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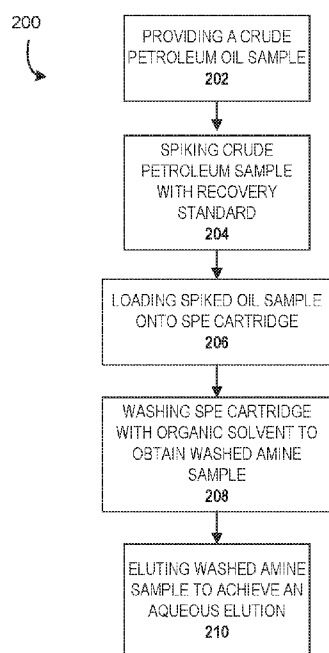


FIG. 2

(57) Abstract: A method for sample preparation to quantify amines, the method comprising: (a) providing a hydrocarbon sample, wherein the hydrocarbon sample comprises a known standard; (b) loading the hydrocarbon sample onto a solid phase extraction (SPE) cartridge; (c) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and (d) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis. A method for sample preparation to quantify amines, the method comprising: (a) providing a crude petroleum oil sample; (b) spiking the crude petroleum oil sample with a recovery standard to provide a spiked oil sample; (c) loading the spiked oil sample onto a solid phase extraction (SPE) cartridge; (d) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and (e) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis.

EXTRACTION OF AMINES FROM HYDROCARBONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Appl. Serial No. 62/588,557, filed November 20, 2017, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention relates to methods for sample preparation to quantify amines, and more particularly, to a method for sample preparation for quantifying amines in oils using solid phase extraction techniques for improved accuracy, throughput, and robustness.

BACKGROUND OF THE INVENTION

[0003] Amines represent a broad class of nitrogen containing organic compounds which are found biogenic in petroleum and also used ubiquitously as chemical treatment solutions in the hydrocarbon processing industry. Additionally, amines can react or degrade to produce an array of similar secondary structures. It is well known that amines can have negative fouling and corrosion effects towards process equipment. Therefore, the amine status of process streams is often an essential piece of information for solving problems in critical areas of a refinery.

[0004] Sample preparation is a critical step in determining amines in oils to remove interfering matrix and enable robust instrumental analysis. It is not technically feasible to analyze amines directly in hydrocarbons with the necessary robustness, sensitivity, and selectivity. For example, direct analysis on a crude petroleum sample can damage or destroy analytical equipment and includes classes of compounds that cannot easily be analyzed. Most native oil samples examined show very low, or insignificant levels of amines (total amines <5 µg/mL). This makes it challenging to know if these samples contain truly low levels, or if the method utilized to quantify amines is not able to capture “native amines” (i.e., unknown losses of target amines).

[0005] Further, amines are believed to have limited stability in oils, which can lead to inaccurate quantitation if sample handling is not appropriate. There are several known sources of potential amine loss including: surface adsorption to glass surfaces, evaporation, precipitation or salting out, reaction with matrix components, encapsulation in emulsions, and partitioning out of the bulk solution into trace amounts of water. Additionally, other unknown sources of amine loss may exist given the complexity and reactive nature of hydrocarbon samples. As such, sampling and handling procedures play an essential role in the accuracy of amine quantitation.

[0006] In conventional liquid extraction processes, problems arise due to the complexity of hydrocarbon phases. For instance, the possibility of emulsions or micelles can insulate amines from the extraction solvent, which can lead to incomplete recovery. Additionally, the isolated extract contains a significant amount of hydrocarbon impurities that can negatively impact analytical processes and equipment. Other factors that lead to problems include, but are not limited to, (1) amine loss or reaction due to instability during the liquid extraction process, (2) non-compatible sample matrix for the analytical method, (3) signal suppression in analytical instruments, (4) poor reproducibility and sensitivity, or (5) other unknown factors.

[0007] Alternative sample preparations strategies often include filtration, asphaltene precipitation, centrifugation, or dilution. However, these common approaches do not provide a sufficiently clean extract for robust, sensitive, and precise analytical measurement. For instance, methods for asphaltene precipitation and sample dilution compromise the sensitivity by reducing the concentration of target analytes. Methods for centrifugation or filtration do not remove enough hydrocarbon impurities to enable robust chromatographic analyses.

