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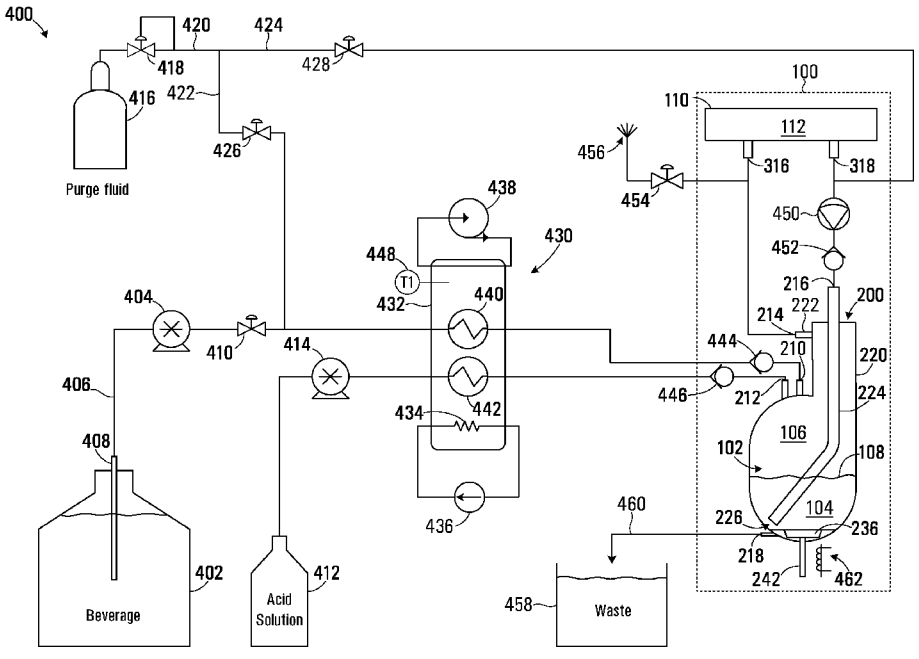


FIG. 4

(57) Abstract: A method for rapid determination of a concentration of free sulfur dioxide (SO_2) in a liquid is disclosed. The method involves receiving a liquid sample in an enclosed volume and, while a temperature of the liquid sample remains below 35°C, conditioning the liquid sample to cause gasified SO_2 to accumulate in a headspace of the enclosed volume above a surface of the liquid sample. The method further involves directing UV light having a wavelength between 250 nm and 320 nm through a gaseous sample taken from the headspace, and measuring an attenuation of the UV light due to absorption within the gaseous sample The concentration of gaseous SO_2 within the gaseous sample is determined from the measured attenuation.

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SYSTEM AND METHOD FOR RAPID DETERMINATION OF FREE SULFUR DIOXIDE CONCENTRATION IN A LIQUID

RELATED APPLICATIONS

This application claims the benefit of provisional patent application 63/270,706 entitled "SYSTEM AND METHOD FOR RAPID DETERMINATION OF FREE SULFUR DIOXIDE CONCENTRATION IN A LIQUID", filed on October 22, 2021 and incorporated herein by reference in its entirety.

BACKGROUND

1. Field

This disclosure relates generally to the determination of a free sulfur dioxide concentration in a liquid, and more particularly to a rapid determination of free sulfur dioxide concentration.

2. Description of Related Art

Sulfur dioxide (SO_2) concentration within a liquid is an important parameter in several industries. In the beverage industry and particularly for fermented beverages such as wine, beer, and cider, SO_2 may be considered to be desirable in limited concentrations. In its dissolved form, SO2 has antimicrobial and antioxidant effects. Some beverages may also include SO_2 that is bound to other constituents of the beverage such as aldehydes or ketones. The bound SO_2 is effectively inactive and not considered to be part of the free SO_2 that acts to prevent spoilage. Sulfites are however also considered to be food allergens and in some people may cause breathing difficulty, sneezing, hives, migraine, or other problems. This has led to certain jurisdictions placing limitations on total SO_2 concentration in beverages such as wine. The concentration of SO_2 in a beverage may thus be an important parameter to maintain and/or monitor.

Other industries also have a need for SO_2 concentration measurement. For example, boilers for heating water may be susceptible to tube fouling and sulfites may be added to mitigate this problem. The sulfite concentration may thus need monitoring to ensure that an effective concentration is maintained. Sulfites may also be used in water treatment industries where it is necessary to measure and control sulfite levels.

There is thus a need for improved techniques for measuring SO_2 concentration.

SUMMARY

In accordance with one disclosed aspect there is provided a method for rapid determination of a concentration of free sulfur dioxide (SO_2) in a liquid. The method involves receiving a liquid sample in an enclosed volume, the liquid sample including a quantity of the liquid, and a quantity of acid to promote gasification of SO_2 within the liquid. The method also involves, while a temperature of the liquid sample remains below 35°C, conditioning the liquid sample to cause gasified SO_2 to accumulate in a headspace of the enclosed volume above a surface of the liquid sample to provide a gaseous sample. The method further involves directing UV light through the gaseous sample, the UV light having a wavelength within a spectral range of between 250 nm and 320 nm. The method also involves measuring an attenuation of the UV light due to absorption within the gaseous sample and determining the concentration of gaseous SO_2 within the gaseous sample from the measured attenuation, the gaseous SO_2 concentration being indicative of the free SO_2 concentration within the liquid sample.

