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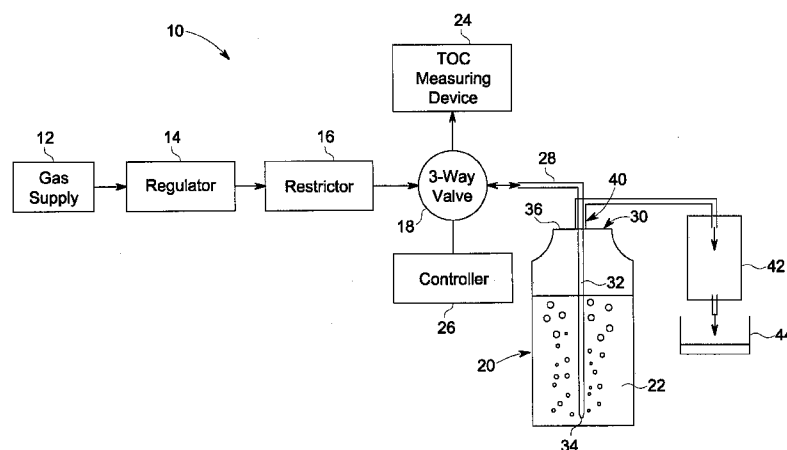


FIG. 1

(57) Abstract: A method for an in-vial sparging process and measuring process is provided. The method includes providing a vial having an aqueous sample contained therein. The aqueous sample is then acidified to convert the carbonate and bicarbonate to carbon dioxide (CO₂). A purge gas is then injected into the aqueous sample to perform an in-vial sparging process. A portion of the aqueous sample is then transferred to a TOC measuring device to measure the amount of total organic carbon in the sparged sample. The TOC measuring device then produces an output from that indicates the amount of total organic carbon within the aqueous sample after the in-vial sparging process.

METHOD AND APPARATUS FOR CARBON DIOXIDE REMOVAL IN AQUEOUS SAMPLE BY IN- VIAL SPARGING FOR TOC MEASUREMENT

FIELD OF THE INVENTION

[0001] This invention relates generally to the method and apparatus of sparging an aqueous sample so as to precisely measure the remaining total organic carbon (TOC).

BACKGROUND OF THE INVENTION

[0002] Total organic carbon (TOC) is a well-established water quality parameter that quantifies the overall concentration of organic substances, all of which are typically regarded as contaminants. In most water (or any other aqueous) samples, such as drinking water, raw water, wastewater, industrial process streams, and the like, the total carbon (TC) is the sum of the amount of total organic carbon (TOC) and the amount of inorganic carbon (IC) present in the sample. It is typically not analytically possible to measure only the amount of organic carbon when there is also inorganic carbon present in the sample. Thus, general measuring techniques measure the amount of total carbon in the sample, the amount of inorganic carbon in the sample, and then calculate the difference therebetween to determine the amount of organic carbon.

[0003] One potential problem regarding TOC analysis is where the concentration of IC is significantly greater than the concentration of TOC. For example, a TOC/IC ratio less than 0.10 (<0.1) is considered a high concentration of IC relative to TOC. Such a high ratio and concentration of IC in samples will cause IC and TOC measurements to be unstable. If the IC is not removed from a sample of a fluid prior to performing a TOC measurement on the fluid sample, a false positive test relating to the level of TOC may occur.

[0004] The inorganic carbon can be removed from the aqueous sample through a sparging process. Inorganic carbon is typically the result of dissolved limestone or bicarbonate. An exemplary sparging process involves acidifying the aqueous sample to convert the carbonates and bicarbonates into free carbon dioxide (CO_2). The carbon dioxide is then degassed from the aqueous sample by pumping a CO_2 -free gas into the aqueous sample to remove the inorganic carbon present therein, leaving only the organic

carbon. The amount of remaining organic carbon can then be measured. However, typical sparging processes need a special and costly sparger in a TOC device together with a mixer, a purge gas distributor, and the like, which together consumes a large volume of purge gas.

[0005] A need therefore exists for a less costly process and apparatus for sparging to remove inorganic carbon from an aqueous sample prior to a TOC measurement. A need also therefore exists for a system that is capable of performing in-vial sparging to remove IC in the aqueous sample so as to obtain highly accurate and precise TOC measurements.

BRIEF SUMMARY OF THE INVENTION

[0006] In an aspect of the present invention, a method for measuring an amount of total organic carbon in an aqueous sample is provided. The method includes providing a vial having the aqueous sample contained therein. The method further includes acidifying the aqueous sample. A purge gas is then injected into the aqueous sample to perform an in-vial sparging process. A measuring device for measuring an amount of total organic carbon in the aqueous sample is provided. A portion of the aqueous sample is transferred to the measuring device. The amount of total organic carbon in the transferred portion of the aqueous sample is measured. An output from the measuring device that indicates the amount of total organic carbon within the aqueous sample after the in-vial sparging process is produced.

[0007] In another aspect of the method above, the purge gas is injected into the aqueous sample at a rate of between about twenty milliliters per minute (20 mL/min) and five hundred milliliters per minute (500 mL/min).

[0008] In another aspect of the method above, the purge gas is injected into the aqueous sample at a rate of about one hundred milliliters per minute (100 mL/min).

[0009] In another aspect of the method above, the purge gas is injected into the aqueous sample for between about two minutes (2 min) and twenty minutes (20 min).

[0010] In another aspect of the method above, the purge gas is injected into the aqueous sample for about three minutes (3 min).

[0011] In another aspect of the method above, the purge gas is injected into the aqueous sample at a rate of between about one hundred milliliters per minute (100

mL/min) and one hundred fifty milliliters per minute (150 mL/min) for about three minutes (3 min).

[0012] In another aspect of the method above, the purge gas is injected into the aqueous sample to perform a second in-vial sparging process.

[0013] In another aspect of the method above, thirty-five milliliters (35 mL) of the aqueous sample is disposed within said vial.

[0014] In another aspect of the method above, the purge gas is injected into the vial at a pressure of between about one pounds per square inch (1 psi) and seven pounds per square inch (7 psi).

[0015] In another aspect of the method above, the sparging process includes injecting the purge gas into the vial at a pressure of between about three pounds per square inch (3 psi) and three-and-a-half pounds per square inch (3.5 psi).

[0016] In another aspect of the method above, acidifying the aqueous sample comprises introducing phosphoric acid (H_3PO_4) into the aqueous sample.

[0017] In another aspect of the method above, acidifying the aqueous sample comprises reducing the pH level of the aqueous sample to less than about 4 pH.

[0018] In another aspect of the method above, the purge gas is one of nitrogen gas (N_2), zero gas (comprising 20% O_2 and 80% N_2), and a non- CO_2 gas.

[0019] In yet another aspect of the present invention, a method for performing an in-vial sparging process is provided. The method also includes providing a vial having the aqueous sample contained therein. The aqueous sample is acidified in the vial. A purge gas is injected into the aqueous sample in said vial to volatilize carbon dioxide (CO_2) contained within the aqueous sample. The volatilized carbon dioxide is removed from the vial.

[0020] In still another aspect of the present invention, an apparatus for performing an in-vial sparging process and measuring process is provided. The apparatus includes a pressure regulator fluidly connected to a purge gas supply. A restrictor is fluidly connected to the pressure regulator, and the restrictor is configured to receive purge gas from the pressure regulator. A three-way valve is fluidly connected to the restrictor. A TOC measuring device is fluidly connected to the three-way valve, and a vial for receiving an aqueous sample is fluidly connected to the three way valve.

[0021] Advantages of the present invention will become more apparent to those skilled in the art from the following description of the embodiments of the invention which have been shown and described by way of illustration. As will be realized, the invention is capable of other and different embodiments, and its details are capable of modification in various respects.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0022] These and other features of the present invention, and their advantages, are illustrated specifically in embodiments of the invention now to be described, by way of example, with reference to the accompanying diagrammatic drawings, in which:

[0023] FIG. 1 is a schematic diagram of an exemplary embodiment of an in-vial sparging system.

[0024] FIG. 2 is an exemplary embodiment of the tip of a needle for use in the in-vial sparging system of FIG. 1.