[0008] Therefore, what is needed in the art is a sample preparation method or procedure for isolating amines from hydrocarbons (i.e. crude oil and refinery cuts), to improve the reliability and accuracy of the quantitative results.

SUMMARY OF THE INVENTION

[0009] The present invention provides a method for sample preparation to quantify amines is provided. The method comprises: (a) providing a hydrocarbon sample,

wherein the hydrocarbon sample comprises a known standard; (b) loading the hydrocarbon sample onto a solid phase extraction (SPE) cartridge; (c) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and (d) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis.

[0010] In one embodiment, the hydrocarbon sample is a crude petroleum sample. In another embodiment, the hydrocarbon sample is selected from the group consisting of a refinery fluid, refinery cuts, a production fluid, drilling fluids, completion fluids, production fluids, crude oil, feed streams to desalting units, outflow from desalting units, refinery heat transfer fluids, gas scrubber fluids, refinery unit feed streams, refinery intermediate streams, finished product streams, and combinations thereof.

[0011] In some embodiment, the organic solvent comprises toluene, acetone, isopropanol, methanol, acetonitrile, benzene, butanol, ethanol, heptane, hexane, pentane, tetrahydrofuran, n-propanol, xylene, dichloromethane, ethyl acetate, or combinations thereof. In some embodiments, the acidified solution includes a 50%methanol/50%water solution, acetonitrile, ethanol, isopropanol, water, or combinations thereof. In some embodiments, the aqueous elution comprising amines.

[0012] In some embodiments, the aqueous elution comprises amines selected from the group consisting of monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine.

[0013] In some embodiments, the analysis occurs at the point of sampling. In some embodiments, approximately 50-150% of amines are recovered. In other embodiments, approximately 80-120% of amines are recovered.

[0014] In one exemplary embodiment, the present invention further provides a method for sample preparation to quantify amines. The method comprises: (a) providing a crude petroleum oil sample; (b) spiking the crude petroleum oil sample with a recovery standard to provide a spiked oil sample; (c) loading the spiked oil sample onto a solid phase extraction (SPE) cartridge; (d) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and (e) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis.

[0015] In one embodiment, the spiked oil sample provides for approximately 50-150% recovery of amines. In another embodiment, the spiked oil sample provides for approximately 80-120% recovery of amines.

[0016] In one embodiment, the recovery standard is dibutylamine, monoethanolamine, monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, dimethylaminopropylamine, isotope labelled surrogates of these amine structures (ex. monoethanolamine-d4), or mixtures thereof. In one embodiment, the organic solvent comprises toluene, acetone, isopropanol, methanol, acetonitrile, benzene, butanol, ethanol, heptane, hexane, pentane, tetrahydrofuran, n-propanol, xylene, dichloromethane, ethyl acetate, or combinations thereof.

[0017] In one embodiment, the SPE cartridge is a silica-based cartridge. In other embodiments, the SPE cartridge is a diol cartridge, cyano cartridge, amine diamine, or aminopropyl cartridge, magnesium silicate cartridge, alumina cartridge, or cation exchange cartridge.

[0018] In one embodiment, the acidified solution includes a 50%methanol/50%water solution, acetonitrile, ethanol, isopropanol, water, or combinations thereof. In one embodiment, the aqueous elution comprising amines. In other embodiments, the aqueous elution comprises amines selected from the group consisting of monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings, wherein:

[0020] FIG. 1 is a flowchart illustrating an exemplary method in accordance with an illustrative embodiment of the disclosed system and method;

[0021] FIG. 2 is a flowchart illustrating an exemplary method in accordance with an illustrative embodiment of the disclosed system and method;

[0022] FIGS. 3A-3C depict various oil samples and spiked amines samples used in solid phase extractions used in accordance with an illustrative embodiment of the disclosed system and method;

[0023] FIG. 4 is a chart depicting the average amine recovery from an aqueous control sample in accordance with an illustrative embodiment of the disclosed system and method;

[0024] FIG. 5 is a chart depicting the average amine recovery from all oil sample types in accordance with an illustrative embodiment of the disclosed system and method; and

[0025] FIG. 6 is a chart depicting the average amount of amine recovery from a sample in accordance with an illustrative embodiment of the disclosed system and method.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. The endpoints of all ranges reciting the same characteristic are independently combinable and inclusive of the recited endpoint. All references are incorporated herein by reference.