The liquid may include a beverage.

The liquid may include dissolved or entrained carbon dioxide (CO_2) and conditioning the liquid sample may involve causing at least some CO_2 within the liquid sample to accumulate in the headspace and determining the attenuation of the UV light may involve determining the attenuation of the UV light in the presence of CO_2 in the gaseous sample.

The method may involve causing the liquid sample to have a temperature within a temperature range of between 18°C and 35°C.

Receiving the liquid sample may involve receiving the liquid sample at a temperature of below 18°C.Receiving the liquid sample may involve passing the liquid sample through a heat exchanger to heat the liquid sample to a temperature within the temperature range.

The method may involve drawing the gaseous sample from the headspace and delivering the gaseous sample to a flow cell and directing the UV light through the gaseous sample may involve directing UV light through the flow cell.

Conditioning the liquid sample may involve sparging the liquid sample by drawing the gaseous sample from the headspace and recirculating the gaseous sample back below the surface of the liquid sample to cause free SO_2 in the liquid sample to be released into the headspace.

Sparging the liquid sample may involve delivering the recirculated gaseous sample to the enclosed volume at a location proximate a lower end of the enclosed volume.

Delivering the recirculated gaseous sample may involve directing the recirculated gaseous sample generally downwardly in the enclosed volume and with a component directed toward a lateral wall of the enclosed volume.

Recirculating the gaseous sample may involve passing the gaseous sample through a flow cell having an optical path therethrough and directing UV light through a gaseous sample may involve directing UV light through the optical path of the flow cell.

Drawing the gaseous sample may involve drawing the gaseous sample from a location above and spaced apart from the surface of the liquid sample to reduce a likelihood of liquid or foam from the liquid sample entering the recirculated gaseous sample and reaching the flow cell.

The enclosed volume may involve a passage that extends the headspace of the enclosed volume upwardly away from the surface of the liquid sample and drawing the gaseous sample may involve drawing the gaseous sample from a location proximate an upper end of the passage.

Drawing the gaseous sample may involve drawing the gaseous sample from the passage in a lateral direction.

Receiving the liquid sample may involve causing a liquid dosage system to draw the quantity of liquid from a container, and wherein a first portion of the quantity of liquid is delivered to the enclosed volume by operating the liquid dosage system , and a second portion of the quantity of liquid is delivered to the enclosed volume by flushing the liquid dosage system using a pressurized fluid. The liquid dosage system may be a liquid dosage pump. The pressurized fluid may be a pressurized gas.

The method may involve opening a vent valve in fluid communication with the headspace of the enclosed volume while flushing the liquid dosage system to permit pressurized fluid to escape. The pressurized fluid may be a pressurized gas.

The enclosed volume may include a drain port sealed by a drain valve at the bottom of the enclosed volume and the method may further involve, after the concentration of gaseous SO_2 within the gaseous sample has been determined, causing the drain valve to open to permit the liquid sample to be drained from the enclosed volume.

The drain valve may have a frustoconical shape and may be received in a frustoconical valve seat at the bottom of the enclosed volume and the valve may be configured to open by lifting upwardly out of the valve seat such that when being drained the liquid sample is completely drained to the bottom of the enclosed volume.

The method may involve flushing the enclosed volume by delivering a fluid to the enclosed volume that causes any remnants of the liquid sample to be forced out of the drain.

Directing UV light may involve directing UV light produced by a UV light emitting diode through the gaseous sample.

Measuring the attenuation of the UV light may involve generating modulated UV light, generating a measurement signal in response to receiving the UV light at a photodetector after passing through the gaseous sample, processing the measurement signal to extract components that are synchronized with the modulated UV light to determine an attenuation of the UV light, and determining the attenuation by comparing the level of attenuated UV light with a level of the generated modulated UV light.

Generating modulated light may involve generating UV light that may be intensity modulated at a reference frequency and processing the measurement signal may involve processing the measurement signal to extract components that are synchronized with the reference frequency to determine the attenuation of the UV light.

The photodetector may include a silicon carbide photodetector that is responsive to wavelengths of UV light in a narrow band including the 280 nanometer wavelength of the UV light.

The method may involve converting the measurement signal produced by the photodetector into a digital representation for receipt by a processor circuit and processing the measurement signal may involve mathematically processing the measurement signal in the processor circuit.

The method may involve splitting the UV light into a first beam of UV light and a second beam of UV light and directing UV light through the gaseous sample may involve directing the first beam of UV light along a measurement optical path through the gaseous sample in a measurement channel and may further involve directing the second beam of UV light through a reference optical path in a reference channel to generate a reference signal for extracting the measurement signal from noise.

The method may involve balancing the measurement channel and the reference channel while no gaseous sample is present.

Determining the concentration of gaseous SO_2 may involve producing an output absorption signal by taking a ratio of the measurement signal values and the reference signal and determining the SO_2 concentration based on fitting an exponential function to the output absorption signal.

The quantity of acid may include a quantity of phosphoric acid to lower a pH of the liquid sample to below pH 3.

