift of the chromatographic pattern such that components with heavier boiling ranges have a higher relative ratio when compared to unaltered liquids. The effect of exposure is more pronounced with lighter, more volatile ignitable liquids. Lighter ignitable liquids, as a result, can have greater skewing when compared to heavier products and products which have broad boiling ranges are affected more than narrow range products (refer to appendix figures X.1 and X.2)(17).

20.5 *Extraneous Compounds* – Burned or pyrolyzed substrate material(s) can contribute extraneous compounds to the patterns such as oxygenated compounds, alkanes, cycloalkanes, alkenes, alkylbenzenes, condensed ring aromatic hydrocarbons or polynuclear aromatics. The amount and type of pyrolysis and combustion products formed during a fire are dependent on the substrate material(s) and the fire conditions (11, 12, 13).

20.5.1 The additional presence of these extraneous compounds is acceptable when the requirements for an identification of ignitable liquid class have been met.

20.5.2 Benzene is a light aromatic compound naturally present in crude oil which is removed during the refinery process. Commercial ignitable liquid products containing benzene are extremely rate; however, benzene is commonly found in many mass-produced products, industrial adhesives, and as a pyrolysis product of many substrates, including some flooring materials and some plastics. For these reasons, the finding of benzene should not be considered significant unless present in a liquid form and comparable to a reference ignitable liquid.

20.6 *Polyolefin or Asphalt Decomposition* – Carefully review extracts that meet the criteria for heavy petroleum distillates for 1-alkene or 1, (*n*-1) diene compounds associated with the *n*-alkanes present. Generally, this feature would indicate the presence of polyolefin or asphalt decomposition products rather than heavy petroleum distillates (refer to appendix figure X.3)(20).

20.6.1 Polyolefin decomposition products typically do not exhibit the same pattern of branched alkanes as heavy petroleum distillates.

20.7 *Degradation* – Microorganisms (e.g., bacteria and mold) can exist in various substrates, such as soil. When present and metabolically active, they preferentially degrade mono-substituted aromatic compounds such as ethylbenzene and *n*-propylbenzene, *n*-alkanes present in gasoline and distillates, or a combination of both [4-6]. Consider degradation effects when debris samples contain substrates expected to contain microorganisms (refer to appendix figure

X.4)(17).

20.8 *Considerations for Extraction Techniques*

20.8.1 Passive headspace adsorption using activated charcoal (Practice E1412) will preferentially adsorb aromatic compounds over alkane compounds, particularly in samples where the activated charcoal becomes overloaded by a large quantity of ignitable liquid. For example, when a large quantity of an HPD is extracted, the increased aromatics can give the false appearance of gasoline contribution (refer to appendix figure X.5).

20.8.2 Adsorption based extraction techniques often will not allow for differentiation between narrower and wider range heavy petroleum distillates (for example kerosene and diesel fuel). This is especially true in the case of samples extracted from charred matrices. Additional extraction procedures can be performed, such as solvent extraction (Practice E1386), to attempt to differentiate between such products (refer to appendix figure X.6).

20.8.3 Adsorption-based extraction techniques may provide an HPD pattern from a heavy oil/lubricant product containing heavy normal and isoparaffinic aliphatic compounds. Additional extraction procedures can be performed, such as solvent extraction (Practice E1386), to attempt to differentiate between such products (refer to appendix figure X.7).

21. Dissimilarity [7]

21.1 When the requirements for identification of an ignitable liquid class are not met, a negative finding is appropriate.

21.2 The presence of only some compounds common to a particular class of ignitable liquid product does not necessarily indicate the presence of that liquid in the debris at the time of the fire. For example, the pyrolyzates of some polymers can include toluene and xylenes and the pyrolyzates of polyolefin plastic may include a homologous series of normal alkanes.

22. Control or Comparison Samples

22.1 Some ignitable liquid compounds may be found in some substrates. Examples include normal alkane products found in linoleum and in carbonless paper forms; isoparaffinic products found in some linoleum; distillates found in some printed materials; and solvents used in some adhesives and coatings. (14, 15, 16, 18)

22.2 Comparison and control samples can provide information that can aid in the interpretation of data and in determining whether an ignitable liquid is incidental or foreign to the substrate.

