greases, etc., have been suggested but various drawbacks have existed which have hindered their effectiveness. Many currently available markers cannot be used as both forensic markers, detected by, but not limited to analysis by Gas Chromatography (GC), and simple field test markers detected by, but not limited to, development or extraction of the marker. Many known markers are easily removed from the fluid to which they are added destroying the integrity of the marker system. Many currently available markers cannot be easily combined to detect marker product with a component that cannot be laundered from the fuel. And current methods of lab analysis of these markers ends to be very expensive.

[0007] In view of the above, it would be desirable to provide a composition useful as a marker and that could be detected not only in the field, but also in the lab. It would be desirable to combine field test technology with existing chromatography techniques to provide not only field test results but also a laboratory confirmation of the marker presence, using common lab techniques, such as, but not limited to, analysis by GC. Additionally, the marker should be able to accomplish the above and remain resistant to undesired extraction or removal (laundering) by unscrupulous persons. Additionally it would be desirable to provide a marker composition that could be used in a wide variety of fluids, including, but not limited to, petroleum products, alcohols, etc. Petroleum products may include, but are not limited to, fuels, lubes, greases, etc. It would also be desirable to provide economical detection methods not requiring advanced training of the operator.

SUMMARY ~~OF THE INVENTION~~

[0008] ~~In an aspect, the~~The present disclosure provides a method of identifying marked hydrocarbon fluids that have been laundered, wherein unlaundered marked hydrocarbon fluids contain a gas chromatography marker and a spectroscopic marker. The gas chromatography marker includes a non-pyrrolidinone nitrogen-containing compound. The method includes: a) introducing a first portion of a hydrocarbon fluid sample that is suspecting of having been laundered into a gas chromatography system, thereby resulting in a gas chromatography report of the hydrocarbon fluid sample; b) spectroscopically analyzing a second portion of the hydrocarbon fluid sample, thereby resulting in a spectroscopic report of the hydrocarbon fluid sample; c) identifying the presence or absence of the gas chromatography marker using the gas chromatography report and identifying the presence or absence of the spectroscopic marker using the spectroscopic report; and d) based on the identifying of step c): if the gas chromatography marker and the spectroscopic marker are identified as present, then indicating that the hydrocarbon fluid sample is marked and unlaundered; if the gas chromatography

marker is identified as present and the spectroscopic marker is identified as absent, then indicating that the hydrocarbon fluid sample is marked and laundered; and if the gas chromatography marker and the spectroscopic marker are identified as absent, then indicating the hydrocarbon fluid is unmarked.

[0008a] In one aspect, the present disclosure provides a method of identifying marked hydrocarbon fluids that have been laundered, wherein unlaundered marked hydrocarbon fluids contain a gas chromatography marker and a spectroscopic marker, the gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine, the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities, the method comprising: a) introducing a first portion of a hydrocarbon fluid sample that is suspecting of having been laundered into a gas chromatography system, thereby resulting in a gas chromatography report of the hydrocarbon fluid sample; b) spectroscopically analyzing a second portion of the hydrocarbon fluid sample, thereby resulting in a spectroscopic report of the hydrocarbon fluid sample; c) identifying the presence or absence of the gas chromatography marker using the gas chromatography report and identifying the presence or absence of the spectroscopic marker using the spectroscopic report; and d) based on the identifying of step c): if the gas chromatography marker and the spectroscopic marker are identified as present, then indicating that the hydrocarbon fluid sample is marked and unlaundered; if the gas chromatography marker is identified as present and the spectroscopic marker is identified as absent, then indicating that the hydrocarbon fluid sample is marked and laundered; and if the gas chromatography marker and the spectroscopic marker are identified as absent, then indicating the hydrocarbon fluid is unmarked.

[0009] ~~In another aspect, the~~The present disclosure provides a method of marking a subset of hydrocarbon fluids in circulation within a market and detecting presence of the marking. The method includes: a) adding a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound to the subset of the hydrocarbon fluids in circulation within the market; b) selecting a sample of one of the hydrocarbon fluids in circulation within the market; c) introducing at least a portion of the sample of one of the hydrocarbon fluids in

circulation within the market into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; and d) identifying the presence or absence of the non-pyrrolidinone nitrogen-containing compound in the sample using the gas chromatography report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids.

[0009a] In another aspect, the present disclosure provides a method of marking a subset of hydrocarbon fluids in circulation within a market and detecting the presence of the marking, the method comprising: a) adding a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound to the subset of the hydrocarbon fluids in circulation within the market, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine; b) selecting a sample of one of the hydrocarbon fluids in circulation within the market; c) introducing at least a portion of the sample of one of the hydrocarbon fluids in circulation within the market into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; d) identifying the presence or absence of the non-pyrrolidinone nitrogen-containing compound in the sample using the gas chromatography report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids; e) adding a spectroscopic marker to the subset of the hydrocarbon fluids in circulation within the market, wherein the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities; f) spectroscopically analyzing at least a second portion of the sample of one of the hydrocarbon fluids in circulation within the market, thereby resulting in a spectroscopic report of the sample; and g) identifying the presence or absence of the spectroscopic marker in the sample using the spectroscopic report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids.