[0025] FIG. 3 is a schematic diagram of an exemplary in-vial sparging and measuring process of the present invention.

[0026] FIG. 4A is a graphical representation of test results comparing sparging time relative to concentration of inorganic carbon and inorganic carbon removal rate with a starting inorganic carbon concentration of 100 ppm.

[0027] FIG. 4B is a table of the test results forming the basis of the chart in FIG. 4A.

[0028] FIG. 5A is a graphical representation of test results comparing sparging time relative to concentration of inorganic carbon and inorganic carbon removal rate with a starting inorganic carbon concentration of 5.9 ppm.

[0029] FIG. 5B is a table of the test results forming the basis of the chart in FIG. 5A.

[0030] FIG. 6A is a graphical representation of test results comparing sparging time relative to concentration of inorganic carbon and inorganic carbon removal rate with a starting inorganic carbon concentration of 680 ppb.

[0031] FIG. 6B is a table of the test results forming the basis of the chart in FIG. 6A.

[0032] FIG. 7A is a graphical representation of test results comparing sparging time relative to gas flow rate of a purge gas relative to the removal rate of inorganic carbon.

[0033] FIG. 7B is a table of the test results forming the basis of the chart in FIG. 7A in addition to total volume of purge gas used for the sparging process.

[0034] It should be noted that all the drawings are diagrammatic and not drawn to scale. Relative dimensions and proportions of parts of these figures have been shown exaggerated or reduced in size for the sake of clarity and convenience in the drawings. The same reference numbers are generally used to refer to corresponding or similar features in the different embodiments. Accordingly, the drawing(s) and description are to be regarded as illustrative in nature and not as restrictive.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0035] Referring to FIG. 1, an exemplary embodiment of an in-vial sparging and measuring system 10 is shown. The system 10 includes a gas supply 12 for providing a purge gas. The purge gas is used to remove the inorganic carbon within an aqueous sample. In an embodiment, the gas supply can be any purge gas, such as nitrogen gas (N₂) or zero gas (composed of 20% O₂ and 80% N₂). It should be understood by one of ordinary skill in the art that the purge gas can be any other gas for the oxidization of the inorganic carbon in an aqueous sample. In an embodiment, the gas supply 12 supplies the purge gas at a pressure of between about twenty and two hundred pounds per square inch (20-200 psi). Typically, the gas supply 12 supplies the purge gas at more than thirty pounds per square inch (>30 psi). The gas supply 12 is operatively connected to a pressure regulator 14.

[0036] In the embodiment illustrated in FIG. 1, the pressure regulator 14 is configured to receive the purge gas from the gas supply 12. The pressure regulator 14 is configured to regulate the pressure of the gas exiting therefrom. In an exemplary embodiment, the pressure regulator 14 reduces the incoming gas pressure to provide an outgoing gas pressure of about thirteen pounds per square inch (13 psi). It should be understood by one of ordinary skill in the art that the pressure regulator 14 can be configured to step down the incoming gas pressure so as to provide an outgoing gas pressure of between about three to fifteen pounds per square inch (3-15 psi), or provide an outgoing pressure that is at any pressure less than the pressure of the gas introduced

into the pressure regulator 14. In an embodiment, the pressure regulator 14 is operatively connected to a restrictor 16.

[0037] As illustrated in the embodiment of FIG. 1, the restrictor 16 receives the purge gas at the reduced pressure from the pressure regulator 14. The restrictor 16 is configured to control the gas flow rate exiting therefrom. The gas flow rate from the restrictor 16 has a direct effect on the rate of removal of the inorganic carbon within the aqueous sample. While it may be ideal to maximize the gas flow rate from the restrictor 16, the cost of any unnecessary or additional purge gas used for the sparging process may negatively offset the cost advantages resulting from the in-vial sparging and measuring system 10. Thus, it is important to determine the optimal gas flow rate and length of time for supplying the purge gas to the aqueous sample necessary to produce the pre-determined amount of removal of inorganic carbon within the sample while using the minimum total amount of purge gas. It should be understood that process conditions may fluctuate, so one skilled in the art may configure the system 10 to provide a small amount of additional purge gas over the minimum to ensure the desired amount of inorganic carbon removal efficiency is achieved. In an embodiment, the restrictor 16 is formed of a tube (not shown) extending between the regulator 14 and a three-way valve 18. The dimensions of the tube can be configured to produce a pre-determined gas flow rate therethrough based upon a given gas pressure supplied by the regulator 14.

[0038] During testing of the present in-vial sparging and measuring system 10, a 2.56 inch polyetheretherkeytone (PEEK®) tube having an inside diameter of 0.009 inches was used to connect the pressure regulator 14 and the three-way valve 18, thereby acting as a gas flow restrictor 16 to provide a desired gas flow rate therefrom. In another embodiment, the restrictor 16 can be a gas flow restrictor valve having an orifice that is sized and shaped to provide a pre-determined gas flow rate therefrom with a regulated gas pressure introduced thereto. It should be understood by one of ordinary skill in the art that any gas flow restrictor commonly known in the art configured to provide a given gas flow rate of purge gas therefrom can be used. In an embodiment, the restrictor 16 is configured to produce a resulting gas flow rate of between about ten milliliters per minute to about three hundred milliliters per minute (10-300 mL/min). In another embodiment, the restrictor 16 is configured to produce a resulting gas flow rate of between about sixty

and one hundred fifty milliliters per minute (60-150 mL/min). In yet another embodiment, the restrictor 16 is configured to produce a resulting gas flow rate of between about one hundred ten and one hundred thirty milliliters per minute (110-130 mL/min). It should be understood by one of ordinary skill in the art that the restrictor 16 can be configured to provide any pre-determined gas flow rate or range of gas flow rates to the three-way valve 18. During recent testing, it was determined that the purge gas flow rate is sensitive to the pressure of the purge gas flowing from the three-way valve 18 to the vial 20. In an embodiment, the pressure of the purge gas exiting the restrictor 16 and passing through the three-way valve 18 to be introduced into the vial 20 during the purging process is between about one pound per square inch (1 psi) and about seven pounds per square inch (7 psi). In another embodiment, the pressure of the purge gas exiting the restrictor 16 and passing through the three-way valve 18 to be introduced into the vial 20 during the purging process is between about three pounds per square inch (3 psi) and about three-and-a-half pounds per square inch (3.5 psi).

[0039] In the embodiment shown in FIG. 1, a three-way valve 18 is operatively connected to the restrictor 16 to receive purge gas from the gas supply 12 for selectively controlling three distinct flow regimes through the valve. The three-way valve 18 is also fluidly connected to a vial 20 configured to receive and contain an aqueous sample 22. The three-way valve 18 is further fluidly connected to a total organic carbon ("TOC") measuring device 24 that is configured to measure the total organic carbon in a fluid. The three distinct flow regimes of the three-way valve 18 include: (1) a first position for introduction of purge gas into the vial 20 for an in-vial sparging process, (2) a second position for transfer a portion of the sample 22 to the TOC measuring device 24 for a measuring process, (3) and a third position that is a closed position through which no fluids pass. Although the exemplary embodiment illustrated in FIG. 1 shows the three-way valve 18 being fluidly connected to a single vial 20, it should be understood by one of ordinary skill in the art that the three-way valve 18 may be connected to any number of vials 20 or other containers configured to receive and contain an aqueous sample to be sparged and measured. It should further be understood by one of ordinary skill in the art that the system 10 can be configured such that the three-way valve 18 can be fluidly connected to a single vial 20 or other container or device, simultaneously fluidly

connected to a plurality of vials 20, or sequentially fluidly connected to a single or a plurality of vials 20.

[0040] In an embodiment, the three-way valve 18 is manually controllable. In another embodiment, the three-way valve 18 is electronically controllable. In yet another embodiment, the three-way valve 18 is controllable by a controller 26, computer, or electronic system. For example, the three-way valve can be a valve having serial number 075MP24-32-4M manufactured by Bio-Chem Fluidics of Boonton, New Jersey or a valve having serial number CTV-3-1/4 UKG manufactured by Takasago of Tokyo, Japan. It should be understood by one of ordinary skill in the art that the three-way valve can be any mechanism capable of providing three distinct flow regimes that are selectively controllable in any manner.