22.2.1 The submission of a comparison or control sample is not required for an ignitable liquid determination. (refer to E3245)

22.3 Identification of an ignitable liquid in the comparison or control sample are reported.

22.4 Ignitable compounds known to be used in the manufacture of materials, or found in pyrolysis of control or comparison materials, are not reported without explanation of possible origin (i.e. toluene from shoes, terpenes from wood).

22.5 Examine a control sample of any absorbent and packaging materials used during the extraction process.

23. Precision and Bias

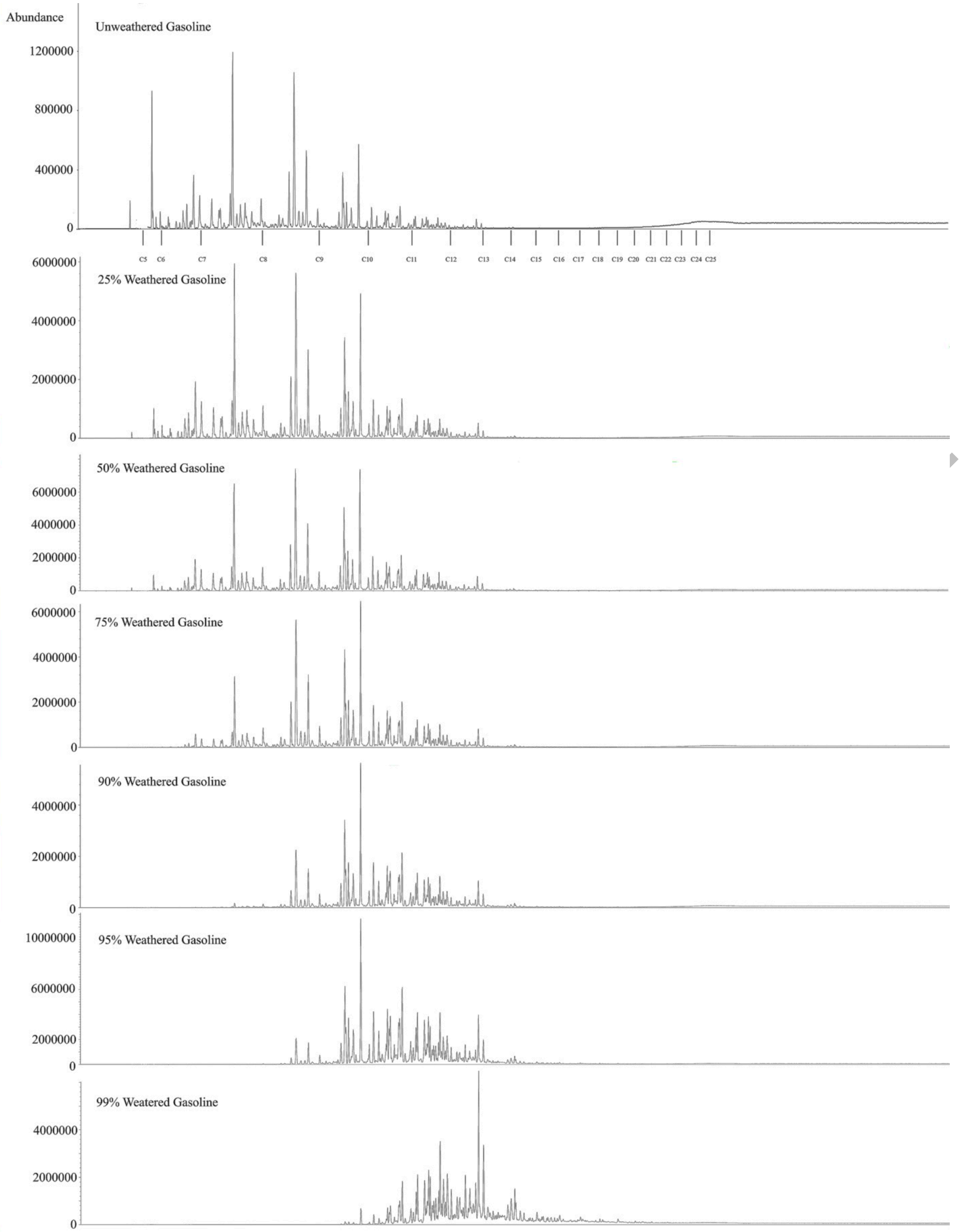
23.1 This test method is qualitative. A quantitative evaluation of precision and bias is not required for this qualitative determination.