[0027] The terms “comprises”, “comprising”, “includes”, “including”, “has”, “having”, “containing”, “contains” or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article or apparatus that comprises a list of elements is not necessarily limited to only those elements, but may include other elements not expressly listed or inherent to such process, method, article or apparatus.

[0028] The present technology generally provides a method for a sample preparation procedure for quantifying amines in oils using solid phase extraction techniques for improved accuracy, throughput, and robustness. The method further provides for isolating amines from hydrocarbons by using solid phase extraction (SPE) techniques. This method improves accuracy by mitigating several sources of potential amine loss, enhancing robustness by generating a cleaner, more concentrated extract, and

increasing sample throughput by allowing extraction steps to be conducted simultaneously on, for example, 12 or 24 samples. Although SPE is a well-known sample preparation method, it has only been sparingly applied to hydrocarbon samples (crude oil and refinery streams) for a handful of analytical targets. Often complex hydrocarbon samples are thought to be or determined to be incompatible with SPE due various factors including but not limited to: (1) saturation of binding sites to capture target analyte, (2) insufficient resolution of target analytes and matrix, (3) or clogging of SPE cartridges. Furthermore, amines are known to have particularly challenging chromatographic properties due to their small size and high polarity. Therefore, it was surprisingly found that a SPE material was capable of providing adequate retention without irreversibly absorbing the target amines compounds.

[0029] The disclosed system and methods describe a procedure which improves the accuracy of amine quantitation by mitigating potential losses during sample preparation. This is accomplished by rapidly extracting amines into a more stable environment without the need for complex equipment.

[0030] The present technology provides a method 100 for sample preparation to quantify amines. With reference to FIG. 1, a flowchart illustrating an exemplary method 100 comprises the steps of (a) providing a hydrocarbon sample, wherein the hydrocarbon sample comprises a known standard (step 102); (b) loading the hydrocarbon sample onto a solid phase extraction (SPE) cartridge (step 104); (c) washing the SPE cartridge with an organic solvent to obtain a washed amine sample (step 106); and (d) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis (step 108).

[0031] The present technology provides a method or procedure for sample preparation which improves the accuracy of amine quantitation by mitigating potential losses during sample preparation. By rapidly extracting amines into a more stable environment without the need for complex equipment, the accuracy of amine quantitation is improved. Thus, the present disclosed method reduces the time of extraction, mitigates potential surface adsorption losses, minimizes evaporative losses, prevents emulsions, and increases contact with the extraction media to improve the overall recovery and accuracy compared with state-of-the-art procedures.

[0032] While, for purposes of simplicity of explanation, the methodologies illustrated in FIGS. 1-2 are shown and described as a series of acts, it is to be understood and appreciated that the subject disclosure is not limited by the order of acts, as some acts may, in accordance with the disclosure, occur in a different order and/or concurrently with other acts from that shown and described herein. For example, those skilled in the art will understand and appreciate that a methodology could alternatively be represented as a series of interrelated states or events. Moreover, not all illustrated acts may be required to implement a methodology in accordance with the disclosure.

[0033] As shown in step 102, the method 100 comprises providing a hydrocarbon sample. In some embodiments, samples are obtained by transferring a portion of a process stream into a container, such that the amount collected is enough to represent a mean of the potential process fluid variations at that point in time. For instance, in some embodiments, 500 mL of crude oil might be collected at a refinery from an atmospheric tower pre-heater into a glass container. In other embodiments, at least 2 mL of crude oil may be collected.

[0034] In some embodiments, a known standard is added to the hydrocarbon sample to provide means to monitoring the process efficiency. Sample matrices can vary widely across the hydrocarbon processing industry; therefore, amine instability effects may also be equally variable. By monitoring the recovery of a known standard, the extraction process can be validated on a sample by sample basis. For example, in some embodiments, monoethanolamine-d4 (MEA-d4) was added to a sample aliquot by spiking it with a 50 µg/mL source standard prepared in tetrahydrofuran to give a final concentration of 5 µg/mL MEA-d4 in sample.