[0041] In an embodiment, the three-way valve 18 is connected to a one-sixteenth inch (1/16 in) tube 28, which is connected to a needle 32 that is insertable through the opening 30 and into the vial 20. If a sample 22 is present within the vial 20, a tip 34 of the needle 32 is positioned near the bottom surface of the vial 20. While the tip 34 may be positioned at any location within the vial 20, the tip 34 is preferably positioned adjacent to the bottom surface of the vial 20 such that when the purge gas is introduced into the sample 22, the distance that bubbles of the purge gas must travel through the sample 22 to the surface of the sample maximizes the amount of volatilization produced by the bubbles of purge gas. Recent tests have shown that the depth at which the tip of the needle is positioned within the vial does not have a significant effect on the inorganic carbon removal efficiency. In an embodiment, the vial 20 includes a cap 36 that seals the opening 30 thereof. Accordingly, the tip 34 of the needle 32 is configured to penetrate the cap 36 while maintaining the seal between the contents of the vial 20 and the ambient environment. In another embodiment, the vial 20 does not include a cap such that the contents of the vial 20 are exposed to the ambient environment surrounding the vial 20. It should be understood by one of ordinary skill in the art that the three-way valve 18 may be fluidly connected to the vial 20 by way of a tube (not shown) that is simply immersible into the vial 20. The tube may be integrally formed with the cap 36 or may be immersible through an uncapped opening 30.

[0042] In an embodiment, the vial 20 is capable of holding between about two to two hundred fifty milliliters (2-250 mL) therein. In another embodiment, the vial 20 is capable of holding between about twenty to one hundred milliliters (20-100 mL) therein. In yet another embodiment, the vial 20 is capable of holding about forty milliliters (40 mL) therein. It should be understood by one of ordinary skill in the art that the vial 20 should be sized to receive a sufficient volume of an aqueous sample 22 therein to allow an in-vial sparging process and subsequent TOC measurement of a portion of the aqueous sample 22.

[0043] In the embodiment illustrated in FIG. 1, the needle 32 is introducible into the vial 20 through the opening 30 thereof. In another embodiment, the needle 32 is integrally formed with the cap 36 so as to maintain a seal between the needle 32 and the cap 36 to prevent any fluid leakage therebetween. As illustrated in FIG. 2, the needle 32 is configured to have at least one hole 38 formed therein. In an embodiment, the needle 32 includes a single hole 38 through the tip 34 for allowing the purge gas from the three-way valve 18 to be released therethrough. In another embodiment, the needle 32 includes two or more holes 38 formed therein for allowing the purge gas from the three-way valve 18 to be released therethrough. In yet another embodiment, the needle 32 includes twenty-four (24) holes 38 formed along the axial length thereof. It should be understood by one skill in the art that the needle 32 may include any number of holes 38 formed therethrough to allow the purge gas to be introduced into the sample 22 contained in the vial 20 for an in-vial sparging process. Through testing, it was determined that having multiple holes formed through the needle 32 was preferable to a single hole formed therethrough for delivering purge gas to the aqueous sample. When the same gas flow rate is used, a needle having the plurality of holes formed therethrough produced a larger quantity of smaller bubbles which, in turn, increased the amount of surface area of purge gas that contacts the aqueous sample. The increased surface area of purge gas bubbling up through the aqueous sample increased the removal rate of inorganic carbon from the aqueous sample. Through testing, it was also determined that the inorganic carbon removal efficiency is independent upon the depth of the needle 32 within the vial 20.

[0044] In the embodiment illustrated in FIG. 1, a vent needle 40 is configured to concentrically surround a portion of the needle 32 adjacent to the opening 30 of the vial

20. In an embodiment, the vent needle 40 has the same cross-sectional shape as the needle 32. The vent needle 40 is adapted to surround the needle 32 in a substantially concentric manner, having a small gap between the inner surface of the vent needle 40 and the outer surface of the needle 32 to allow gas or liquid to vent through the gap between the vent needle 40 and the needle 32. In an embodiment, the vent needle 40 is operatively connected to the cap 36 attached to the opening 30 of the vial 20 and provides a seal between the vent needle 40 and the cap 36 to prevent any fluids to escape the vial 20. In another embodiment, the vent needle 40 is operatively connected to the cap 36 at a position adjacent to the needle 32 without surrounding the hose. The vent needle 40 is operatively and fluidly connected to the vial 20 as well as a buffer container 42 which is configured to receive an overflow of the aqueous sample 22 as well as the gaseous byproducts of an in-vial sparging process. The buffer container 42 also acts to balance the pressure within the vial 20 during an in-vial sparging process. The buffer container 42 can also isolate inorganic carbon and total organic carbon in ambient air and prevent them from dissolving back into the aqueous sample.

[0045] As shown in FIG. 1, a beaker 44 is fluidly connected to the buffer container 42. When the three-way valve 18 is opened during an in-vial sparging process to introduce purge gas into the vial 20, a small portion of the aqueous sample 22 may escape through the vent tubing 40, which passes through the buffer container 42 and is collected in the beaker 44.

[0046] FIG. 3 illustrates a schematic of an exemplary embodiment of an in-vial sparging and measuring process 11. In a first step 60, an aqueous sample 22 is collected in a container such as a vial 20, a bottle, tube, or any other device for containing a fluid. In an embodiment, the vial 20 is open such that the aqueous sample is continually exposed to the ambient environment. In another embodiment, the vial 20 is closed such that the aqueous sample 22 is sealed from the ambient environment. The aqueous sample 22 is acidified to a pH level less than about 4 pH by adding an acid such as phosphoric acid (H_3PO_4) that causes the inorganic carbon within the aqueous sample to produce carbon dioxide (CO_2). In an embodiment, this acidification can be done during the collection of the aqueous sample in the vial 20 or at any other time prior to injecting the purge gas during an in-vial sparging process.

[0047] Once the aqueous sample 22 is collected in the vial 20, the vial 20 is then placed into a device for receiving the vial 20 and securing the vial 20 therein. If the sparging and measuring processes are to be conducted on the aqueous sample 22 in an open vial 20, the needle 32, tube, or other means for injecting purge gas into the aqueous sample 22 is attached such that the purge gas transfer means is submerged within the aqueous sample 22. If the sparging and measuring processes are to be conducted on the aqueous sample 22 in a closed vial 20, the cap 36 can either now be secured to the vial 20 or the cap 36 may have been previously attached thereto when the aqueous sample 22 was introduced into the vial 20.

[0048] Once the vial 20 containing the aqueous sample 22 is secured the means for transferring purge gas into the vial 20 and for removing a portion of the aqueous sample 22 therefrom is fluidly connected to the vial 20. In an embodiment, a needle 32 is inserted through the cap 36 of the vial 20 and the tip 34 is submerged in the aqueous sample 22. In another embodiment, a tube is disposed within the vial and is submerged in the aqueous sample 22. Once the means for injecting a purge gas into the vial 20 is fluidly connected thereto, an in-vial sparging process can be performed on the aqueous sample 22 contained within the vial 20.

[0049] In a second step 62, as illustrated in FIG. 3, the in-vial sparging process is performed. The in-vial sparging process includes providing a purge gas to the regulator 14 to control the gas pressure of the purge gas which then passes through the restrictor 16 to control the flow rate of the purge gas. The in-vial sparging process begins when the three-way valve 18 is selectively switched from a third position in which the valve is closed to a first position that allows the purge gas to be directed through the needle 32, and then exit the hole or holes 38 formed through the needle 32 to result in the purge gas being injected into the aqueous sample 22. The three-way valve 18 remains in the first position for a pre-determined amount of time to allow the purge gas to bubble up through the aqueous sample 22 in the vial 20.