24. Keywords

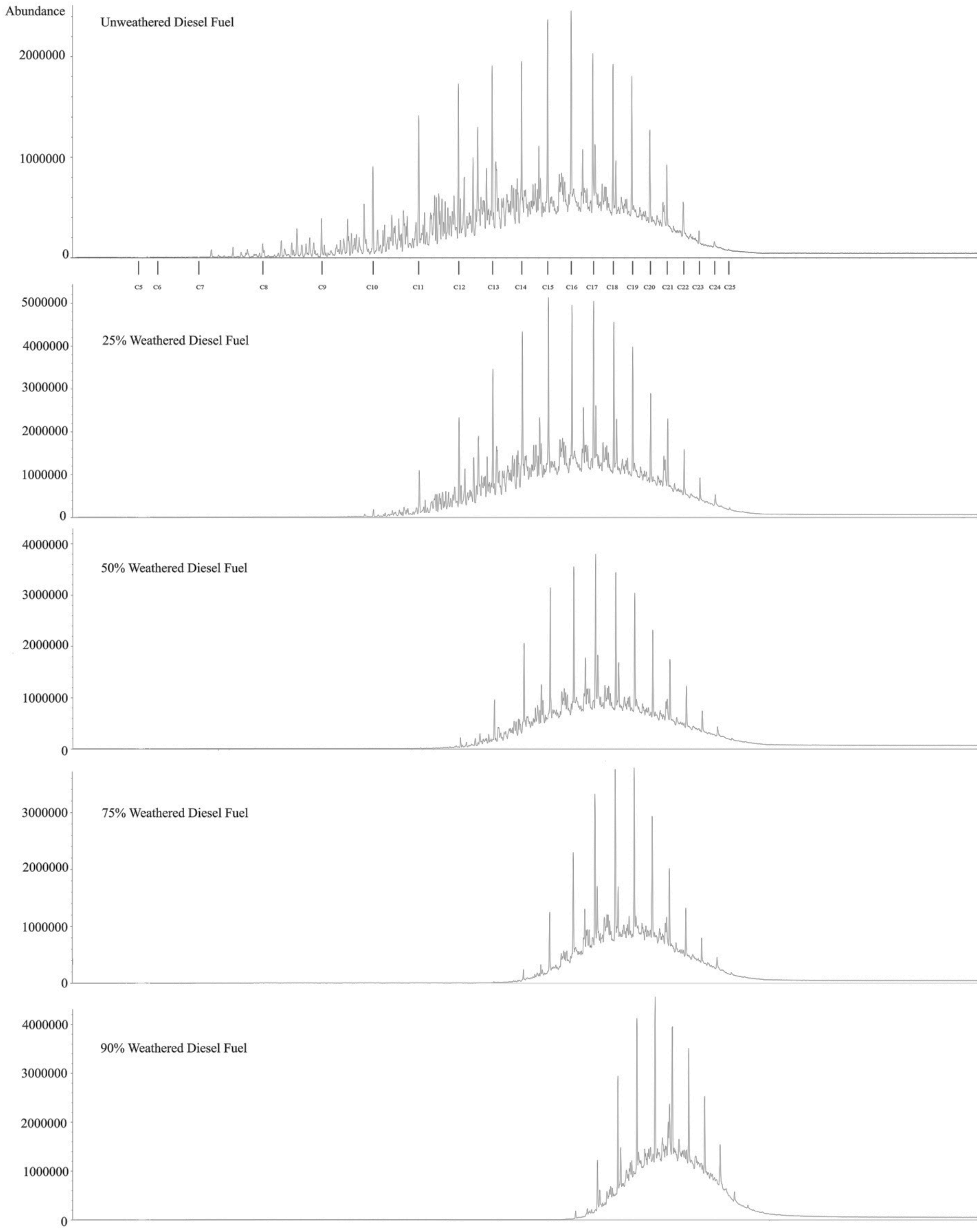
24.1 fire debris samples; forensic sciences; gas chromatography; ignitable liquid residues; mass spectrometry.