In accordance with another disclosed aspect there is provided a system for rapid determination of a concentration of free sulfur dioxide (SO_2) in a liquid. The system includes an enclosed volume operable to receive a liquid sample, the liquid sample including a quantity of the liquid, and a quantity of acid to promote gasification of SO_2 within the liquid. The system also includes a liquid sample conditioner operably configured to condition the liquid sample to cause gasified SO_2 to accumulate in a headspace of the enclosed volume above a surface of the liquid sample while a temperature of the liquid sample remains below 35°C. The system further includes a flow cell in fluid communication with the headspace of the enclosed volume, the flow cell being operable to receive a gaseous sample taken from the headspace of the enclosed volume, the flow cell having an optical path therethrough. The system also includes a UV light source having a wavelength within a spectral range of between 250 nm and 320 nm, the UV light source being disposed to direct UV light through the optical path of the flow cell, a photodetector disposed to receive UV light passing through the gaseous sample and to generate measurement signal representing an attenuation of the UV light due to

absorption within the gaseous sample. The system further includes a processor operably configured to determine the concentration of gaseous SO_2 within the gaseous sample based on the attenuation signal, the gaseous SO_2 concentration being indicative of the free SO_2 concentration within the liquid sample.

The liquid may include a beverage.

Other aspects and features will become apparent to those ordinarily skilled in the art upon review of the following description of specific disclosed embodiments in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate disclosed embodiments,

Fig. **1** is a block diagram of a system for rapid measurement of a free sulfur dioxide (SO_2) in a liquid according to a first disclosed embodiment;

Fig. **2A** is a perspective view of a reactor vessel used in the system of Fig. **1**;

Fig. **2B** is an exploded view of a reactor vessel of Fig. **2A**;

Fig. **2C** is a cross sectional view of an enclosed volume of the reactor vessel taken along a line **2C-2C** in Fig. **2A**;

Fig. **2D** is a cross sectional view of the enclosed volume of the reactor vessel taken along a line **2D-2D** in Fig. **2A**;

Fig. **3** is a schematic view of an optical subsystem and controller for implementing the system shown in Fig. **1**;

Fig. **4** is a schematic view of a SO_2 monitoring system for a beverage including the system shown in Fig. **1**;

Fig. **5A** is a process flowchart showing blocks of code for directing the processor circuit of Fig. **4** to perform an initialization process;

Fig. **5B** is a process flowchart showing blocks of code for directing the processor circuit of Fig. **4** to perform a SO_2 concentration measurement;

Fig. **5C** is a process flowchart showing blocks of code for directing the processor circuit of Fig. **4** to perform a purge process;

Fig. **6** is a process flowchart showing blocks of code for directing the processor circuit of Fig. **4** to perform a channel balancing process;

Fig. **7** is a graphical depiction of signals generated by the system during a first time period t_i of the measurement process of Fig. **5B**;

Fig. **8** is a graphical depiction of signals generated by the system during a second time period t_m of the measurement process of Fig. **5B**; and

Fig. **9** is a process flowchart showing blocks of code for directing the processor circuit of Fig. **4** to implement a digital signal process in accordance with one disclosed embodiment.

DETAILED DESCRIPTION

Referring to Fig. **1**, a system for rapid measurement of a concentration of free sulfur dioxide (SO_2) in a liquid according to a first disclosed embodiment is shown generally at **100**. The SO_2 measurement system **100** includes an enclosed volume **102** operable to receive a liquid sample **104**. The liquid sample includes a quantity of the liquid and a quantity of acid. In the embodiment shown in Fig. **1**, the quantity of liquid and quantity of acid are separately received in the enclosed volume **102** and thus mix within the enclosed volume to form the liquid sample **104**. In other embodiments the liquid and acid may be mixed prior to being received in the enclosed volume **102**. The acid is added to promote gasification of the free SO_2 within the liquid. In one embodiment phosphoric acid may be added in a quantity selected to lower a pH of the liquid sample to a pH below pH 3. The quantities of liquid and acid are selected such that a headspace **106** remains above a surface **108** of the liquid sample **104**. In some embodiments, the size of the headspace **106** as a proportion of the liquid sample **104** may vary from the proportions shown in Fig. **1** and in particular the size of the headspace may occupy a significantly lesser proportion of the enclosed volume **102**.

The system **100** also includes a flow cell **110** and a liquid sample conditioner. The flow cell **110** is in fluid communication with the headspace **106** and receives the gaseous sample taken from the headspace. The gaseous sample flows through an interior volume **112** of the flow cell. In this embodiment a return line **114** in fluid communication with the flow cell **110** acts as the liquid sample conditioner. That is, the return line 114 may be used to condition the liquid sample. The return line **114** recirculates the gaseous sample to cause sparging of the liquid sample **104**. The sparging action of the recirculating gaseous sample in combination with the effect of the acid on hydrolysis accelerates gasification of the free SO_2 from the liquid sample **104** into the headspace **106**. In other embodiments the liquid sample **104** may be sparged using a fluid other than the gaseous sample or the liquid sample may be otherwise conditioned by mechanical mixing, cavitation, vibration, or other means.