[0050] In general, the in-vial sparging process is a process in which an aqueous sample that has previously been acidified which has converted the carbonate and bicarbonate to CO_2 is subsequently injected with a purge gas that is CO_2 -free to remove the CO_2 through volatilization. The volatilized CO_2 is then transferred out of the vial 20

through the vent needle 40. Because a high concentration of inorganic carbon relative to the concentration of total organic carbon within a fluid can cause an inaccurate measurement of the total organic carbon within the fluid, it is an objective of the in-vial sparging process to remove as much of the inorganic carbon from the fluid so as to provide a more accurate measurement of the total organic carbon concentration in the fluid. The desired amount of inorganic carbon to be removed from an aqueous sample 22 should be enough to provide a reliable total organic carbon concentration measurement of the post-sparged aqueous sample. In one embodiment of an in-vial sparging process, the removal rate of inorganic carbon from the aqueous sample should be greater than about ninety percent (>90%) for solutions containing two hundred fifty parts per billion (250 ppb) of inorganic carbon, and more particularly, greater than about ninety-five percent (>95%) for solutions containing two parts per million (2 ppm) of inorganic carbon. Ideally, the inorganic carbon removal rate is greater than ninety-nine percent (>99%), but such a removal rate may be cost prohibitive given the volume of purge gas necessary to achieve such a removal rate. It should be understood by one skilled in the art that given a pre-determined set of sparging parameters, the removal rate of inorganic carbon from the aqueous sample can vary between different samples. In another embodiment of an in-vial sparging process, the parameters of the sparging process are configured such that the removal of inorganic carbon within the aqueous sample results in a concentration of inorganic carbon that is less than one hundred parts per billion (<100 ppb). As stated above, the parameters of such an in-vial sparging process can vary.

[0051] In an embodiment, once the in-vial sparging process of the second step 62 has been completed, the three-way valve 18 is then selectively switched to the third position in which the three-way valve 18 is closed. Alternatively, the third step 64 or selectively switching the three-way valve to a second position wherein a portion of the sparged aqueous sample is transferred through the valve to the TOC measuring device 24. In an embodiment, a portion of the sparged aqueous sample – about one-tenth to about twenty milliliters (~0.10-20 mL) is transferred from the vial 20 to the TOC measuring device 24. It should be understood by one of ordinary skill in the art that any volume of the sparged aqueous sample sufficient to be accurately measured in the TOC measuring device 24 can be transferred thereto. After the transfer of a portion of the sparged aqueous sample to

the TOC measuring device 24 is complete, the three-way valve 18 can be selectively switched to the third position in which the valve is closed.

[0052] As shown in FIG. 3, the fourth step 66 involves a measuring process for measuring the amount or concentration of total organic carbon present in the portion of post-sparged aqueous sample transferred to the TOC measuring device 24 in the third step 64. The results of the total organic carbon measuring process of the fourth step 66 can be output in a variety of different formats, such as by printing to a printer (not shown), writing the data to a hard disc or disc drive, displaying the results on a graphical user interface, or any other means of providing the data in a user-readable format.

[0053] Subsequent to the total organic carbon measuring process of the fourth step, the optional fifth step 68 involves selectively switching the three-way valve to the first position to allow the purge gas to flow therethrough to the vial 20 so as to perform a secondary sparging process. This secondary sparging process is configured to transfer any aqueous solution remaining in the needle 32 back into the vial 20 to prevent cross-contamination between successive measurement samples in the TOC measuring device 24. It has been found that there is insignificant cross-contamination between successive sample measurements when the secondary sparging process is performed, and any such cross-contamination is likely attributable to the wet tubing. In an embodiment, this secondary sparging process can be performed for about fifteen seconds (15 sec) or any other time sufficient to completely transfer the remaining aqueous sample in the tube 28 needle 32 back into the vial 20. Also, this secondary sparging process can fully fill the buffer container 42 with CO₂-free purge gas to isolate CO₂ and organic matter in ambient air dissolving back into the successive sample.

[0054] In order to assess the inorganic removal rate, simulated tests were undertaken using the in-vial sparging and measuring system 10 to determine some process parameters that produce an acceptable amount of inorganic carbon removal from an aqueous sample. The following examples reflect the tests and corresponding results from different sets of tests using the in-vial sparging and measuring system 10 illustrated in FIG. 1 and the in-vial sparging and measuring process 11 illustrated in FIG. 3.

EXAMPLE 1

[0055] In a first set of tests configured to determine whether or not a correlation exists between the removal efficiency of inorganic carbon from an aqueous sample and the amount of sparging time in which the purge gas is introduced into the aqueous sample. The conditions of the process were:

[0056] Vials: 40 mL vials having 35 mL-38 mL of aqueous sample

[0057] Acidification: 0.4 mL of 6M H_3PO_4

[0058] Purge gas: Zero gas

[0059] Purge gas flow rate: 80-100 mL/min

[0060] IC concentrations: (1) 100 ppm, (2) 5.9 ppm and (3) 680 ppb inorganic carbon as sodium carbonate (Na_2CO_3)

[0061] The variable for each of the three concentrations of inorganic carbon removal efficiencies was the sparging time of between thirty seconds and twenty minutes (~30 sec – 20 min). The results of a first set of vials having an inorganic carbon concentration of about 100 ppm inorganic carbon as sodium carbonate (Na_2CO_3) are shown in FIGS. 4A-4B, the results of a second set of vials having an inorganic carbon concentration of about 5.9 ppm inorganic carbon as sodium carbonate (Na_2CO_3) are shown in FIGS. 5A-5B, and the results of a third set of vials having an inorganic carbon concentration of about 680 ppb inorganic carbon as sodium carbonate (Na_2CO_3) are shown in FIGS. 6A-6B.

[0062] The tests indicated that the removal efficiency of the in-vial sparging and measuring process increases: (1) from 94.18% to 99.95% when the sparging time is increased from 2 minutes to 5 minutes at 100 ppm inorganic carbon concentration, (2) from 91.74% to 99.73% when the sparging time is increased from 2 minutes to 5 minutes at 5.9 ppm inorganic carbon concentration, and (3) from 89.22% to 98.56% when the sparging time is increased from 2 minutes to 5 minutes at 680 ppb inorganic carbon concentration. Accordingly, it was determined that a sparging time does affect the inorganic carbon removal efficiency and a sparging time of between about 2 minutes and 5 minutes should result in a removal rate of inorganic carbon in an aqueous sample that is sufficient to provide an accurate measurement of total organic carbon in the TOC measuring process. However, depending upon the gas flow rate of the purge gas during

the in-vial sparging process may warrant more or less sparging time to produce an acceptable inorganic carbon removal efficiency.

[0063] Given this range of time for the in-vial sparging process, the gas flow rate and total purge gas volume can be optimized so as to minimize the total purge gas volume over the given sparging time to produce an acceptable inorganic carbon removal efficiency.

EXAMPLE 2

[0064] In a second set of tests configured to determine whether or not a correlation exists between the removal efficiency of inorganic carbon from an aqueous sample and the gas flow rate of the purge gas is introduced into the aqueous sample. The conditions of the process were:

[0065] Vials: 40 mL vials having 35 mL-38 mL of aqueous sample

[0066] Acidification: 0.4 mL of 6M H_3PO_4

[0067] IC concentration: 100.8 ppm inorganic carbon

[0068] Purge gas: N_2 gas

[0069] Sparging time: 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 10, 15, and 20 minutes

[0070] The variable for this second set of tests was the gas flow rate of the purge gas during an in-vial sparging process, wherein the gas flow rates tested were: (1) 50 mL/min, (2) 100 mL/min, and (3) 200 mL/min. Samples of the aqueous sample were taken at each of the above-identified time intervals to test the inorganic carbon concentration after sparging of the given time at each of the different gas flow rates. The results of the three different gas flow rates with respect to the removal rate of the inorganic carbon and relative to the sparging time are shown in the chart in FIGS. 7A-7B.

[0071] The tests indicate that the gas flow rate at a given sparging time of about 2 minutes results in an inorganic carbon removal rate of: (1) 72.72% at a gas flow rate of 50 mL/min, (2) 94.18% at a gas flow rate of 100 mL/min, and (3) 98.46% at a gas flow rate of 200 mL/min. The removal rate of inorganic carbon improves significantly when the sparging time is increased from 2 minutes to 5 minutes, wherein the inorganic carbon removal rate at a gas flow rate of about 5 minutes is: (1) 95.68% at a gas flow rate of 50 mL/min, (2) 99.95% at a gas flow rate of 100 mL/min, and (3) 99.99% at a gas flow rate of 200 mL/min.