[0035] Contrary to other conventional sample preparation methods, in some embodiments, the present method is suitable for field environments and can be executed at the point of sampling. However, it should be understood by one skilled in the art that the present method may be executed (1) away from the point of sampling (e.g. in a laboratory), or (2) in multiple phases/locations (e.g. sample loading is conducted at point of sampling, and subsequent steps are carried out in a laboratory or elsewhere). However, as in some embodiments, immediate sample preparation in the field improves accuracy and does not require sample heating or extended sample storage periods (which worsens the stability of

target analytes, as required by other conventional methods). In some embodiments, sample extraction and/or analysis takes place in the field, can be automated, or achieved by online-analysis.

[0036] In some embodiments, the hydrocarbon sample is a crude petroleum sample. In some embodiments, the hydrocarbon sample is selected from the group consisting of a refinery fluid, refinery cuts, a production fluid, drilling fluids, completion fluids, production fluids, crude oil, feed streams to desalting units, outflow from desalting units, refinery heat transfer fluids, gas scrubber fluids, refinery unit feed streams, refinery intermediate streams, finished product streams, and combinations thereof.

[0037] As shown in step 104, the hydrocarbon sample is loaded onto a solid phase extraction (SPE) cartridge. Compared to liquid extractions, loading the hydrocarbon sample onto a SPE cartridge lessens certain instability effects (e.g. amine evaporation and reactivity), provides better separation of matrix and target analytes, and allows parallel processing of several samples without need for specialized equipment. In some embodiments, the present method employs solid phase extraction techniques to enable accurate, sensitive and robust analysis in the sample preparation.

[0038] In some embodiments, the hydrocarbon sample is loaded onto a pre-conditioned cartridge where a large portion of the sample components absorb to the solid phase packing. Pre-conditioning the SPE cartridge may include rinsing the solid phase packing with a liquid, which will eventually promote retention of target analytes. For example, in some embodiments, rinsing the SPE cartridge with 2 cartridge volumes of toluene improved recovery and precision while avoiding asphaltene precipitation.

[0039] In some embodiments, the solid phase extraction (SPE) cartridge is selected from the group consisting of diol, cyano, amine, diamine, aminopropyl, magnesium silicate, alumina, or cation exchange-type cartridges. In other embodiments, the SPE cartridge is a normal phase bonded silica or other adsorption medium. In some embodiments, Van der Waals, electrostatic, and/or hydrogen bonding forces are exploited to establish a strong yet reservable interaction between the target amines and solid phase packing. These forces can be fine-tuned by appropriate stationary and mobile phase selection. For instance, in some embodiments, a pH modifier (e.g. acid) was found to be

essential to disrupt the binding interactions between target amines and the solid phase in order to elute the amines in the final step.

[0040] As shown in step 106, the SPE cartridge is washed with an organic solvent to obtain a washed amine sample. The undesired hydrocarbons and nonpolar molecules are washed away using different organic solvents. Any hydrocarbons other than the target amines are undesirable because they can potentially foul downstream equipment or interfere with subsequent analytical testing. Therefore, the general rule holds that the cleaner the extract the more reliable and robust the analysis. In some embodiments, the optimal extent of the SPE washing phase was found to be highly dependent on the starting sample. In some embodiments, three rinse cycles with incremental polarity solvents, such as, but not limited to, toluene, acetone, and isopropanol, were used.

[0041] It should be understood that any organic solvent could be used to wash the SPE cartridge. In some embodiments, the organic solvent comprises toluene, acetone, isopropanol, methanol, acetonitrile, benzene, butanol, ethanol, heptane, hexane, pentane, tetrahydrofuran, n-propanol, xylene, dichloromethane, ethyl acetate, or combinations thereof.

[0042] As shown in step 108, the washed amine sample is subsequently eluted with an acidified solution to achieve an aqueous elution (i.e. eluates) for analysis. Amines may be eluted from the SPE cartridge by any known solvent or combination of solvents that allow proper resolution of various amine species as they elute from the column. In some embodiments, the acidified solution includes a 50%methanol/50%water solution, acetonitrile, ethanol, isopropanol, water, or combinations thereof. In some embodiments, the specific conditions can be fine-tuned by screening samples spiked with target amines of interest and evaluating which composition provides the highest recovery or best accuracy.

[0043] In some embodiments, the acidified solution is prepared between pH 2-4, in other embodiments, between pH 1-4, and in other embodiments, between pH 1-6. In such embodiments, the acidified solution comprises phosphoric acid, hydrochloric acid, sulfuric acid, acetic acid, nitric acid, nitrous acid, citric acid, carbonic acid, methanesulfonic acid, sulfonic acid, or combinations thereof.

