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

[0008] 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] 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,

[0010] 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 ina 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. 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] 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] 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] 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] 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] 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 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 example of the disclosure. Such example does not necessarily represent the full scope of the disclosure, however, and reference is made therefore to the claims and herein for interpreting the scope of the disclosure.

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;

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, 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 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 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 claim 1, wherein the identifying of step b) includes comparing the gas chromatography report to a reference report.

11. The method of 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 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.

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

14. The method of claim 1, wherein the spectroscopic marker is present in the hydrocarbon fluid in an amount of between 0.1 ppm and 500 ppm.

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;

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.

16. The method of claim 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.

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

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.