[0072] Accordingly, it was determined that the gas flow rate of the purge gas during the in-vial sparging process does affect the inorganic carbon removal efficiency. At a sparging time of about 2 minutes, the gas flow rate of 200 mL/min provides for an inorganic carbon removal efficiency above ninety-five percent (>95%). However, for a sparging time of about 3 minutes, the purge gas flow rate of 100 mL/min and 200 mL/min both provide for an inorganic carbon removal efficiency above ninety-five percent (>95%). It should be understood by one of ordinary skill in the art that either of the above conditions, or any conditioned in between, that provide an inorganic carbon removal efficiency above ninety-five percent (>95%) are sufficient to remove enough inorganic carbon to produce an acceptable inorganic carbon removal efficiency.

EXAMPLE 3

[0073] During the second set of tests above, the tests were also configured to determine an acceptable set of process parameters that would minimize the total amount of purge gas yet result in an acceptable inorganic carbon removal efficiency above ninety-eight percent (>98%). The total volume of purge gas consumed – which includes a secondary 15 second sparging process, as described in the fifth step 68 above – was empirically determined. As shown in FIG. 7B, the sparging parameters that produced an inorganic carbon removal efficiency above ninety-eight percent (>98%) while consuming the smallest volume of purge gas was when the in-vial sparging process was performed at a gas flow rate of 100 mL/min for 3 minutes on an aqueous sample having an inorganic concentration of 100 ppm, resulting in a total consumption of 325 mL of purge gas. While these process conditions produce an acceptable inorganic carbon removal efficiency, it should be understood by one of ordinary skill in the art that these conditions are only exemplary yet they should act to illustrate the effects that gas flow rate, sparging time, and total volume of purge gas consumed have on the inorganic carbon removal efficiency.

[0074] While preferred embodiments of the present invention have been described, it should be understood that the present invention is not so limited and modifications may be made without departing from the present invention. The scope of the present invention is defined by the appended claims, and all devices, process, and methods that

come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein.

CLAIMS

1. A method for performing TOC measurements comprising:
providing a vial having said aqueous sample contained therein;
acidifying said aqueous sample;
injecting a purge gas into said aqueous sample to perform an in-vial sparging process;
providing a measuring device for measuring an amount of total organic carbon in said aqueous sample;
transferring a portion of said aqueous sample to said measuring device;
measuring said amount of total organic carbon in said transferred portion of said aqueous sample; and
producing an output from said measuring device that indicates said amount of total organic carbon within said aqueous sample after said in-vial sparging process.
2. The method of Claim 1, wherein said purge gas is injected into said aqueous sample at a rate of between about twenty milliliters per minute (20 mL/min) and five hundred milliliters per minute (500 mL/min).
3. The method of Claim 1, wherein said purge gas is injected into said aqueous sample at a rate of about one hundred milliliters per minute (100 mL/min).
4. The method of Claim 1, wherein said purge gas is injected into said aqueous sample for between about two minutes (2 min) and twenty minutes (20 min).
5. The method of Claim 1, wherein said purge gas is injected into said aqueous sample for about three minutes (3 min).
6. The method of Claim 1, wherein said purge gas is injected into said aqueous sample at a rate of between about one hundred milliliters per minute (100 mL/min) and one hundred fifty milliliters per minute (150 mL/min) for about three minutes (3 min).

7. The method of Claim 1 further comprising injecting a purge gas into said aqueous sample to perform a second in-vial sparging process after said measuring step.
8. The method of Claim 1, wherein thirty-five milliliters (35 mL) of said aqueous sample is disposed within said vial.
9. The method of Claim 1, wherein said purge gas injected into said vial is injected at a pressure of between about one pounds per square inch (1 psi) and seven pounds per square inch (7 psi).
10. The method of Claim 1, wherein sparging includes injecting said purge gas into said vial at a pressure of between about three pounds per square inch (3 psi) and three-and-a-half pounds per square inch (3.5 psi).
11. The method of Claim 1, wherein acidifying said aqueous sample comprises introducing phosphoric acid (H_3PO_4) into said aqueous sample.
12. The method of Claim 1, wherein acidifying said aqueous sample comprises reducing a pH level of said aqueous sample to less than about 4 pH.
13. The method of Claim 1, wherein said purge gas is one of nitrogen gas (N_2), zero gas (comprising 20% O_2 and 80% N_2), and a CO_2 -free gas.
14. A method for performing an in-vial sparging process comprising:
 - providing a vial having said aqueous sample contained therein;
 - acidifying said aqueous sample in said vial;
 - injecting a purge gas into said aqueous sample in said vial to volatilize carbon dioxide (CO_2) contained within said aqueous sample in said vial; and
 - removing said volatilized carbon dioxide from said vial.

15. An apparatus for performing an in-vial sparging process and measuring process, said apparatus comprising:

- a pressure regulator fluidly connected to a purge gas supply;
- a restrictor fluidly connected to said pressure regulator, said restrictor configured to receive purge gas from said pressure regulator;
- a three-way valve fluidly connected to said restrictor;
- a TOC measuring device fluidly connected to said three-way valve; and
- a vial for receiving an aqueous sample, said vial being fluidly connectable to said three-way valve for receiving said purge gas during an in-vial sparging process.

16. The apparatus of Claim 15 further comprising a needle disposable within said vial, said needle being fluidly connected to said three-way valve.