[0010] ~~In a further aspect, the~~The present disclosure further provides a method of identifying a hydrocarbon fluid containing a gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound. The method includes: a) introducing a sample of the hydrocarbon fluid into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; and b) identifying the presence of the non-pyrrolidinone nitrogen-containing compound in the hydrocarbon fluid using the gas chromatography report.

[0010a] In another aspect, the present disclosure provides a method of identifying a hydrocarbon fluid containing a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound and a spectroscopic marker, wherein the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine, the method comprising: a) introducing a sample of the hydrocarbon fluid into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; b) identifying the presence of the non-pyrrolidinone nitrogen-containing compound in the hydrocarbon fluid using the gas chromatography report; c) spectroscopically analyzing a second sample of the hydrocarbon fluid, thereby resulting in a spectroscopic report of the second sample; and d) identifying the presence of the spectroscopic marker in the hydrocarbon fluid using the spectroscopic report.

[0011] ~~In yet another aspect, the~~The present disclosure provides a marker composition. The marker composition includes: a gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound; and a solvent.

[0012] ~~In yet a further aspect, the~~The present disclosure further provides a marker composition. The marker composition includes: a gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound; and a spectroscopic marker.

[0013] ~~In an additional aspect, the~~The present disclosure provides a marked hydrocarbon fluid. The marked hydrocarbon fluid includes a hydrocarbon fluid and the marker compositions as described herein. The marker composition is present in an amount sufficient to provide a concentration of the non-pyrrolidinone nitrogen-containing compound in the marker hydrocarbon fluid of between 0.1 ppm and 500 ppm, to provide a concentration of the spectroscopic marker in the marker hydrocarbon fluid of between 0.1 ppm and 500 ppm, or a combination thereof.

[0014] ~~In yet another aspect, the~~The present disclosure provides a kit. The kit includes the

marker composition as described herein and a reference gas chromatography report for the non-pyrrolidinone nitrogen-containing compound of the marker composition.

[0015] ~~In yet a further aspect, the~~ The present disclosure provides a system for identifying hydrocarbon fluids marked with a gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound. The system includes a gas chromatography with nitrogen phosphorus detector (GC-NPD) system; and a computer. The computer has a processor and a memory. The memory has stored thereon a reference gas chromatography report for the non-pyrrolidinone nitrogen-containing compound and instructions that, when executed by the processor, cause the processor to receive a gas chromatography report from the GC-NPD system and identify the present or absence of the gas chromatography marker based on a comparison with the reference gas chromatography report.

[0016] The foregoing and other aspects and advantages of the ~~invention~~ disclosure will appear from the following description. In the description, reference is made to the accompanying drawings which form a part hereof, and in which there is shown by way of illustration a preferred ~~embodiment~~ example of the disclosure~~invention~~. Such ~~embodiment~~ example does not necessarily represent the full scope of the disclosure~~invention~~, however, and reference is made therefore to the claims and herein for interpreting the scope of the disclosure~~invention~~.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] In order to assist the understanding of this invention, reference will now be made to the appended drawings, in which like reference characters refer to like elements. The drawings are exemplary only, and should not be construed as limiting the invention.

[0018] Figure 1 is a system, in accordance with various aspects of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Before the present materials and methods are described, it is understood that this disclosure is not limited to the particular methodology, protocols, materials, and reagents described, as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

[0020] As used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. As well, the terms “a” (or “an”), “one or more” and “at least one” can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably.

CLAIMS

1. A method of identifying a hydrocarbon fluid containing a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound and a spectroscopic marker, wherein the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine, the method comprising:

a) introducing a sample of the hydrocarbon fluid into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; and

b) identifying the presence of the non-pyrrolidinone nitrogen-containing compound in the hydrocarbon fluid using the gas chromatography report;.

c) spectroscopically analyzing a second sample of the hydrocarbon fluid, thereby resulting in a spectroscopic report of the second sample; and

d) identifying the presence of the spectroscopic marker in the hydrocarbon fluid using the spectroscopic report.

2. The method of claim 1, wherein the gas chromatography system is a gas chromatography with nitrogen phosphorus detector (GC-NPD) system and step a) is introducing the sample into the GC-NPD system.

3. The method of claim 2, wherein the GC-NPD system includes a flame thermionic detector or an alkali flame-ionization detector.

4. The method of claim 2 or 3, wherein the gas chromatography report resulting from step a) includes an intensity value that is proportional to an amount of nitrogen or phosphorus in the sample.

5. The method of claim 4, wherein the intensity is time-variable as a function of elution times of components of the sample.

6. The method of claim 5, wherein the identifying of step b) includes monitoring the intensity value at one or more predetermined elution times.

7. The method of claim 1, wherein the gas chromatography system is a gas chromatography-mass spectrometry (GC-MS) system, a gas chromatography-Hall electrolytic

conductivity detector (GC-HECD) system, a gas chromatography-flame ionization detector (GC-FID) system, a gas chromatography-electron capture detector (GC-ECD) system, a gas chromatography-photoionization detector (GC-PID) system, or a combination thereof, and step a) is introducing the sample into the GC-MS system, the GC-HECD system, the GC-FID system, the GC-ECD system, the GC-PID system, or the combination thereof.