Appendix
(Nonmandatory Information)

X1. Weathered Gasoline

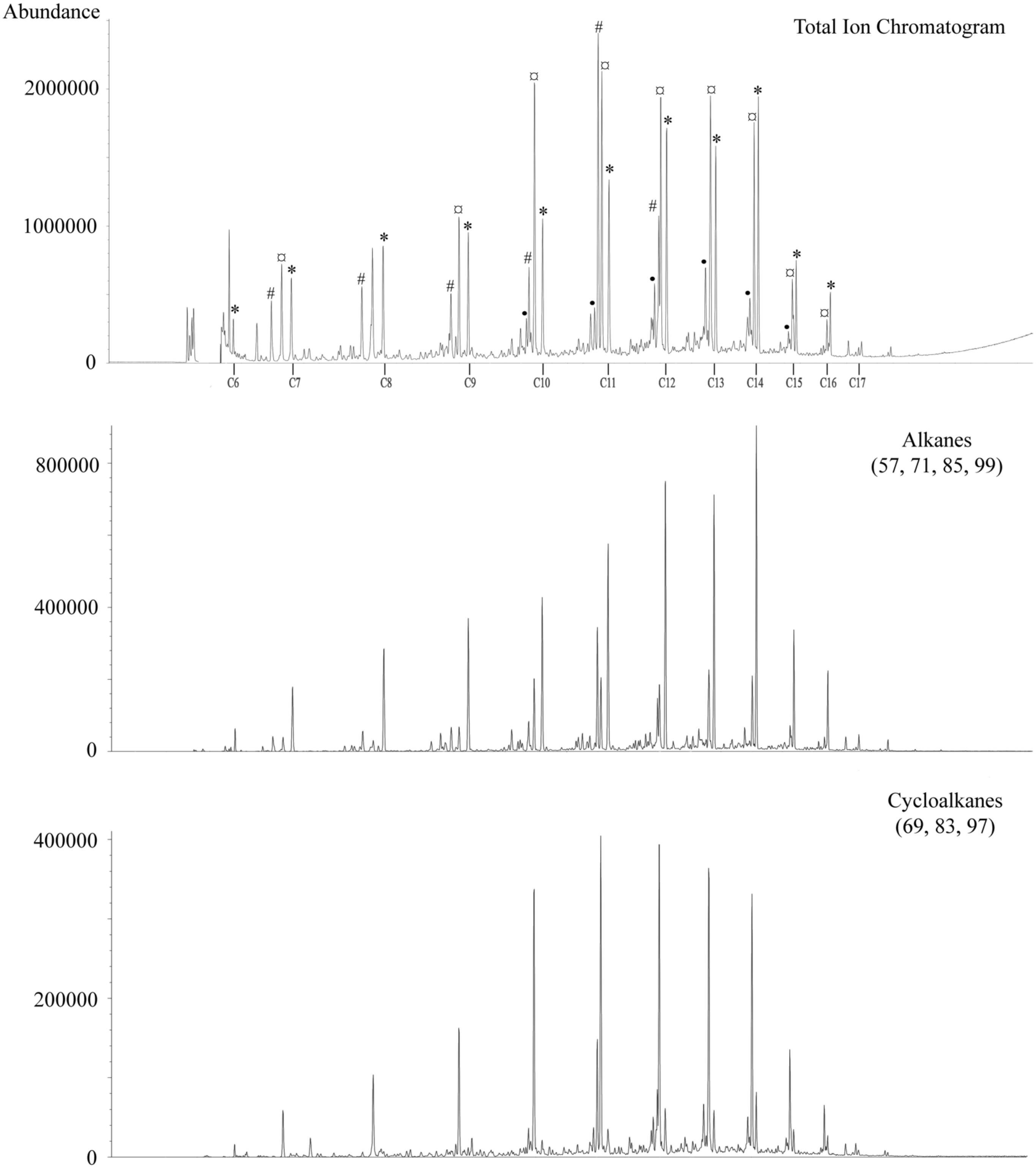


X2. Weathered HPD



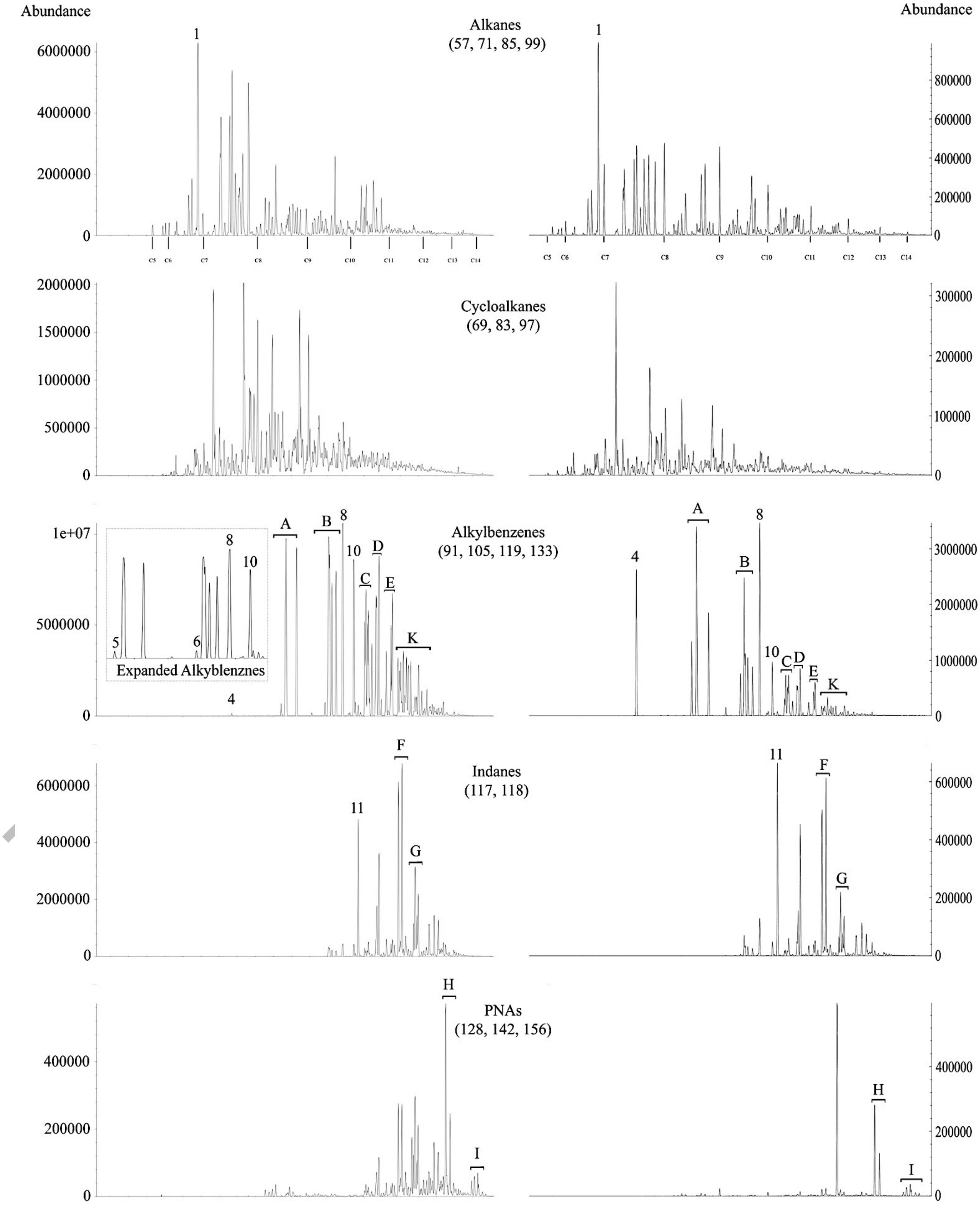
X3. Polyolefin or Asphalt Decomposition

The presence of alkanes proceeded by alkenes and alkylidenes indicates thermal degradation of plastics. Legend: # - aldehydes, ¤ -alkenes, * - alkanes, • - alkylidenes



X.4. Microbial Degradation

The image on the right is a reference gasoline sample. The image on the left is microbially degraded gasoline produced by placing gasoline onto potting soil into a vapor proof can and leaving it at room temperature for three days prior to extraction.