17. The apparatus of Claim 16, wherein said needle includes at least one hole formed therethrough.

18. The apparatus of Claim 16, wherein said needle includes a plurality of holes formed therethrough.

19. The apparatus of Claim 15 further comprising a buffer container fluidly connected to said vial.

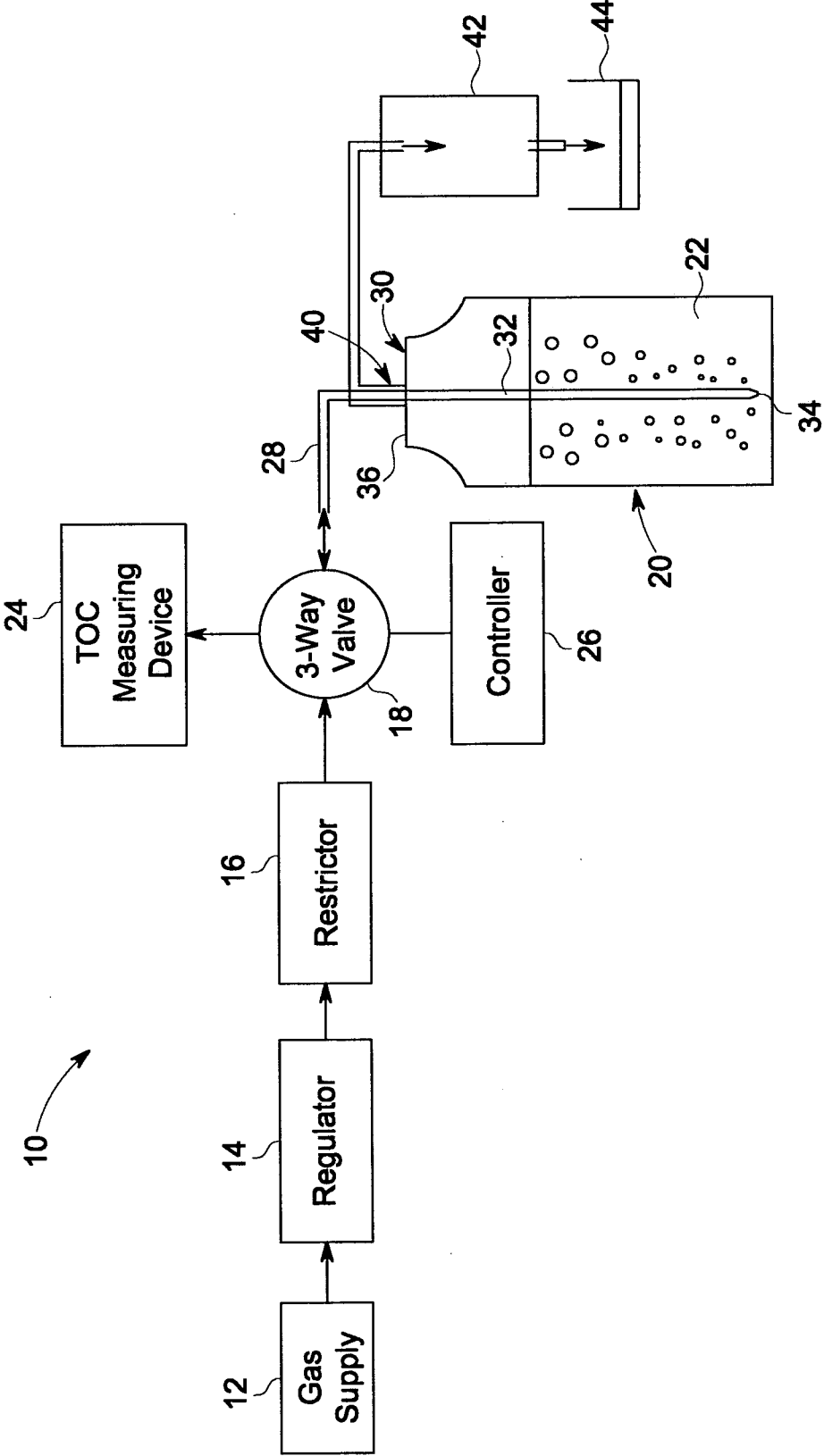


FIG. 1

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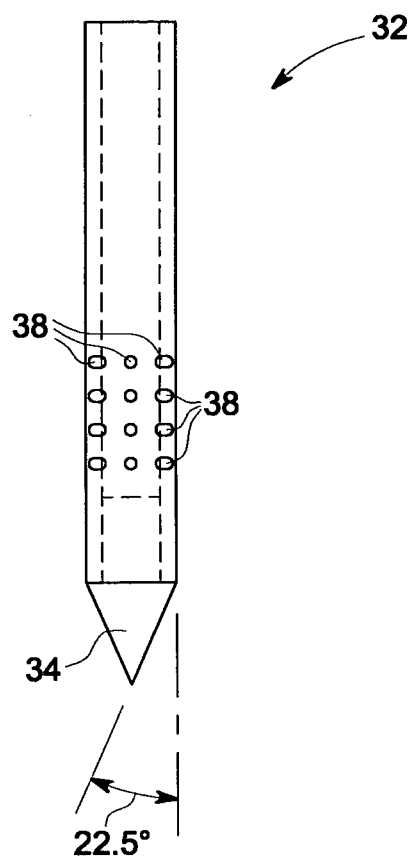


FIG. 2

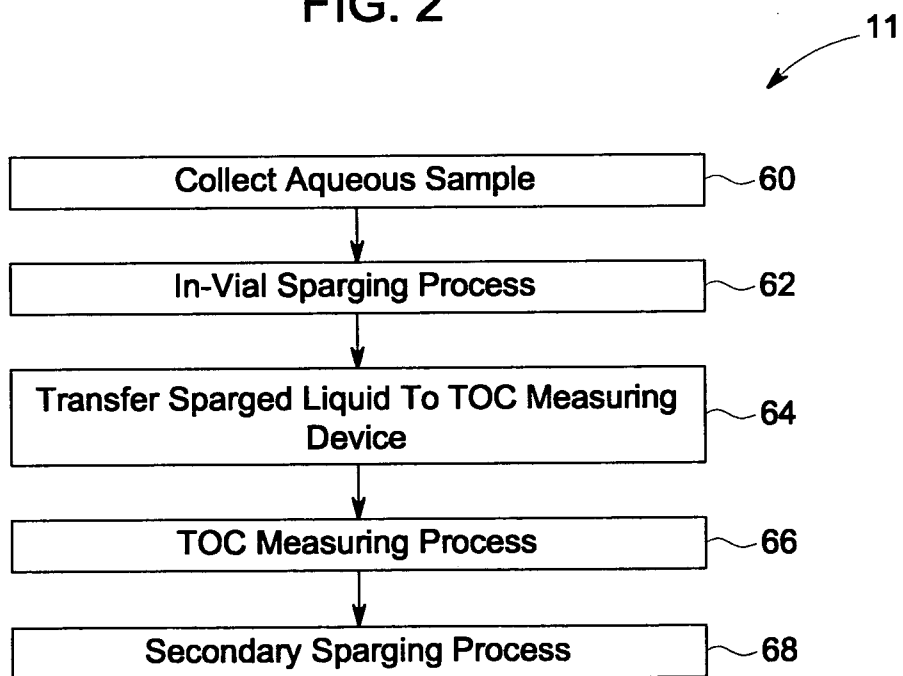


FIG. 3

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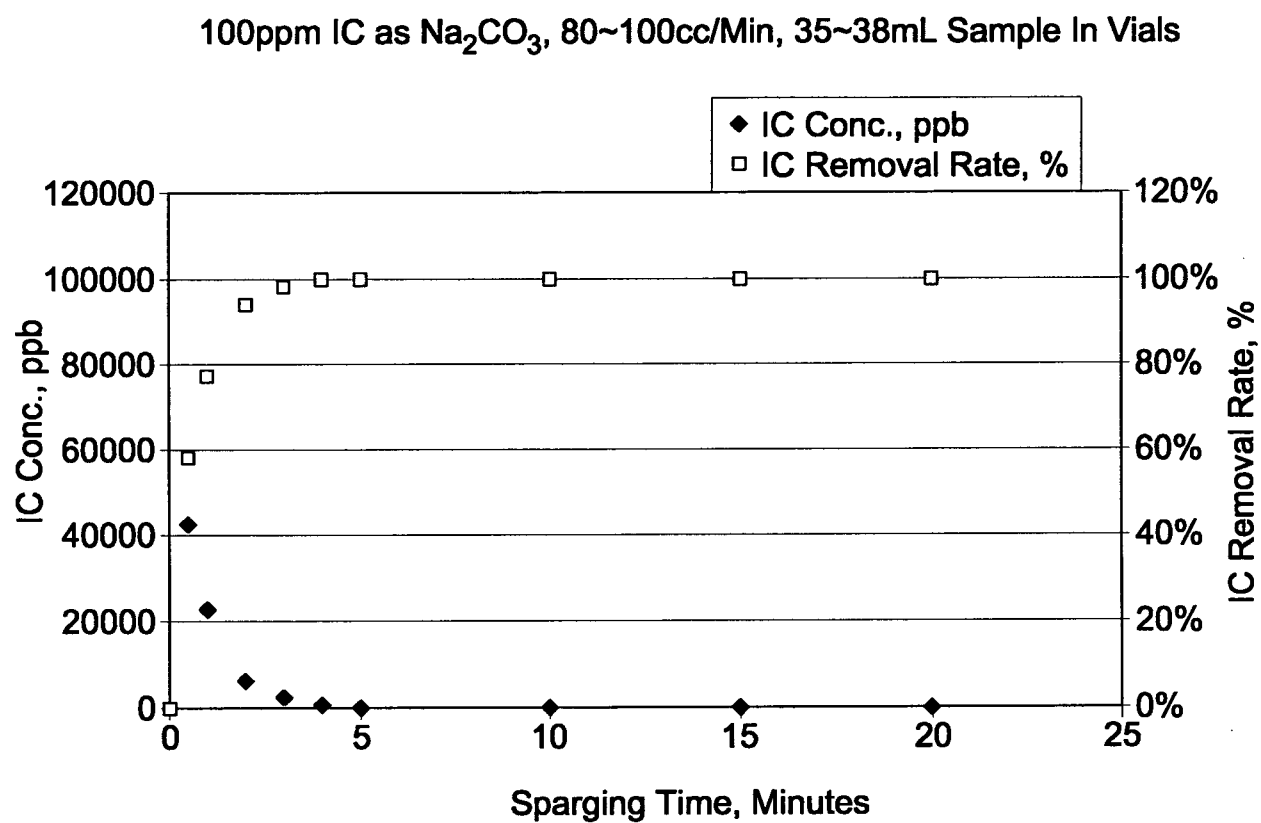