8. The method of ~~any one of the preceding claims~~claim 1, wherein the gas chromatography system includes a fused silica column, a polyethylene glycol column, a cyano propyl column, a trifluorpropyl column, a substituted polysiloxane column, or a combination thereof and the introducing of step a) includes introducing the sample into the fused silica column, the polyethylene glycol column, the cyano propyl column, the trifluorpropyl column, the substituted polysiloxane column, or the combination thereof.

9. The method of ~~any one of the preceding claims~~claim 1, wherein the introducing of step a) includes introducing the sample with a carrier gas selected from the group consisting of nitrogen, helium, and combinations thereof.

10. The method of ~~any one of the preceding claims~~claim 1, wherein the identifying of step b) includes comparing the gas chromatography report to a reference report.

11. The method of ~~any one of the preceding claims~~claim 1, wherein the non-pyrrolidinone nitrogen-containing compound is present in the hydrocarbon fluid in an amount of between 0.1 ppm and 500 ppm.

~~12. The method of any one of the preceding claims, the hydrocarbon fluid further comprising a spectroscopic marker, the method further comprising:~~

~~c) spectroscopically analyzing a second sample of the hydrocarbon fluid, thereby resulting in a spectroscopic report of the second sample; and~~

~~d) identifying the presence of the spectroscopic marker in the hydrocarbon fluid using the spectroscopic report.~~

~~13.~~12. The method of ~~claim 12~~claim 1, wherein the spectroscopically analyzing of step c) includes conducting fluorescence spectroscopy, UV-Vis spectroscopy, Raman spectroscopy, near infrared spectroscopy, or a combination thereof.

~~14.~~13. The method of ~~claim 12 or 13~~claim 1, wherein the identifying of step d) includes comparing the spectroscopic report to a reference spectrum.

~~15.~~14. The method of ~~any one of claims 12 to the immediately preceding claim~~claim 1, wherein the spectroscopic marker is present in the hydrocarbon fluid in an amount of between 0.1 ppm and 500 ppm.

~~16.~~15. A method of marking a subset of hydrocarbon fluids in circulation within a market and detecting the presence of the marking, the method comprising:

a) adding a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound to the subset of the hydrocarbon fluids in circulation within the market, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine;

b) selecting a sample of one of the hydrocarbon fluids in circulation within the market;

c) introducing at least a portion of the sample of one of the hydrocarbon fluids in circulation within the market into a gas chromatography system, thereby resulting in a gas chromatography report of the sample; ~~and~~

d) identifying the presence or absence of the non-pyrrolidinone nitrogen-containing compound in the sample using the gas chromatography report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids~~.~~;

e) adding a spectroscopic marker to the subset of the hydrocarbon fluids in circulation within the market, wherein the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities;

f) spectroscopically analyzing at least a second portion of the sample of one of the hydrocarbon fluids in circulation within the market, thereby resulting in a spectroscopic report of the sample; and

g) identifying the presence or absence of the spectroscopic marker in the sample using the spectroscopic report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids.

~~17.~~16. The method of claim ~~16~~15, wherein the gas chromatography system is a gas chromatography with nitrogen phosphorus detector (GC-NPD) system and step c) is introducing the sample into the GC-NPD system.

~~18.~~17. The method of claim ~~17~~16, wherein the GC-NPD system includes a flame thermionic detector or an alkali flame-ionization detector.

~~19. The method of claim 17 or 18, wherein the gas chromatography report resulting from step c) includes an intensity value that is proportional to an amount of nitrogen or phosphorus in the sample.~~

20. The method of claim 19, wherein the intensity is time-variable as a function of elution times of components of the sample.

21. The method of claim 20, wherein the identifying of step d) includes monitoring the intensity value at one or more predetermined elution times.

22. The method of any one of claims 16 to the immediately preceding claim, wherein the gas chromatography system is a gas chromatography-mass spectrometry (GC-MS) system, a gas chromatography-Hall electrolytic conductivity detector (GC-HECD) system, a gas chromatography-flame ionization detector (GC-FID) system, a gas chromatography-electron capture detector (GC-ECD) system, a gas chromatography-photoionization detector (GC-PID) system, or a combination thereof, and step c) is introducing the sample into the GC-MS system, the GC-HECD system, the GC-FID system, the GC-ECD system, the GC-PID system, or the combination thereof.

23. The method of any one of claims 16 to the immediately preceding claim, wherein the gas chromatography system includes a fused silica column a polyethylene glycol column, a cyano propyl column, a trifluorpropyl column, a substituted polysiloxane column, or a combination thereof and the introducing of step c) includes introducing the sample into the fused silica column, the polyethylene glycol column, the cyano propyl column, the trifluorpropyl column, the substituted polysiloxane column, or the combination thereof.

24. The method of any one of claims 16 to the immediately preceding claim, wherein the introducing of step c) includes introducing the sample with a carrier gas selected from the group consisting of nitrogen, helium, and combinations thereof.