X.5. Considerations for Extraction Techniques; Preferential Adsorption of Aromatics using ASTM E1412

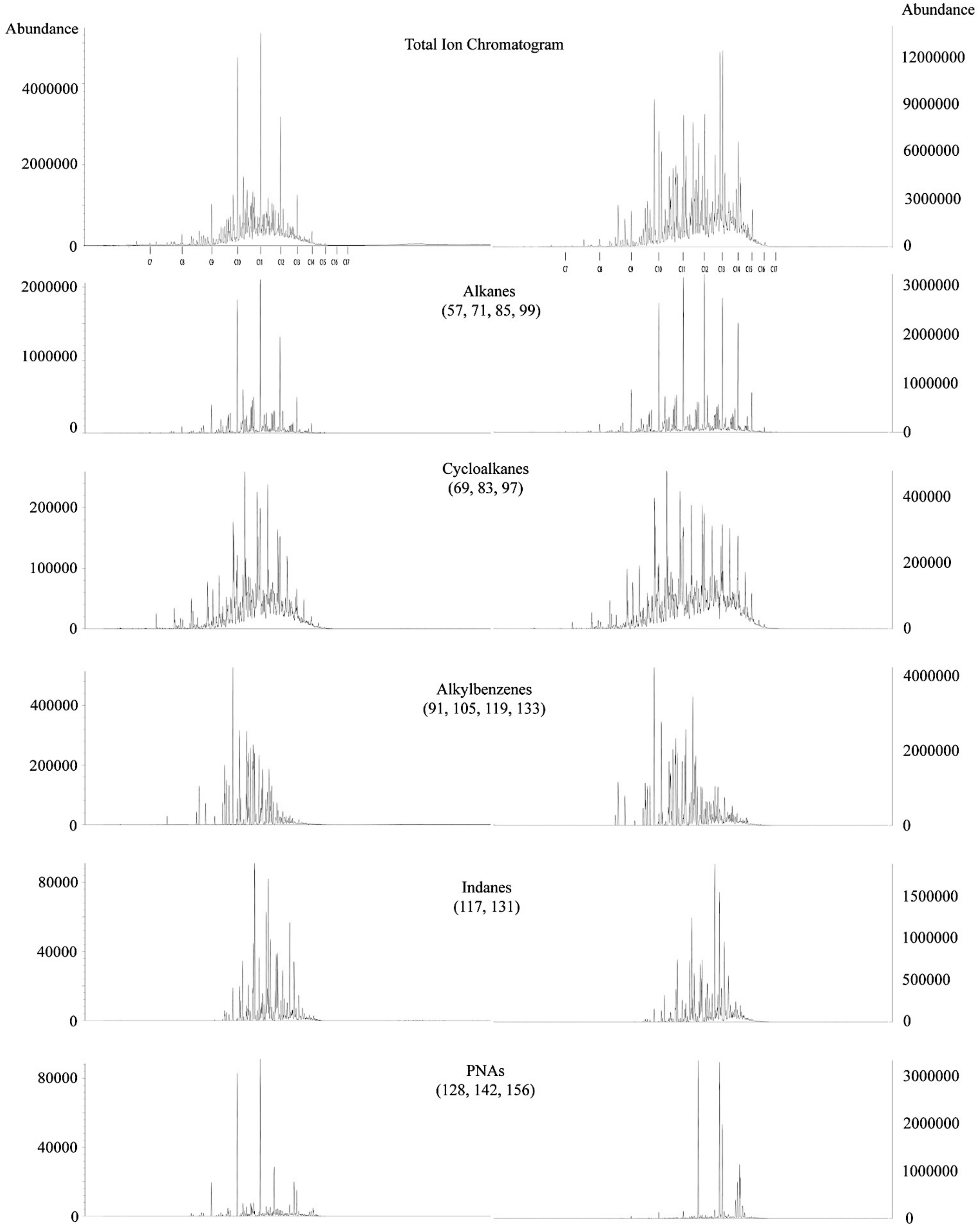
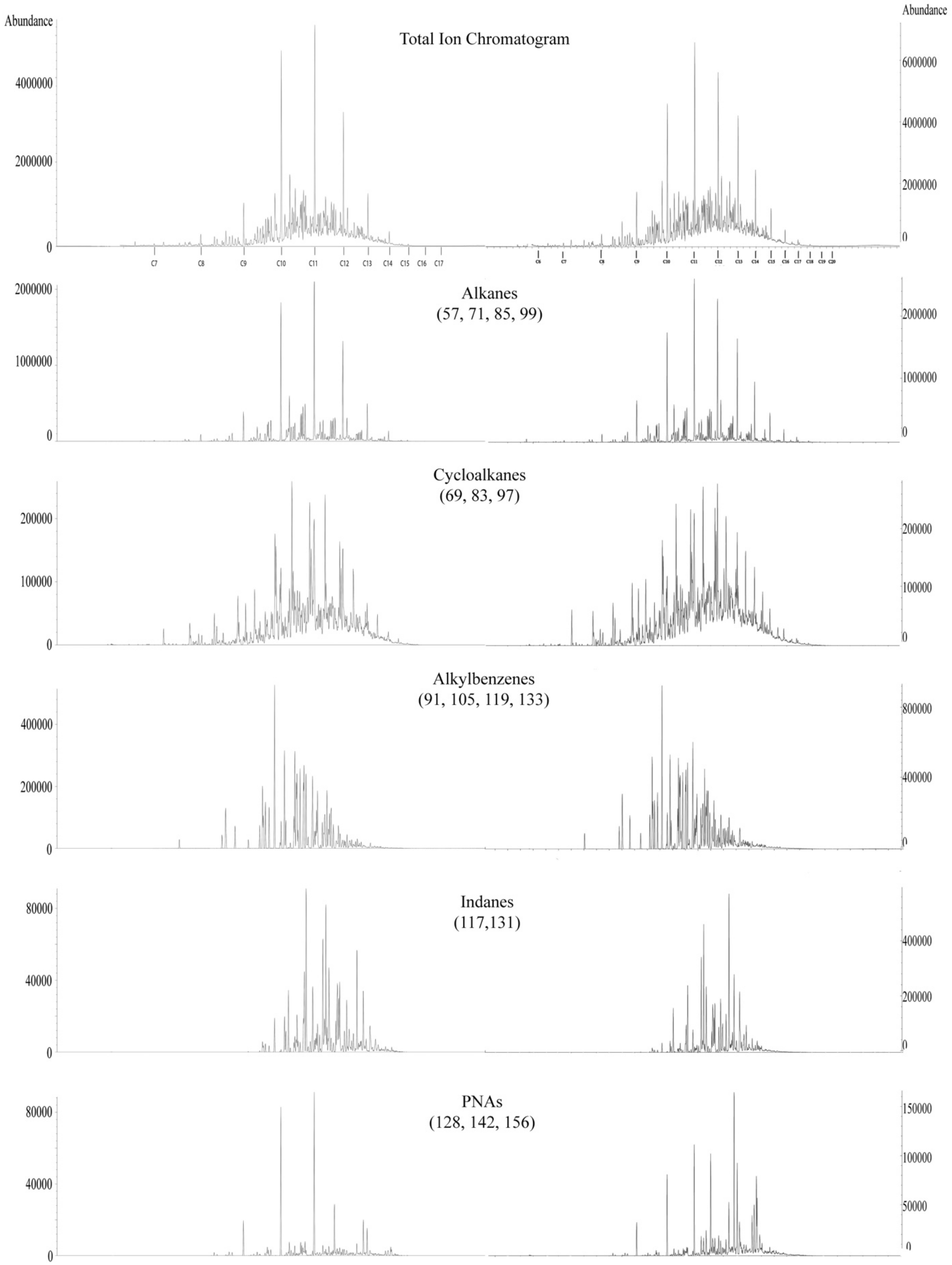