[0044] The eluates can be identified and/or quantified using any suitable apparatus known in the art and used to identify and/or quantify each species. In some embodiments, apparatuses for ion chromatography, mass spectrometry, nuclear magnetic resonance, surface enhanced Raman scattering, ultra-violet spectrophotometry, fluorescence, conductivity, and combinations thereof can be used for identifying and/or quantifying the each species of interest.

[0045] The resultant aqueous elution comprises amines. In some embodiments, the aqueous elution comprises amines selected from the group consisting of monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine.

[0046] In some embodiments, the amount of known standard recovered (i.e., recovery standard) provides quantitative validation of the extraction efficiency on a sample by sample basis. This allows sample matrices prone to false negative interferences to be identified. For instance, certain hydrocarbon samples may be highly reactive or have extremely poor solubility for amines such that endogenous target amines may not be able to be recovered. These types of samples can be identified if using a recovery standard to monitor the extraction process which ultimately avoids misleading false negative results.

[0047] In some embodiments, the disclosed system and method recovers approximately 50-150% of amines. In other embodiments, the disclosed system and method recovers approximately 80-120% of amines.

[0048] The present invention further provides a method 200 for sample preparation to quantify amines. With reference to FIG. 2, a flowchart illustrating an exemplary method 200 comprises the steps of (a) providing a crude petroleum oil sample (step 202); (b) spiking the crude petroleum oil sample with a recovery standard to provide a spiked oil sample (step 204); (c) loading the spiked oil sample onto a solid phase extraction (SPE) cartridge (step 206); (d) washing the SPE cartridge with an organic solvent to obtain a washed amine sample (step 208); and (e) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis (step 210).

[0049] As shown in step 202, the method 200 comprises providing a crude petroleum oil sample. The present disclosed method allows for more accurate amine

recoveries by mitigating certain instability and/or encapsulation effects. Amines are reactive compounds and their reactivity is only enhanced by long sample storage periods, exposure to organic solvents, and at elevated temperatures. With conventional amine liquid extraction techniques, target amines are diluted since complete extractions (>90% total mass) require samples to be extracted in volumes greater than the initial sample volume. This dilution causes the amines contained therein to be lower than standard detection limits, thus resulting in worse sensitivity and precision.

[0050] As shown in step 204, the method 200 comprises spiking the crude petroleum oil sample with a recovery standard to provide a spiked oil sample. The recovery standard comprises known amount of target amines. By spiking the sample with a recovery standard, the overall process efficiency of the disclosed method is monitored. In some embodiments, the recovery standard is spiked into all oil samples prior to processing and is homogeneously distributed throughout each sample. This allows incompatible samples to be identified where either the sample matrix creates an unstable environment for amine targets or disrupts the extraction process in some manner. Thus, false negative results are avoided by monitoring all samples with a recovery standard.

[0051] In some embodiments, the recovery standard is introduced to provide quality assurance of each sample. In some embodiments, the recovery standard is dibutylamine, monoethanolamine, monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, dimethylaminopropylamine, isotope labelled surrogates of these amine structures (e.g. monoethanolamine-d4), or mixtures thereof.

[0052] In other embodiments, the recovery standard can be utilized as an internal standard to correct for random and systematic errors during sample preparation and analysis. In such embodiments, it can be assumed that the target analyte and internal standard behave identically, and the signal ratio of the two will remain constant to despite experimental errors which may occur.

[0053] In some embodiments, the spiked oil sample provides for approximately 50-150% recovery of amines. In other embodiments, the spiked oil sample provides for approximately 80-120% recovery of amines.

[0054] As shown in step 206, the method 200 comprises loading the spiked oil sample onto a solid phase extraction (SPE) cartridge. In some embodiments, the SPE cartridge is a silica-based cartridge. In other embodiments, the SPE cartridge is a diol, cyano, amine, diamine, aminopropyl, magnesium silicate, alumina, or cation exchange - type cartridge.

[0055] As shown in step 208, the method 200 further comprises washing the SPE cartridge with an organic solvent to obtain a washed amine sample. By washing the SPE cartridge, the amines of interest will be retained on the cartridge and interfering compounds will be washed away to waste. In some embodiments, the amines of interest include, but are not limited to, monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine. In some embodiments, the method is applicable to derivatives of these amines as well as other aliphatic and/or hydroxy amines.