25. The method of any one of claims 16 to the immediately preceding claim, wherein the identifying of step d) includes comparing the gas chromatography report to a reference report.

26. The method of any one of claims 16 to the immediately preceding claim, wherein the adding of step a) includes adding the gas chromatography marker in an amount necessary to provide the non-pyrrolidinone nitrogen-containing compound in the subset of the hydrocarbon fluids in an amount of between 0.1 ppm and 500 ppm.

27. The method of any one of claims 16 to the immediately preceding claim, the method further comprising:

e) adding a spectroscopic marker to the subset of the hydrocarbon fluids in circulation within the market;

f) spectroscopically analyzing at least a second portion of the sample of one of the hydrocarbon fluids in circulation within the market, thereby resulting in a spectroscopic report of the sample; and

~~g) identifying the presence or absence of the spectroscopic marker in the sample using the spectroscopic report, thereby identifying whether the sample is from within or without the subset of hydrocarbon fluids.~~

~~28. The method of claim 27, wherein the spectroscopically analyzing of step f) includes conducting fluorescence spectroscopy, UV-Vis spectroscopy, Raman spectroscopy, near infrared spectroscopy, or a combination thereof.~~

~~29. The method of claim 27 or 28, wherein the identifying of step g) includes comparing the spectroscopic report to a reference spectrum.~~

~~30. The method of any one of claims 27 to the immediately preceding claim, wherein the adding of step e) includes adding the spectroscopic marker to the subset of the hydrocarbon fluids in an amount of between 0.1 ppm and 500 ppm.~~

~~31.~~ 18. A method of identifying marked hydrocarbon fluids that have been laundered, wherein unlaundered marked hydrocarbon fluids contain a gas chromatography marker and a spectroscopic marker, the gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound, wherein the non-pyrrolidinone nitrogen-containing compound is a core structure with zero, one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length, wherein the core structure is pyrrole, pyrazole, pyrazolone, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, piperidone, piperidine, piperazine, pyrazine, pyridazinone, imidazole, imidazolidone, oxazole, oxazoline, or oxazolidine, the non-pyrrolidinone nitrogen-containing compound and the spectroscopic marker are different chemical entities, the method comprising:

a) introducing a first portion of a hydrocarbon fluid sample that is suspecting of having been laundered into a gas chromatography system, thereby resulting in a gas chromatography report of the hydrocarbon fluid sample;

b) spectroscopically analyzing a second portion of the hydrocarbon fluid sample, thereby resulting in a spectroscopic report of the hydrocarbon fluid sample;

c) identifying the presence or absence of the gas chromatography marker using the gas chromatography report and identifying the presence or absence of the spectroscopic marker using the spectroscopic report; and

d) based on the identifying of step c):

if the gas chromatography marker and the spectroscopic marker are identified as present, then indicating that the hydrocarbon fluid sample is marked and unlaundered;

if the gas chromatography marker is identified as present and the spectroscopic marker is identified as absent, then indicating that the hydrocarbon fluid sample is marked and laundered; and

if the gas chromatography marker and the spectroscopic marker are identified as absent, then indicating the hydrocarbon fluid is unmarked.

~~32. The method of claim 31, wherein the gas chromatography system is a gas chromatography with nitrogen phosphorus detector (GC-NPD) system and step a) is introducing the first portion into the GC-NPD system.~~

~~33. The method of claim 32, wherein the GC-NPD system includes a flame thermionic detector or an alkali flame-ionization detector.~~

~~34. The method of claim 32 or 33, wherein the gas chromatography report resulting from step a) includes an intensity value that is proportional to an amount of nitrogen or phosphorus in the sample.~~

~~35. The method of claim 34, wherein the intensity is time-variable as a function of elution times of components of the sample.~~

~~36. The method of claim 35, wherein the identifying the presence or absence or the gas chromatography marker portion of step c) includes monitoring the intensity value at one or more predetermined elution times.~~

~~37. The method of any one of claims 31 to the immediately preceding claim, wherein the gas chromatography system is a gas chromatography-mass spectrometry (GC-MS) system, a gas chromatography-Hall electrolytic conductivity detector (GC-HECD) system, a gas chromatography-flame ionization detector (GC-FID) system, a gas chromatography-electron capture detector (GC-ECD) system, a gas chromatography-photoionization detector (GC-PID) system, or a combination thereof, and step a) is introducing the first portion into the GC-MS system, the GC-HECD system, the GC-FID system, the GC-ECD system, the GC-PID system, or the combination thereof.~~

~~38. The method of any one of claims 31 to the immediately preceding claim, wherein the gas chromatography system includes a fused silica column and the introducing of step a) includes introducing the sample into the fused silica column.~~

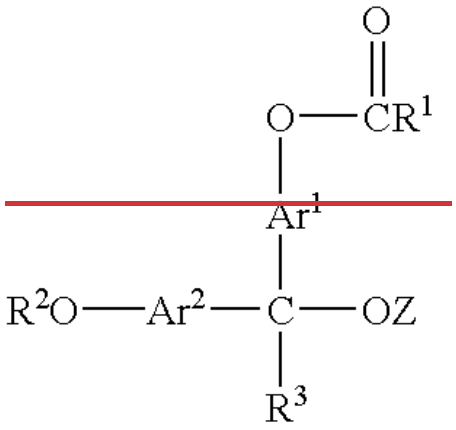
~~39. The method of any one of claims 31 to the immediately preceding claim, wherein the introducing of step a) includes introducing the sample with a carrier gas selected from the group consisting of nitrogen, helium, and combinations thereof.~~

40. The method of any one of claims 31 to the immediately preceding claim, wherein the identifying the presence or absence of the gas chromatography marker portion of step c) includes comparing the gas chromatography report to a reference report.