Image on the left shows one drop of kerosene extracted with ASTM E1412. Image on the right is an ASTM E1412 extraction of 5 mL of the same product.

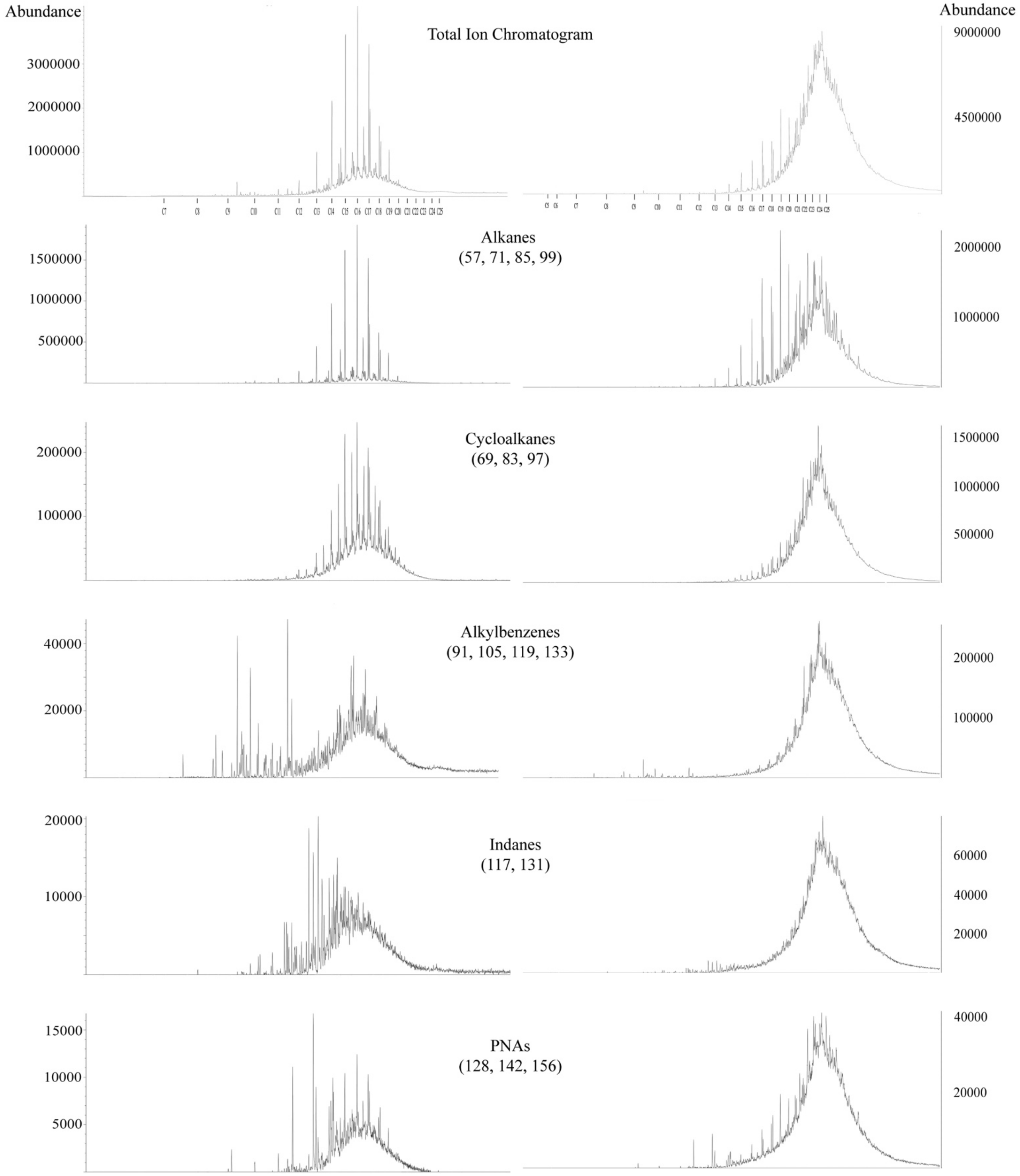
X.6. Considerations for Extraction Techniques; Kerosene vs. Diesel using ASTM E1412

Image on the left is an extraction of kerosene; image on the right is diesel fuel. Both samples were extracted using ASTM E1412.



X.7. Considerations for Extraction Techniques; Oil or Lubricant Product

Image on the left is transmission fluid extracted using ASTM E1412. On the right is the same product diluted in solvent.



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