In this embodiment the liquid sample conditioner operates to condition the liquid sample **104** while a temperature of the liquid sample remains below 35°C. A substantial portion of the free SO_2 will be effectively gasified at temperatures below 35°C while the bound SO_2 will substantially remain bound to other constituents. At temperatures above 35°C the bound SO_2 may begin to be released and will add to the free SO_2 thus increasing the apparent free SO_2 level in the liquid. While in some cases it may be necessary to evaluate total SO_2 in a liquid, the disclosure herein relates to evaluation of only the free SO_2 concentration that is effective in preventing spoilage. As such, in this embodiment, the determination is made at temperatures below 35°C.

The flow cell **110** includes a measurement optical path **118** extending through the interior volume **112**. The system **100** also includes a UV light source **116** having a wavelength within a spectral range of between 250 nm and 320 nm. The UV light source **116** is disposed to direct UV light through the optical path of the flow cell **110**. The system **100** also includes a measurement photodetector **120** disposed to receive UV light passing through the gaseous sample within the interior volume **112** of the flow cell **110**. The measurement photodetector **120** generates a measurement signal representing an attenuation of the UV light due to absorption within the gaseous sample.

The system **100** also includes a processor **124** operably configured to determine the concentration of gaseous SO_2 within the gaseous sample based on the attenuation signal. The gaseous SO_2 concentration is indicative of the free SO_2 concentration within the liquid sample. The processor **124** may be implemented using an analog electronic circuit, a digital electronic circuit, or a processor circuit.

SO_2 has a spectral absorption peak in the infrared wavelength region and also in the UV wavelength region around about 200 nm. However some liquids and particularly beverages such as wine may include varying concentrations of entrained or dissolved carbon-dioxide (CO_2). Some systems that have been previously implemented for measurement of SO_2 concentration in beverages use infrared wavelengths where CO_2 also exhibits significant spectral absorption. At these wavelengths it may thus be necessary to either eliminate CO_2 from the gaseous sample or attempt to separate the absorptive effects of CO_2 to determine the absorption due to SO_2 alone.

In this embodiment the spectral range of the UV light source **116** is specifically selected to be between 250 nm and 320 nm. Advantageously, relatively inexpensive UV sources and optical elements are available in this wavelength range. SO_2 also has a relatively prominent absorption peak in this wavelength range but CO_2 has effectively negligible absorption. This advantageously avoids the need to remove CO_2 from the liquid sample or otherwise compensate for the presence of CO_2 in the gaseous sample. In this embodiment the determination of SO_2 concentration may thus be made in the presence of CO_2 in the gaseous sample. The elimination of the need to remove CO_2 from the liquid sample also has the effect of reducing the time taken to obtain measurement results for the SO_2 concentration. During conditioning at least some CO_2 within the liquid sample thus accumulates in the headspace, and the attenuation of the UV light is determined in the presence of CO_2 in the gaseous sample.

Referring to Fig. **2A**, in one embodiment the enclosed volume **102** may be implemented using a two-part reactor vessel **200**. The reactor vessel **200** includes an upper housing portion **202** and a lower housing portion **204**. The upper housing portion **202** and the lower housing portion **204** are shown separated in Fig. **2B** and the enclosed volume **102** includes a portion **102'** formed in the lower housing portion **204** and remaining portion **102''** formed within the upper housing portion **202**. The lower housing portion **204** includes an o-ring seal **208** for sealing between the upper and lower housing portions when fastened together using bolts **206**, as shown in Fig. **2A**.

The upper housing portion **202** of the enclosed volume **102** includes a liquid inlet **210** for receiving the quantity of liquid and an acid inlet **212** for receiving the quantity of acid. The liquid inlet **210** and the acid inlet **212** are each connected via a conduit to respective openings **232** and **234** in the enclosed volume **102** for delivering the constituents of the liquid sample **104**.

The upper housing portion **202** also includes a gas outlet **214** for receiving the gaseous sample taken from the headspace within the enclosed volume **102**. The upper housing portion **202** further includes a gas inlet **216** for recirculating the gaseous sample through the liquid sample as described in more detail below. The lower housing portion **204** includes a drain outlet **218** for draining and flushing the liquid sample from the enclosed volume **102** when the SO_2 determination has been completed.

The enclosed volume **102** that is formed within the reactor vessel **200** is shown in first and second cross sectional views in Fig. **2C** and **2D** taken along respective lines **2C-2C** and **2D-2D** in Fig. **2A**. In Fig. **2C** and **2D** the enclosed volume **102** is shown schematically with portions of the reactor vessel **200** that define the enclosed volume and the interior conduits omitted for sake of illustration. Referring to Fig. **2C** the enclosed volume **102** has a vertically elongated generally oval shape and that receives the liquid sample **104**. In this embodiment, the reactor vessel includes a passage **220** that extends the headspace **106** upwardly within the enclosed volume **102** away from the surface **108** of the liquid sample **104**. The gas outlet **214** is provided by a gas conduit **222** proximate the top of the passage **220**. The gas conduit **222** also extends laterally from the passage **220** through the upper housing portion **202**.