41. The method of any one of claims 31 to the immediately preceding claim, wherein the spectroscopically analyzing of step b) includes conducting fluorescence spectroscopy, UV-Vis spectroscopy, Raman spectroscopy, near infrared spectroscopy, or a combination thereof.

42. The method of any one of claims 31 to the immediately preceding claim, wherein the identifying the presence or absence of the spectroscopic marker portion of step c) includes comparing the spectroscopic report to a reference spectrum.

43. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is:



wherein Ar^1 and Ar^2 each independently represent a substituted or unsubstituted phenylene group or a substituted or unsubstituted naphthylene group; R^1 represents a straight or branched chain alkyl group having 1 to 22 carbon atoms; R^2 represents a hydrogen atom or a group of the formula $C(O)R^4$ where R^4 is a hydrogen atom or a straight or branched chain alkyl group having 1 to 22 carbon atoms; R^3 represents a hydrogen atom, a straight or branched chain alkyl group having 1 to 12 carbon atoms, a straight or branched chain alkoxy group having 1 to 12 carbon atoms, a hydroxyl group, a substituted or unsubstituted phenyl group or a substituted or unsubstituted naphthyl group; and Z represents a hydrogen atom or a group of atoms that combine with Ar^2 or R^3 to form a lactone ring.

44. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is a blue dye, a red dye, or a yellow dye.

45. The method of claim 44, wherein the spectroscopic marker is Solvent Red 164 or Solvent Yellow 124.

~~46. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is a phthalein.~~

~~47. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is a phthalein dibutyrate.~~

~~48. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is a phthalein ester.~~

~~49. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is selected from the group consisting of fluorescein dibutyrate, cresolphthalein, o-cresolphthalein dibutyrate, and thymolphthalein.~~

~~50. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is selected from the group consisting of cresolphthalein dibutyrate ester, cresolphthalein monobutyrate ester, cresolphthalein diisopropylate ester, cresolphthalein di-n-propylate ester, cresolphthalein dihexanoate ester, cresolphthalein dipentanoate ester, and cresolphthalein dilaurate ester.~~

~~51. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is selected from the group consisting of naphtholphthalein dibutyrate ester, thymolphthalein dibutyrate ester, and thymolphthalein dipropanoate ester.~~

~~52. The method of any one of claims 12 to 15 and 27 to 42, wherein the spectroscopic marker is selected from the group consisting of sec-butylphenolphthalein dibutyrate ester and di-sec-butylphenolphthalein dibutyrate ester.~~

~~53. The method of any one of the preceding claims, wherein the non-pyrrolidinone nitrogen-containing compound includes two or more nitrogen atoms per compound.~~

~~54. The method of any one of the preceding claims, wherein the non-pyrrolidinone nitrogen-containing compound includes three, four, five, six, seven, eight, nine, ten, or more nitrogen atoms per compound.~~

~~55. The method of any one of the preceding claims, wherein the non-pyrrolidinone nitrogen-containing compound includes one, two, or three alkyl or alkenyl side chains of 1 to 12 carbon atoms in length.~~

~~56. The method of any one of the preceding claims, wherein the non-pyrrolidinone nitrogen-containing compound is selected from the group consisting of a pyrrole, a pyrazole, a pyrazolone, a pyridine, a pyridazine, a pyrimidine, a pyrroline, a pyrrolidine, a piperidone, a piperidine, a piperazine, a pyrazine, a pyridazinone, an imidazole, an imidazolidone, an oxazole, an oxazoline, an oxazolidine, a tertiary amine, or a combination thereof.~~

~~57. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrrole.~~

~~58. The method of claim 57, wherein the pyrrole is 1-methylpyrrole.~~

~~59. The method of claim 57, wherein the pyrrole is 1-benzylpyrrole.~~

~~60. The method of claim 57, wherein the pyrrole is 1-phenylpyrrole.~~

~~61. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrazole.~~

~~62. The method of claim 61, wherein the pyrazole is 1,3,5-trimethylpyrazole.~~

~~63. The method of claim 61, wherein the pyrazole is 1-phenylpyrazole.~~

~~64. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrazolone.~~

~~65. The method of claim 64, wherein the pyrazolone is 3-methyl-1-phenyl-pyrazolone.~~