[0056] As shown in step 210, the method 200 comprises eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis. In some embodiments, the aqueous elution, or clean amine extract, is obtained by eluting with an acidified water/methanol solution. These amines are then subsequently analyzed by a suitable instrumental analytical technique. Such analytical techniques include, but are not limited to, apparatuses for ion chromatography, mass spectrometry, nuclear magnetic resonance, surface enhanced Raman scattering, ultra-violet spectrophotometry, fluorescence, conductivity, and combinations thereof can be used for identifying and/or quantifying the each species of interest.

[0057] In order that those skilled in the art will be better able to practice the present disclosure, the following examples are given by way of illustration and not by way of limitation.

EXAMPLES

[0058] FIGS. 3A-3C describe an SPE validation experiment used for the presently disclosed method. Approximately 15ml of an oil sample was transferred to a plastic tube, (FIG. 3A). Subsequently, approximately 1µg/ml of various amines were

spiked into each sample (FIG. 3B). At the point of extraction, two additional amines were spiked into each sample, (FIG. 3C). This SPE validation experiment was replicated five times using solid phase extraction over a period of three days. FIG. 4 depicts the average amine recovery from an aqueous control sample. FIG. 5 depicts the average amine recovery from all oil types. The data demonstrates that amines are instable in oil samples and can quickly partition into other phases, for example, solid surfaces or water. FIG. 6 depicts the amine recovery from a diesel sample containing approximately 20 μ g of each amine. Sampling was obtained over a period of two days.

[0059] Further, it was determined that cyclohexylamine is fully eluted by methanol, and methoxypropylamine (MOPA) is at least partially eluted by methanol when utilizing the present disclosed method. All other amines were found to elute in 100% water with 10 mM phosphoric acid. The same result was obtained for toluene, diesel, and crude oil. It was shown that approximately 50% methanol/50% water with acid provided best elution results.

[0060] In the foregoing specification, the invention has been described with reference to specific embodiments thereof. It will be evident that various modifications and changes can be made to the methods and solvents of the invention without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative, rather than a restrictive sense. For example, specific reagents and proportions thereof falling within the claimed parameters, but not specifically identified or tried in particular compositions, are anticipated and expected to be within the scope of this invention

[0061] What is claimed is:

CLAIMS

1. A method for sample preparation to quantify amines, the method comprising:
 - (a) providing a hydrocarbon sample, wherein the hydrocarbon sample comprises a known standard;
 - (b) loading the hydrocarbon sample onto a solid phase extraction (SPE) cartridge;
 - (c) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and
 - (d) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis.
2. The method as recited in claim 1, wherein the hydrocarbon sample is a crude petroleum sample.
3. The method as recited in claim 1, wherein the hydrocarbon sample is selected from the group consisting of a refinery fluid, refinery cuts, a production fluid, drilling fluids, completion fluids, production fluids, crude oil, feed streams to desalting units, outflow from desalting units, refinery heat transfer fluids, gas scrubber fluids, refinery unit feed streams, refinery intermediate streams, finished product streams, and combinations thereof.
4. The method as recited in claim 1, wherein the organic solvent comprises toluene, acetone, isopropanol, methanol, acetonitrile, benzene, butanol, ethanol, heptane, hexane, pentane, tetrahydrofuran, n-propanol, xylene, dichloromethane, ethyl acetate, or combinations thereof.
5. The method as recited in claim 1, wherein the acidified solution includes a 50%methanol/50%water solution, acetonitrile, ethanol, isopropanol, water, or combinations thereof.
6. The method as recited in claim 1, wherein the aqueous elution comprising amines.

7. The method as recited in claim 1, wherein the aqueous elution comprises amines selected from the group consisting of monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine.
8. The method as recited in claim 1, wherein the analysis occurs at the point of sampling.
9. The method as recited in claim 1, wherein approximately 50-150% of amines are recovered.
10. The method as recited in claim 9, wherein approximately 80-120% of amines are recovered.
11. A method for sample preparation to quantify amines, the method comprising:
 - (a) providing a crude petroleum oil sample;
 - (b) spiking the crude petroleum oil sample with a recovery standard to provide a spiked oil sample;
 - (c) loading the spiked oil sample onto a solid phase extraction (SPE) cartridge;
 - (d) washing the SPE cartridge with an organic solvent to obtain a washed amine sample; and
 - (e) eluting the washed amine sample with an acidified solution to achieve an aqueous elution for analysis.
12. The method as recited in claim 11, wherein the spiked oil sample provides for approximately 50-150% recovery of amines.
13. The method as recited in claim 12, wherein the spiked oil sample provides for approximately 80-120% recovery of amines.