In this embodiment the gas inlet **216** is in fluid communication with a sparging tube **224** extending through the passage **220** and the headspace portion of the enclosed volume into the liquid sample **104**. The sparging tube **224** has an opening **226** at a location proximate the bottom of the enclosed volume **102**. A bend **228** in the tube **224** orients the opening such that the flow of the recirculated gaseous sample through the tube is directed generally downwardly and laterally at a sidewall **230** of the enclosed volume **102**. The bend **228** in the tube **224** is selected to cause the opening **226** of the sparging tube **224** to be disposed as far away from the passage **220** and gas conduit **222** as possible.

The lower housing portion **204** includes a drain valve **236**, which has a frustoconical shape and includes an o-ring seal **238**. The drain valve **236** is received within a corresponding frustoconical shaped seat **240** (shown best in Fig. **2D**) and includes a stem **242** that extends downwardly from a base of the enclosed volume **102**. The stem **242** may be coupled to an actuator, such as a pneumatic actuator (not shown) configured to exert a downward force on the stem to cause the drain valve **236** to seal within the seat **240**. As shown in Fig. **2B**, the drain valve **236** thus forms a bottom surface of the enclosed volume **102** within the lower housing portion **204**. When received in the seat **240** as shown in Fig. **2C**, the valve **236** seals the enclosed volume **102** to contain the liquid sample **104**. When the stem **242** is displaced upwardly by the actuator as shown in Fig. **2D**,

the drain valve **236** is unseated and provides an annular opening **244** for draining the liquid sample **104** from the enclosed volume **102** via a catchment volume **246** and through a drain conduit **248**.

The flow cell **110**, UV light source **116**, measurement photodetector **120** and other optical elements of the system **100** form an optical subsystem shown in Fig. **3** at **300**. The optical subsystem **300** may be mounted on an optical breadboard **302** or other mounting arrangement. In one embodiment the flow cell **110** may be implemented using a glass cell **304** having end caps **306** and **308**. A suitable glass cell having threaded ends for receiving end caps is available from Thorlabs Inc. of New Jersey, United States. The end caps **306** and **308** accommodate respective optical windows **310** and **312**, which provide the optical path **118** through the cell **304**. The windows **310** and **312** are mounted between compressible seals **314** that seal off the interior volume **112** of the cell **304**. The cell **304** also includes an inlet port **316** and an outlet port **318**. The inlet port **316** receives the gaseous sample from the gas outlet **214** of the enclosed volume **102**. The outlet port **318** recirculates the gaseous sample back to the gas inlet **216**. In other embodiments the ports **316** and **318** may be reversed since the direction of flow of the gaseous sample through the interior volume **112** of the flow cell **110** may be in either direction. The components of the flow cell 110 may be implemented using one or more off the shelf components and/or customized parts. Using customized parts may improve packaging and integration with the surrounding optical systems.

In this embodiment the UV light source **116** is mounted to the optical breadboard **302** and may be implemented using a single color UV light emitting diode (UV-LED). In one embodiment the UV-LED may have a wavelength of 280 nm and a FWHM wavelength distribution width of about 12 nm. One or more lens elements **320** may be disposed to capture the UV radiation generated by the UV light source **116** and produce a UV light beam **322** that has a diameter selected to pass through the windows **310** and **312** without significant clipping. Other UV light sources such as a UV laser may be implemented in place of the UV-LED.

The optical subsystem **300** also includes a beamsplitter **324** that separates the UV light beam **322** into a measurement beam **326** and a reference beam **328**. In one embodiment the beamsplitter **324** may be configured for a 50:50 split ratio such that the measurement beam **326** and the reference beam **328** have substantially similar intensity. In other embodiments the beamsplitter **324** may be configured for other than a **50**:**50** split ratio. The measurement beam **326** is directed through the cell **300** via the window **310** where it interacts with the gaseous sample in the interior volume **112** of the flow cell **110**, before passing out of the cell via the window **312**. The measurement photodetector **120** is disposed and aligned to receive the measurement beam **326** exiting the flow cell **110** via a one or more lenses **330** that collect and focus the

measurement beam onto the measurement photodetector **120**. The measurement beam **326** thus passes along the measurement optical path **118** through the interior volume **112** of the flow cell **110** that will receive the gaseous sample and forms a measurement channel of the optical subsystem **300**. The reference beam **328** is directed through one or more lenses **332** that collect and focus the reference beam onto a reference photodetector **334**. The reference beam **328** passes through a reference optical path aligned with the reference photodetector 334 but does not pass through the gaseous sample. The reference optical path and the reference photodetector **334** together form a reference channel of the optical subsystem **300**.

In this embodiment the photodetectors **120** and **334** are implemented using Silicon carbide (SiC) photodetectors, which typically have a spectral response limited to wavelengths in the region of about 210 nm to 380 nm. SiC photodetectors are not sensitive to radiation outside this range, which allows the optical system **300** to be operated without additional filtering to prevent stray ambient light from influencing the signals detected by the photodetectors. In other embodiments the photodetectors **120** and **330** may be implemented using other types of photo-sensitive detectors.