FIG. 4A

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Items	Std Vol., mL	Std IC Conc., ppm	6M H ₃ PO ₄ , mL	Gas Flow Rate, mL/Min	Sparging Time, Min	IC, ppb	SD, ppb	RSD, %	Acid, μL/Min	Oxid, μL/Min	ICR, %
					0	100800			0.1	0	0%
1#	35	100ppm IC	0.4	80~100	20	8.1444	1.4861	18.25%	0.1	0	99.99%
2#	35	100ppm IC	0.4	80~100	15	5.6689	2.11562	37.32%	0.1	0	99.99%
3#	35	100ppm IC	0.4	80~100	10	5.4856	1.93473	35.27%	0.1	0	99.99%
4#	35	100ppm IC	0.4	80~100	5	51.578	1.16916	2.27%	0.1	0	99.95%
5#	35	100ppm IC	0.4	80~100	4	190.78	2.27913	1.19%	0.1	0	99.81%
6#	35	100ppm IC	0.4	80~100	3	1770	37.081	2.09%	0.1	0	98.24%
7#	35	100ppm IC	0.4	80~100	2	5870	42.4264	0.72%	0.1	0	94.18%
8#	35	100ppm IC	0.4	80~100	1	22222	551.765	2.48%	0.1	0	77.95%
9#	35	100ppm IC	0.4	80~100	0.5	41944	296.273	0.71%	0.1	0	58.39%

FIG. 4B

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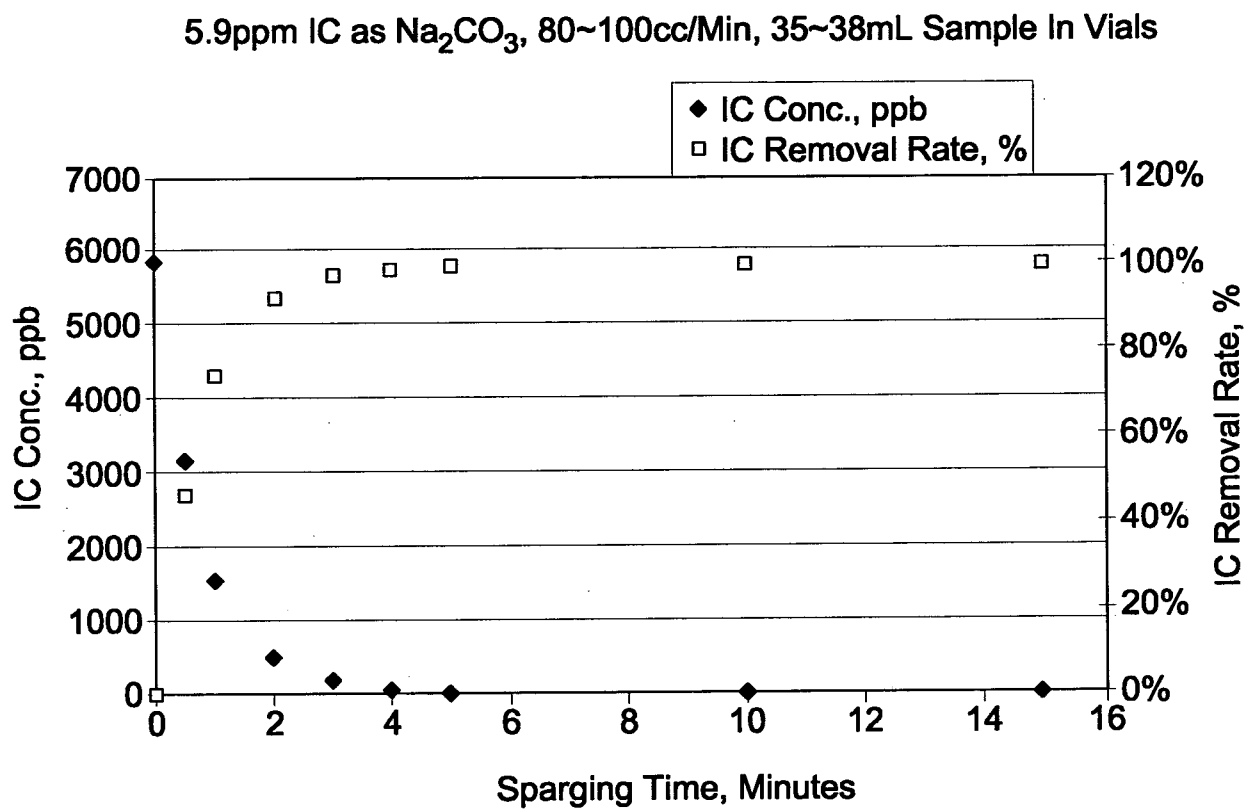


FIG. 5A

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Items	Std Vol., mL	Std IC Conc., ppm	6M H ₃ PO ₄ , mL	Gas Flow Rate, mL/Min	Sparging Time, Min	IC, ppb	SD, ppb	RSD, %	Acid, μL/Min	Oxid, μL/Min	ICR, %
		5.9ppm IC	0		0	5900			0.1	0	0%
1#	35	5.9ppm IC	0.2	80~100	15	10.239	4.6527	45.44%	0.1	0	99.83%
2#	35	5.9ppm IC	0.2	80~100	10	11.182	4.19503	37.52%	0.1	0	99.81%
3#	35	5.9ppm IC	0.2	80~100	5	15.884	3.75089	23.61%	0.1	0	99.73%
4#	35	5.9ppm IC	0.2	80~100	4	62.367	0.58095	0.93%	0.1	0	98.94%
5#	35	5.9ppm IC	0.2	80~100	3	174.78	2.04803	1.17%	0.1	0	97.04%
6#	35	5.9ppm IC	0.2	80~100	2	487.22	10.6628	2.19%	0.1	0	91.74%
7#	35	5.9ppm IC	0.2	80~100	1	1546.7	23.4521	1.52%	0.1	0	73.79%
8#	35	5.9ppm IC	0.2	80~100	0.5	3141.1	50.111	1.60%	0.1	0	46.76%

FIG. 5B

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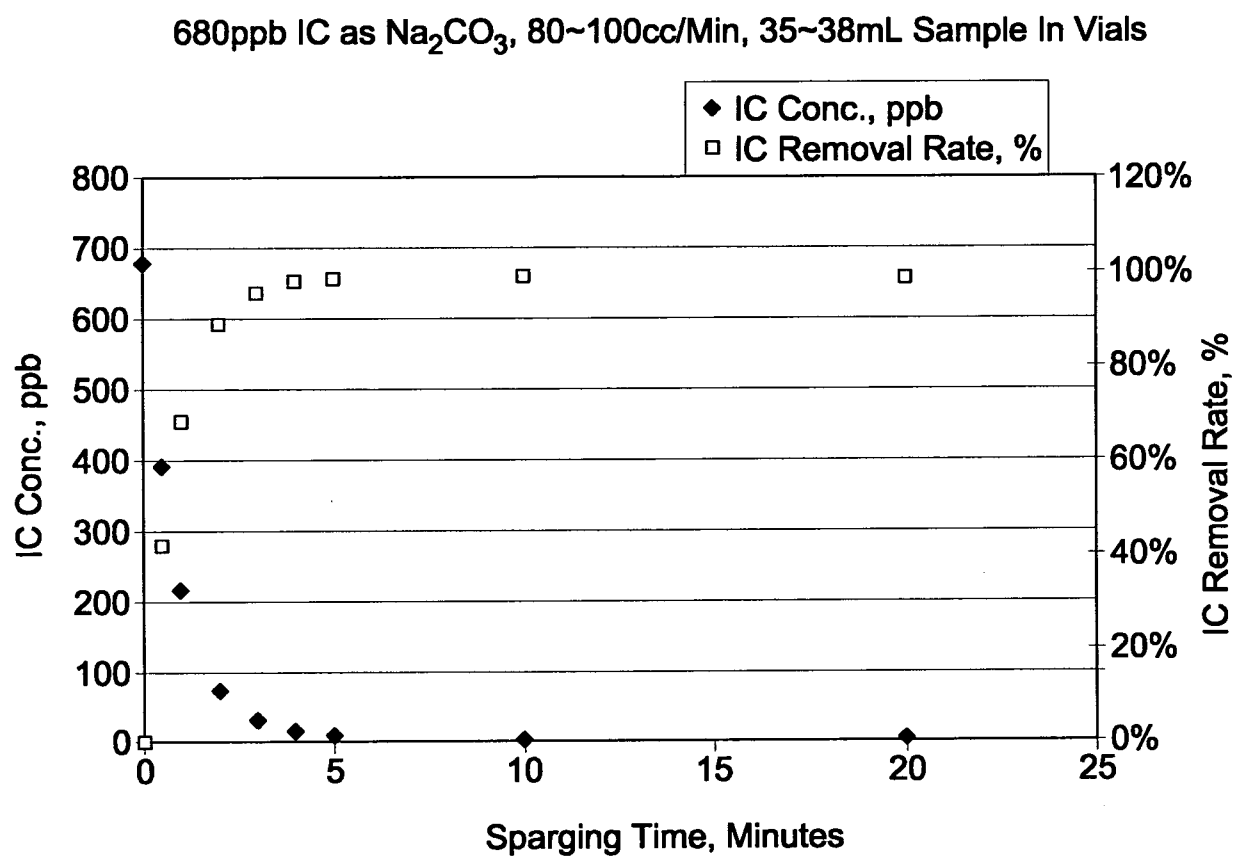