~~66. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyridine.~~

~~67. The method of claim 66, wherein the pyridine is 2-propylpyridine.~~

~~68. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyridazine.~~

~~69. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrimidine.~~

~~70. The method of claim 69, wherein the pyrimidine is 4-methylpyrimidine.~~

~~71. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrroline.~~

~~72. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrrolidine.~~

~~73. The method of claim 72, wherein the pyrrolidine is N-butylpyrrolidine.~~

~~74. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the piperidone.~~

~~75. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the piperidine.~~

~~76. The method of claim 75, wherein the piperidine is 1-methylpiperidine.~~

~~77. The method of claim 75, wherein the piperidine is 1-ethylpiperidine.~~

~~78. The method of claim 75, wherein the piperidine is 1-ethyl-3-methylpiperidine.~~

~~79. The method of claim 75, wherein the piperidine is 1-propyl-4-piperidine.~~

~~80. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the piperazine.~~

~~81. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyrazine.~~

~~82. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the pyridazinone.~~

~~83. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the imidazole.~~

~~84. The method of claim 83, wherein the imidazole is 1-butylimidazole.~~

~~85. The method of claim 83, wherein the imidazole is 2-methylimidazole.~~

~~86. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the imidazolidone.~~

~~87. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the oxazole.~~

~~88. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the oxazoline.~~

~~89. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the oxazolidine.~~

~~90. The method of claim 56, wherein the non-pyrrolidinone nitrogen-containing compound is the tertiary amine.~~

~~91. The method of claim 90, wherein the tertiary amine is trioctylamine.~~

92. A marker composition comprising:

a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound; and

a solvent.

93. The marker composition of claim 92, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the solvent is present in an amount by weight of between 1% and 99%.

94. The marker composition of claim 92, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the solvent is present in an amount by weight of between 25% and 75%.

95. The marker composition of claim 92, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the solvent is present in an amount by weight of between 40% and 60%.

96. The marker composition of claim 92, the marker composition consisting essentially of the gas chromatography marker and the solvent.

97. The marker composition of claim 96, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the solvent is present in an amount by weight of between 1% and 99%.

98. The marker composition of claim 96, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the solvent is present in an amount by weight of between 25% and 75%.

99. The marker composition of claim 96, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the solvent is present in an amount by weight of between 40% and 60%.

100. The marker composition of claim 92, the marker composition consisting of the gas chromatography marker and the solvent.

101. The marker composition of claim 100, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the solvent is present in an amount by weight of between 1% and 99%.

102. The marker composition of claim 100, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the solvent is present in an amount by weight of between 25% and 75%.

~~103. The marker composition of claim 100, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the solvent is present in an amount by weight of between 40% and 60%.~~

~~104. The marker composition of claim 92, the marker composition further comprising a spectroscopic marker.~~

~~105. The marker composition of claim 104, wherein the gas chromatography marker is present in an amount by weight of between 10% and 85%, the spectroscopic marker is present in an amount by weight of between 5% and 80%, and the solvent is present in an amount by weight of between 10% and 85%.~~

~~106. The marker composition of claim 104, wherein the gas chromatography marker is present in an amount by weight of between 20% and 70%, the spectroscopic marker is present in an amount by weight of between 10% and 50%, and the solvent is present in an amount by weight of between 20% and 70%.~~

~~107. The marker composition of claim 104, wherein the gas chromatography marker is present in an amount by weight of between 25% and 60%, the spectroscopic marker is present in an amount by weight of between 15% and 25%, and the solvent is present in an amount by weight of between 25% and 60%.~~

~~108. The marker composition of claim 104, the marker composition consisting essentially of the gas chromatography marker, the spectroscopic marker, and the solvent.~~

~~109. The marker composition of claim 105, wherein the gas chromatography marker is present in an amount by weight of between 10% and 85%, the spectroscopic marker is present in an amount by weight of between 5% and 80%, and the solvent is present in an amount by weight of between 10% and 85%.~~

~~110. The marker composition of claim 105, wherein the gas chromatography marker is present in an amount by weight of between 20% and 70%, the spectroscopic marker is present in an amount by weight of between 10% and 50%, and the solvent is present in an amount by weight of between 20% and 70%.~~

~~111. The marker composition of claim 105, wherein the gas chromatography marker is present in an amount by weight of between 25% and 60%, the spectroscopic marker is present in an amount by weight of between 15% and 25%, and the solvent is present in an amount by weight of between 25% and 60%.~~

~~112. The marker composition of claim 104, the marker composition consisting of the gas chromatography marker, the spectroscopic marker, and the solvent.~~

113. The marker composition of claim 112, wherein the gas chromatography marker is present in an amount by weight of between 10% and 85%, the spectroscopic marker is present in an amount by weight of between 5% and 80%, and the solvent is present in an amount by weight of between 10% and 85%.

114. The marker composition of claim 112, wherein the gas chromatography marker is present in an amount by weight of between 20% and 70%, the spectroscopic marker is present in an amount by weight of between 10% and 50%, and the solvent is present in an amount by weight of between 20% and 70%.

115. The marker composition of claim 112, wherein the gas chromatography marker is present in an amount by weight of between 25% and 60%, the spectroscopic marker is present in an amount by weight of between 15% and 25%, and the solvent is present in an amount by weight of between 25% and 60%.