The system **100** also includes a controller **350** for controlling operation of the system. In the embodiment shown the controller **350** includes a processor circuit **352**. The processor circuit **352** includes a microprocessor **354**, a program memory **356**, a data memory **358**, an Input/Output (I/O) interface **360**, and a USB interface **386**, all of which are in communication with the microprocessor **354**. Program codes for directing the microprocessor **354** to carry out various functions are stored in the program memory **356**, which may be implemented as a solid state memory, random access memory (RAM) and/or a hard disk drive (HDD), or a combination thereof. The I/O interface **360** may include an analog to digital signal converter **388** that is capable of receiving analog or digital input signals, converting analog input signals into digital representations, and generating output signals for controlling the system **100**. The data memory **358** is used to store variables and data associated with operation of the system **100**. In other embodiments (not shown), the controller **350** may be partly or fully implemented using a different processor circuit or using analog and/or digital elements in place of the processor circuit **352**.

The controller **350** also includes a UV source driver **362**, which generates a drive signal for powering the UV light source **116**. The controller **350** also includes a reference frequency generator **364**, which in this embodiment is configured to generate a sinusoidal reference frequency v_{REF} having a fixed frequency. In this embodiment the reference frequency v_{REF} has a frequency of about 1 kHz. The UV source driver **362** includes a modulation input **366** and is configured to modulate the drive signal based on the reference frequency v_{REF}.

The UV light produced by the UV light source **116** will thus have an intensity that is modulated at the reference frequency. The I/O interface **360** also includes an input **368** for receiving the reference signal, which is converted into a digital representation by the analog to digital signal converter **388** and is used for performing synchronous detection as described in more detail below.

In the embodiment shown the controller **350** also includes a signal conditioner **370**, which includes a pair of inputs **372** and **374** for receiving respective signals from the measurement photodetector **120** and the reference photodetector **334**. The signal conditioner receives raw signals from the photodetectors **120** and **334**, conditions the signals, and converts the signals into digital representations thereof. The digital representations are provided to the processor circuit **352** via a data input **376** of the USB interface **386**. In one embodiment the signal conditioner may be implemented using a two channel **24-B**it/**192** kHz Interface, such as the UMC202HD audio interface manufactured by Behringer.

In this embodiment the I/O interface **360** includes one or more outputs **378** that provide a plurality of control signals **380** for controlling the system **100**. For example, the one or more outputs **378** may be used to generate control signals **380** for controlling valves, actuators, and other elements as described in more detail later. The I/O interface **360** also includes one or more inputs **382**, which may be used to receive input signals **384** such as status signals associated with valves, actuators, or other elements, or signals representing various operating parameters such as temperatures of fluids in various parts of the system **100**.

Referring to Fig. **4**, a schematic diagram of a SO_2 monitoring system for a beverage is shown schematically at **400**. The beverage monitoring system **400** includes the SO_2 measurement system **100** of Fig. **1** and further includes elements that interact with the SO_2 measurement system to sample a beverage, deliver and condition the liquid sample **104**, and to flush the liquid sample once the measurement is completed. The beverage monitoring system **400** includes a plurality of fluid flow elements that may be controlled via the control signals **380** generated by the processor circuit **352**. As disclosed above the SO_2 measurement system **100** may alternatively be implemented to perform other non-beverage SO_2 monitoring functions.

In this embodiment the beverage is held in a container **402**, which may be a stainless steel tank, a concrete tank, a wooden barrel, or other beverage container. The monitoring system **400** also includes a beverage dosage pump **404**, which is connected via a liquid sample line **406** to a dip tube **408** inserted into the container **402**. The beverage dosage pump **404** is activated via one of the control signals **380** and is connected to a beverage valve **410**, which is also actuated by one of the control signals **380**. The acid solution is held in a

container **412**. Acid is drawn from the container **412** by an acid dosage pump **414**. The dosage pumps may be implemented using a small peristaltic dosage pump that are actuated by the control signal **380** for a fixed period of time to deliver a desired quantity of beverage or acid. Alternatively, other pumps that are operable to deliver a precise volume of liquid such as piston or syringe pumps may be used in place of the peristaltic pump.

The monitoring system **400** also includes a purge fluid **416** for performing purging functions during and subsequent to measurement of SO_2 concentration. The purge fluid may be a pressurized gas supply such as nitrogen or air connected through a pressure regulator valve **418** to provide a regulated gas feed on a line **420**. The pressure regulator valve **418** may be set to provide a fixed purge pressure. In the embodiment shown, the line **420** is split into two gas lines **422** and **424**. The gas line **422** includes a push valve **426** and the gas line **424** includes a purge valve **428**, which are respectively activated and de-activated via control signals **380** generated by the processor circuit **352** at the output **378** of the I/O interface **360**. The line **422** is connected to the output of the beverage valve **410** and the function of this line is described in more detail below. In other embodiments the purge fluid may be a pressurized liquid such as water.