FIG. 6A

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Items	Std Vol., mL	Std IC Conc., ppb	6M H ₃ PO ₄ , mL	Gas Flow Rate, mL/Min	Sparging Time, Min	IC, ppb	SD, ppb	RSD, %	Acid, μL/Min	Oxid, μL/Min	ICR, %
		680ppb IC	0		0	681	3.66667	0.54%	0.1	0	0%
1#	35	680ppb IC	0.2	80~100	20	6.7111	1.82907	27.25%	0.1	0	99.01%
2#	35	680ppb IC	0.2	80~100	10	4.9644	0.33512	6.75%	0.1	0	99.27%
3#	35	680ppb IC	0.2	80~100	5	9.7933	2.86726	29.28%	0.1	0	98.56%
4#	35	680ppb IC	0.2	80~100	4	13.067	1.78955	13.70%	0.1	0	98.08%
5#	35	680ppb IC	0.2	80~100	3	28.911	0.77208	2.67%	0.1	0	95.75%
6#	35	680ppb IC	0.2	80~100	2	73.422	1.16916	1.59%	0.1	0	89.22%
7#	35	680ppb IC	0.2	80~100	1	214	2.17945	1.02%	0.1	0	68.58%
8#	35	680ppb IC	0.2	80~100	0.5	394.67	5.63471	1.43%	0.1	0	42.05%

FIG. 6B

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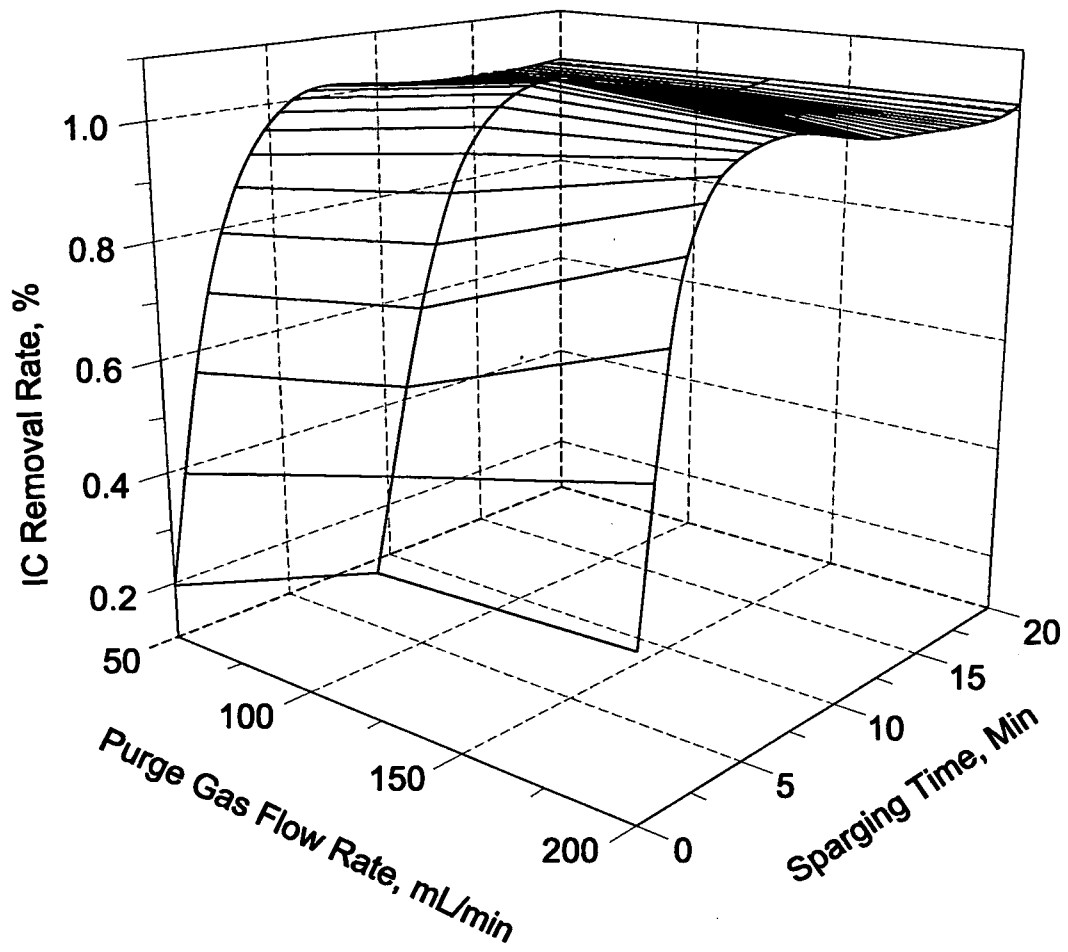


FIG. 7A

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Flow Rate (mL/min)	Sparging Time (min)	IC Removal Rate	Gas Volume (L)
50	0	0	12.5
50	0.5	0.4097	37.5
50	1	0.5724	62.5
50	2	0.7272	112.5
50	3	0.8323	162.5
50	4	0.9086	212.5
50	5	0.9568	262.5
50	10	0.9971	512.5
50	15	0.9998	762.5
50	20	0.9999	1012.5
100	0	0	25
100	0.5	0.5839	75
100	1	0.7795	125
100	2	0.9418	225
100	3	0.9824	325
100	4	0.9981	425
100	5	0.9995	525
100	10	0.9999	1025
100	15	0.9999	1525
100	20	0.9999	2025
200	0	0	50
200	0.5	0.7083	150
200	1	0.874	250
200	2	0.9846	450
200	3	0.9993	650
200	4	0.9997	850
200	5	0.9999	1050
200	10	1	2050
200	15	1	3050
200	20	1	4050

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/000566

A. CLASSIFICATION OF SUBJECT MATTER

G01N33/00 (2006.01) i

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)

IPC: G01N31/-; G01N33/-

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)

CNPAT, EPODOC, WPI, CNKI, GOOGLE SCHOLAR: TOC, organic carbon, acid+, carbon dioxide, CO₂, sparg???, purg???, volatile, bubble, degas???, carrier gas, nitrogen, air, vial, measur???, detect???, analyz???

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US6007777A (TEKMAR COMPANY) 28 Dec. 1999(28.12.1999) column 2 line 53 to column 4 line 39; column 8 lines 8-16 of description; Fig. 1; Fig. 8	1-19
A	US3854881A (COHEN A.) 17 Dec. 1974(17.12.1974) the whole document	1-19
A	US5413763A (JEFFERS J.) 09 May 1995(09.05.1995) the whole document	1-19
A	JP9043225A (SHIMADZU CORP.) 14 Feb. 1997(14.02.1997) the whole document	1-19

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 10 Nov. 2011(10.11.2011)	Date of mailing of the international search report 19 Jan. 2012 (19.01.2012)
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer XU, Yuanyuan Telephone No. (86-10)82245990

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/000566

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