116. The marker composition of any one of claims 92 to 115, wherein the solvent is selected from the group consisting of petroleum naphtha, petroleum naphtha, an alcohol, a glycol ether, dimethyl formamide, dimethyl sulfoxide, xylene, toluene, acetone, ethyl acetate, a petroleum product, and combinations thereof.

117. The marker composition of any one of claims 92 to 115, wherein the solvent is a mixture of petroleum napththa and fuel additives.

118. A marker composition comprising:

a gas chromatography marker comprising a non-pyrrolidinone nitrogen-containing compound; and

a spectroscopic marker.

119. The marker composition of claim 118, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the spectroscopic marker is present in an amount by weight of between 1% and 99%.

120. The marker composition of claim 118, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the spectroscopic marker is present in an amount by weight of between 25% and 75%.

121. The marker composition of claim 118, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the spectroscopic marker is present in an amount by weight of between 40% and 60%.

122. The marker composition of claim 118, the marker composition consisting essentially of the gas chromatography marker and the spectroscopic marker.

~~123. The marker composition of claim 122, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the spectroscopic marker is present in an amount by weight of between 1% and 99%.~~

~~124. The marker composition of claim 122, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the spectroscopic marker is present in an amount by weight of between 25% and 75%.~~

~~125. The marker composition of claim 122, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the spectroscopic marker is present in an amount by weight of between 40% and 60%.~~

~~126. The marker composition of claim 118, the marker composition consisting of the gas chromatography marker and the spectroscopic marker.~~

~~127. The marker composition of claim 126, wherein the gas chromatography marker is present in an amount by weight of between 1% and 99% and the spectroscopic marker is present in an amount by weight of between 1% and 99%.~~

~~128. The marker composition of claim 126, wherein the gas chromatography marker is present in an amount by weight of between 25% and 75% and the spectroscopic marker is present in an amount by weight of between 25% and 75%.~~

~~129. The marker composition of claim 126, wherein the gas chromatography marker is present in an amount by weight of between 40% and 60% and the spectroscopic marker is present in an amount by weight of between 40% and 60%.~~

~~130. The marker composition of any one of claims 92 to the immediately preceding claim, wherein the marker composition is nonaqueous.~~

~~131. The marker composition of any one of claims 92 to the immediately preceding claim, wherein adding the marker composition to a hydrocarbon fluid in an amount of 500 ppm of the non-pyrrolidinone nitrogen-containing compound results in a marked hydrocarbon fluid that, when introduced to a gas chromatography system, produces a gas chromatography signal that is distinguishable from a reference gas chromatography signal for an unmarked hydrocarbon fluid.~~

~~132. The marker composition of any one of claims 92 to the immediately preceding claim, wherein adding the marker composition to a hydrocarbon fluid in an amount of 50 ppm of the non-pyrrolidinone nitrogen-containing compound results in a marked hydrocarbon fluid that, when introduced to a gas chromatography system, produces a gas chromatography signal that is distinguishable from a reference gas chromatography signal for an unmarked hydrocarbon fluid.~~

133. The marker composition of any one of claims 92 to the immediately preceding claim, wherein adding the marker composition to a hydrocarbon fluid in an amount of 5 ppm of the non-pyrrolidinone nitrogen-containing compound results in a marked hydrocarbon fluid that, when introduced to a gas chromatography system, produces a gas chromatography signal that is distinguishable from a reference gas chromatography signal for an unmarked hydrocarbon fluid.

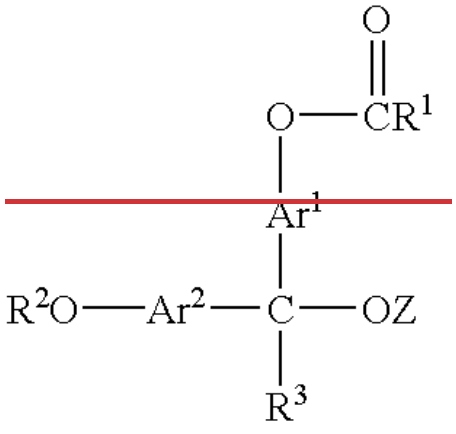
134. The marker composition of any one of claims 131 to 133, wherein the gas chromatography system is a gas chromatography with nitrogen phosphorus detector system and the gas chromatography signal is a gas chromatography with nitrogen phosphorus detector signal.

135. The marker composition of any one of claims 92 to the immediately preceding claim, wherein the gas chromatography marker consists essentially of the non-pyrrolidinone nitrogen-containing compound.

136. The marker composition of any one of claims 92 to the immediately preceding claim, wherein the gas chromatography marker consists of the non-pyrrolidinone nitrogen-containing compound.

137. The marker composition of any one of claims 92 to claim 136, wherein the non-pyrrolidinone nitrogen-containing compound as claimed in any one of claims 55 to 91.

138. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is:



wherein Ar^1 and Ar^2 each independently represent a substituted or unsubstituted phenylene group or a substituted or unsubstituted naphthylene group; R^1 represents a straight or branched chain alkyl group having 1 to 22 carbon atoms; R^2 represents a hydrogen atom or a group of the formula $C(O)R^4$ where R^4 is a hydrogen atom or a straight or branched chain alkyl group having 1 to 22 carbon atoms; R^3 represents a hydrogen atom, a straight or

~~branched chain alkyl group having 1 to 12 carbon atoms, a straight or branched chain alkoxy group having 1 to 12 carbon atoms, a hydroxyl group, a substituted or unsubstituted phenyl group or a substituted or unsubstituted naphthyl group; and Z represents a hydrogen atom or a group of atoms that combine with Ar^2 or R^3 to form a lactone ring.~~

~~139. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is a blue dye, a red dye, or a yellow dye.~~

~~140. The marker composition of claim 139, wherein the spectroscopic marker is Solvent Red 164 or Solvent Yellow 124.~~

~~141. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is a phthalein.~~

~~142. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is a phthalein dibutyrate.~~

~~143. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is a phthalein ester.~~

~~144. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is selected from the group consisting of fluorescein dibutyrate, cresolphthalein, o-cresolphthalein dibutyrate, and thymolphthalein.~~

~~145. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is selected from the group consisting of cresolphthalein dibutyrate ester, cresolphthalein monobutyrate ester, cresolphthalein diisopropylate ester, cresolphthalein di-n-propylate ester, cresolphthalein dihexanoate ester, cresolphthalein dipentanoate ester, and cresolphthalein dilaurate ester.~~

~~146. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is selected from the group consisting of naphtholphthalein dibutyrate ester, thymolphthalein dibutyrate ester, and thymolphthalein dipropanoate ester.~~

~~147. The marker composition of any one of claims 104 to 137, wherein the spectroscopic marker is selected from the group consisting of sec-butylphenolphthalein dibutyrate ester and di-sec-butylphenolphthalein dibutyrate ester.~~

~~148. A marked hydrocarbon fluid comprising:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 92 to 147 in an amount sufficient to provide a concentration of the non-pyrrolidinone nitrogen-containing compound in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~149. A marked hydrocarbon fluid consisting essentially of:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 92 to 147 in an amount sufficient to provide a concentration of the non-pyrrolidinone nitrogen-containing compound in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~150. A marked hydrocarbon fluid consisting of:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 92 to 147 in an amount sufficient to provide a concentration of the non-pyrrolidinone nitrogen-containing compound in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~151. A marked hydrocarbon fluid comprising:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 104 to 147 in an amount sufficient to provide a concentration of the spectroscopic marker in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~152. A marked hydrocarbon fluid consisting essentially of:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 104 to 147 in an amount sufficient to provide a concentration of the spectroscopic marker in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~153. A marked hydrocarbon fluid consisting of:~~

~~a hydrocarbon fluid;~~

~~the marker composition of any one of claims 104 to 147 in an amount sufficient to provide a concentration of the spectroscopic marker in the marked hydrocarbon fluid of between 0.1 ppm and 500 ppm.~~

~~154. The marked hydrocarbon fluid of any one of claims 148 to 153, wherein the hydrocarbon fluid is selected from the group consisting of a petroleum-derived liquid hydrocarbon, gasoline, gasohol, diesel fuel, a petroleum-derived solvent, a petroleum-derived~~

lubricant, a hydraulic fluid, kerosene, jet fuel, heating oil, bunker fuel, and combinations thereof.

155. A kit comprising:

the marker composition of any one of claims 92 to 147; and

a reference gas chromatography report for the non-pyrrolidinone nitrogen-containing compound.

156. A kit comprising:

the marker composition of any one of claims 104 to 147; and

a reference spectroscopic report for the spectroscopic marker.

157. A system for identifying hydrocarbon fluids marked with a gas chromatography marker including a non-pyrrolidinone nitrogen-containing compound, the system comprising:

a gas chromatography with nitrogen phosphorus detector (GC-NPD) system; and

a computer having a processor and a memory, the memory having stored thereon a reference gas chromatography report for the non-pyrrolidinone nitrogen-containing compound and instructions that, when executed by the processor, cause the processor to receive a gas chromatography report from the GC-NPD system and identify the presence or absence of the gas chromatography marker based on a comparison with the reference gas chromatography report.

158. The system of claim 157, the GC-NPD system comprising a flame thermionic detector of an alkali flame-ionization detector.

159. The system of claim 157 or 158, the GC-NPD system comprising a fused silica gas chromatography column.

160. The system of any one of claims 157 to 159, the GC-NPD system further comprising a carrier gas source configured to deliver nitrogen or helium as a carrier gas.

161. The system of any one of claims 157 to 160, the hydrocarbon fluids further marked with a spectroscopic marker, the system further comprising: a spectroscopy system.

162. The system of claim 161, the memory having stored thereon a reference spectroscopy report for the spectroscopic marker and instructions that, when executed by the processor, cause the processor to receive a spectroscopy report from the spectroscopy system and identify the presence or absence of the spectroscopic marker based on a comparison with the reference spectroscopy report.

~~163. The system of claim 161 or 162, wherein the spectroscopy system is a fluorescence spectroscopy system, a UV-Vis spectroscopy system, or a Raman spectroscopy system.~~