The monitoring system **400** also includes a heat exchanger **430**. The heat exchanger **430** may be configured as a water bath **432** which is heated via a heater element **434** connected to a current source **436**. In other embodiments a glycol based coolant may be used in place of water or the water may include an additive such as a corrosion inhibitor. In this embodiment the heat exchanger **430** also includes a circulation pump **438** that circulates the water within the water bath **432** to promote a substantially uniform temperature throughout the bath. The heat exchanger **430** further includes first and second heat exchanger coils **440** and **442**, which may be implemented using coils of thermally conductive tubing immersed in the water bath **432**. The outlet of the beverage valve **410** is connected through the first heat exchanger coil **440**. The first heat exchanger coil **440** is connected via a check valve **444** to the liquid inlet **210** of the reactor vessel **200**. The outlet of the acid dosage pump **414** is connected through the second heat exchanger coil **442**. The second heat exchanger coil **442** is connected via a check valve **446** to the acid inlet **212** of the reactor vessel. The check valves **444** and **446** are located close to the respective liquid inlet **210** and acid inlet **212**. The heat exchanger **430** also includes a temperature sensor **448** (T1) for sensing a temperature of the water in the water bath **432**. The temperature sensor **448** produces a temperature signal that is received by the processor circuit **352** as one of the input signals **384** at the input **382** of the I/O interface **360**.

In other embodiments, various other heat exchanger configurations such as a counter-flow heat exchanger or finned shell and tube heat exchangers may be implemented to provide packaging or performance improvements. A solid-to-liquid heat exchanger utilizing electric heating and cooling via a heating coil or a Peltier thermo-electric device may also be used to eliminate the need for a working fluid and to improve portability of the system.

The gas outlet **214** of the reactor vessel **200** is connected to the inlet port **316** of the flow cell **110** and the outlet port **318** is connected via a recirculation pump **450** and a check valve **452** to the gas inlet **216** of the reactor vessel **200**. In one embodiment, the recirculation pump **450** may be implemented using a diaphragm pump actuated in response to one control signals **380** to cause flow of the gaseous sample through the pump.

The outlet port **318** of the flow cell **110** is also connected to the purge valve **428**, while the inlet port **316** is connected via a vent valve **454** to a vent **456** that is open to the atmospheric environment. The vent valve **454** is configured to open in response to one of the control signals **380** generated by the processor circuit **352**. The vent valve **454** when opened permits gas to escape through the vent **456** from the enclosed volume **102** and interior volume **112** of the flow cell **110** or permits air to enter the enclosed volume and interior volume.

The monitoring system **400** also includes a waste receptacle **458**, which is in communication via a waste line **460** with the drain outlet **218** of the reactor vessel **200**. The drain valve **236** is actuated to open and close by exerting a force on the stem **242** via an actuator **462** such as a solenoid or pneumatic actuator. The actuator **462** is controlled by one of the control signals **380** generated by the processor circuit **352**. The location of the drain valve **236** and seat **240** at the bottom of the enclosed volume **102** ensures that the liquid sample is completely drained to the bottom of the enclosed volume.

The operation of the beverage monitoring system **400** is described further with reference to flowcharts shown in Fig. **5A**, **5B** and **5C** that depict blocks of code for directing the processor circuit **352** to perform the SO_2 concentration measurement. The blocks generally represent codes that may be read from the program memory **356** for directing the microprocessor **354** to perform various functions related to the SO_2 measurement. The actual code to implement each block may be written in any suitable program language, such as Python, C, C++, C#, Java, and/or assembly code, for example.

Referring to Fig. **5A**, an initialization process embodiment is shown generally at **500**. The initialization process **500** may be performed when initially preparing the system for measurement but need not be repeated prior to measurements on each of a plurality of different beverage containers. Initially the enclosed volume **102** of the reactor vessel **200** would have been drained after a previous measurement and should be substantially empty except for some possible residual of liquid sample from the previous measurement. The water bath **432** of the heat exchanger **430** would also have been filled with water.

The initialization process begins at block **502**, which directs the microprocessor **354** activate the heat exchanger **430**. This involves directing the microprocessor **354** to generate the necessary control signals **380** to switch on the circulation pump **438** of the heat exchanger **430** and cause the current source **436** to deliver current to the heater element **434** for heating the water in the water bath **432**. Block **502** also directs the microprocessor **354** to monitor the temperature signal *T1* generated by the temperature sensor **448** by monitoring the applicable input signal **384**.

The process **500** then continues at block **504**, which directs the microprocessor **354** to determine whether the temperature *T1* of the water bath **432** has reached a target temperature. In one embodiment an appropriate target temperature for determining SO_2 in a beverage may be in the range of 18°C to 35°C. Beverages such as wine may ferment at temperatures above 20°C but would be aged at a lower temperature, typically below 18°C. Depending on the point in the winemaking process, there may or may not be a need to heat the beverage prior to SO_2 measurement. As an example, the target temperature may be set to 25°C and block **504** would then direct the microprocessor **354** to maintain the temperature of the water bath **432** at approximately 25°C, within an allowable variance range. If *T1* is outside the variance range, block **504** directs the microprocessor **354** to repeat block **504**. When *T1* is inside the variance range, block **504** directs the microprocessor **354** to block **506**. Block **506** may continue to be executed in parallel with other blocks of the process **500** to maintain the temperature *T1* within the allowable variance range.