14. The method as recited in claim 11, wherein the recovery standard is dibutylamine, monoethanolamine, monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, dimethylaminopropylamine, isotope labelled surrogates, or mixtures thereof.
15. The method as recited in claim 11, wherein the organic solvent comprises toluene, acetone, isopropanol, methanol, acetonitrile, benzene, butanol, ethanol, heptane, hexane, pentane, tetrahydrofuran, n-propanol, xylene, dichloromethane, ethyl acetate, or combinations thereof.
16. The method as recited in claim 15, wherein the SPE cartridge is a silica-based cartridge.
17. The method as recited in claim 16, wherein the SPE cartridge is a diol, cyano, amine, diamine, aminopropyl, magnesium silicate, alumina, or cation exchange -type cartridge.
18. The method as recited in claim 11, wherein the acidified solution includes a 50%methanol/50%water solution acetonitrile, ethanol, isopropanol, water, or combinations thereof.
19. The method as recited in claim 11, wherein the aqueous elution comprising amines.
20. The method as recited in claim 11, wherein the aqueous elution comprises amines selected from the group consisting of monoethylamine, diethanolamine, dimethylethanolamine, methoxypropylamine, n-methylmorpholine, methylamine, aminoethoxyethanol (diglycolamine), cyclohexylamine, ethylenediamine, and dimethylaminopropylamine.

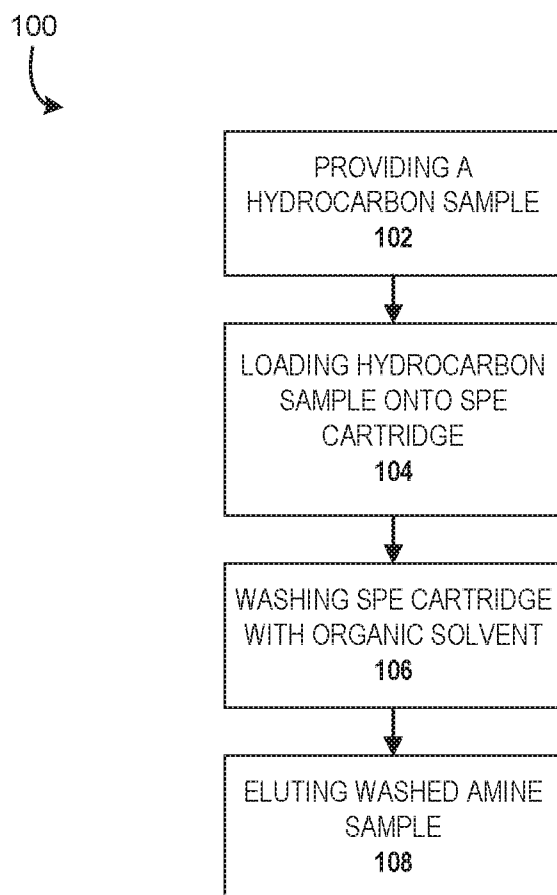


FIG. 1

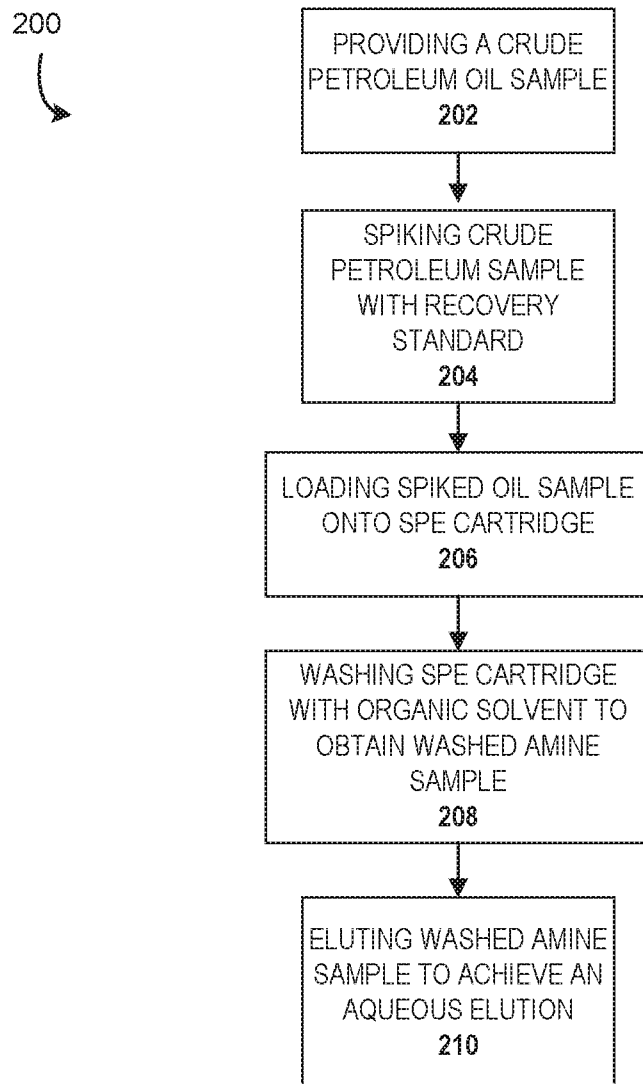


FIG. 2

Sample (15 mL Each)
01-Control (aqueous solution)
02-Raw Crude 1
03-Raw Crude 2
04-Desalted Crude 1
05-Desalted Crude 2
06-LVGO 1
07-LVGO 2
08-VAC Diesel 1
09-VAC Diesel 2
10-Light Straight Run Naphtha
11-Naphthta Product
12-Heavy Naphtha
13-4 Plat Feed

FIG. 3A

Amine	Target [C] (ug/mL)
CYCLO	1.3
DEA	0.5
DGA	1.6
DMAE	1.3
DMAPA	1.2
MEA	0.8
MOPA	0.9
NMM	1.5

FIG. 3B

Amine	Target [C] (ug/mL)
DBA	2.2
MEA-d4	2.5

FIG. 3C

	Amines Spiked in Sample on Day 1								Amines Added Prior to Sample Preparation	
Day	CYCLO	DEA	DGA	DMAE	DMAPA	MEA	MOPA	NMM	MEA-d4	DBA
1	97%	102%	100%	100%	98%	103%	100%	97%	97%	95%
2	103%	98%	100%	100%	102%	98%	100%	103%	103%	105%
3	104%	101%	108%	101%	108%	78%	54%	109%	89%	101%

FIG. 4

	Amines Spiked in Sample on Day 1								Amines Added Prior to Sample Preparation	
Day	CYCLO	DEA	DGA	DMAE	DMAPA	MEA	MOPA	NMM	MEA-d4	DBA
1	88%	65%	69%	90%	69%	71%	77%	104%	80%	83%
2	60%	49%	50%	90%	44%	51%	47%	104%	90%	89%
3	48%	60%	41%	89%	43%	40%	32%	42%	96%	91%

FIG. 5

Sampling Method	MEA	MA	DGA	MOPA	DMAPA
SPE Cartridge	0.5	1	0	0.2	0
Wet Filter	0.7	1.2	3	0.9	0.6

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/059305

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N1/40 G01N33/28
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 106 324 158 A (PETROCHINA CO LTD) 11 January 2017 (2017-01-11) paragraph [0009] - paragraphs [0024], [0071] ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

8 February 2019

Date of mailing of the international search report

22/02/2019

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/059305

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	XIAOHUI LI ET AL: "Characterization of Basic Nitrogen-Containing Compounds in the Products of Lube Base Oil Processing by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry", BULLETIN OF THE KOREAN CHEMICAL SOCIETY, vol. 35, no. 1, 20 January 2014 (2014-01-20), pages 165-172, XP055553509, KR ISSN: 0253-2964, DOI: 10.5012/bkcs.2014.35.1.165 page 165, LC "introduction, line 5-6" -----	1-20
A	JP H09 308803 A (AJINOMOTO KK) 2 December 1997 (1997-12-02) paragraphs [0042], [0046] -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/059305

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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JP H09308803	A	02-12-1997	NONE	