Block **506** then directs the microprocessor **354** to generate a control signal **380** that causes the drain valve **236** to be opened. Block **506** also directs the microprocessor **354** to generate a control signal **380** that causes the vent valve **454** to be opened. The process then continues at block **508**, which directs the microprocessor **354** to generate a control signal **380** to activate the acid dosage pump **414** for priming the acid line connected to the acid inlet **212** of the reactor vessel **200**. In one embodiment the acid dosage pump **414** may be activated for about **4** seconds. Priming of the acid dosage pump **414** and the acid line ensures that the quantity of acid dispensed for a first measurement will be substantially equivalent to the quantity dispensed

in subsequent measurements. During priming, some acid will be delivered through the acid inlet **212** into the enclosed volume **102**. This acid is able to drain through the open drain valve **236** and drain outlet **218** into the waste receptacle **458**. The opening of the vent valve **454** permits air to flow through the vent and prevents a vacuum or pressurization condition from occurring in the enclosed volume **102** that may cause retention of some acid within the enclosed volume. The check valve **446** effectively holds the prime once the priming step is completed, which is one reason for locating the check valve **446** close to the acid inlet **212**. Following block **508**, the initialization process **500** is completed and the microprocessor **354** is directed to block **522** in Fig. **5B** for performing the SO_2 measurement.

Referring to Fig. **5B**, an embodiment of a measurement process is shown generally at **520**. Following the initialization process **500** (or a purge process **560** described later herein) the drain valve **236** and vent valve **454** remain open. The measurement process **520** starts at block **522**, which directs the microprocessor **354** to generate control signals **380** to activate the beverage dosage pump **404** and the beverage valve **410** to deliver a flush volume of beverage to the enclosed volume **102** of the reactor vessel **200**. In one embodiment the flush volume may be about 4 milliliters of beverage. The flush volume when delivered to the enclosed volume **102** has the effect of flushing the enclosed volume to remove traces of residual beverage that remained in the enclosed volume after the previous measurement. The open vent valve **454** facilitates venting of gas within the enclosed volume **102** that is initially displaced by the flush volume and then allows air to flow into the enclosed volume as the flush volume is drained. Once the flush volume of beverage has been delivered and drained, the microprocessor **354** is directed to block **524**.

Block **524** directs the microprocessor **354** to generate control signals **380** to deactivate the beverage dosage pump **404** and close the beverage valve **410**. Block **526** then directs the microprocessor **354** to generate a control signal **380** to open the push valve **426**, which permits pressurized gas from the pressurized gas supply **416** to flow through the gas line **422** and into the line connected to the liquid inlet **210** of the reactor vessel **200**. Since the beverage valve **410** has already been closed at block **524**, this has the effect of pushing any remaining beverage out of the liquid sample line through the liquid inlet **210**, which will then be drained from the enclosed volume **102** through the drain valve **236**. At this point the enclosed volume **102** has been flushed by a small amount of the beverage for which the SO_2 concentration is about to be measured, thus reducing the likelihood of cross-contamination by the prior liquid sample that had been received in the enclosed volume **102**.

The measurement process **520** then continues at block **528** which directs the microprocessor **354** to start recording the signals generated by the measurement photodetector **120** and reference photodetector **334**. Block **528** causes the signal values to be periodically sampled during the remainder of the measurement process **520**. The resulting digital values produced by the signal conditioner **370** of the controller **350** are then received at the data input **376** and stored in the data memory **358**. In one embodiment the samples are taken at a fixed sample rate and the representative values are stored in sequential memory locations for the remainder of the measurement period. For the signal conditioner **370** implemented using the Behringer audio interface the sample rate is **44**.1 kHz). In this embodiment, the reference frequency v_{REF} generated by the reference frequency generator **364** is simultaneously, received at the input **368** of the I/O interface **360**, converted into digital values representing the reference frequency, and stored in the data memory **358**. In one embodiment the samples of the reference frequency may be taken at a fixed interval corresponding to the sample rate of the measurement and reference photodetector signals. In this embodiment the recording of the photodetector signals is commenced before the gaseous sample begins recirculating through the interior volume **112** of the flow cell **110**, which provides data for balancing the measurement channel and reference channel of the optical subsystem **300** before the interior volume **112** receives the gaseous sample. A balancing process that may be executed by the processor circuit **352** after the signals have been received and stored is described later herein.

Block **530** then directs the microprocessor **354** to generate a control signal **380** to close the drain valve in preparation for receiving the liquid sample **104**. The vent valve **454** remains open to allow displaced air in the enclosed volume **102** to escape through the gas outlet **214** and through the vent **456**. The vented air is substantially prevented from passing into the flow cell **110** via the port **316** since the flow path through the port **318** remains blocked by the inactivated recirculation pump **450** and the check valve **452**.

The measurement process **520** then continues at block **532**, which directs the microprocessor **354** to generate control signals **380** to activate the beverage dosage pump **404** and to open the beverage valve **410**. The beverage dosage pump **404** is operated to deliver a desired quantity of beverage through the first heat exchanger coil **440** of the heat exchanger **430** and through the liquid inlet **210** into the enclosed volume **102** of the reactor vessel **200**. Block **532** also directs the microprocessor **354** to generate a control signal to activate the acid pump for delivering the quantity of acid through the second heat exchanger coil **442** of the heat exchanger **430** and through the acid inlet **212** into the enclosed volume **102**. Block **534** then directs the microprocessor **354** to determine whether an acid dosage time has elapsed. In one embodiment the acid dosage pump **414** is operated for a time period sufficient to dispense a quantity of about 7.5 milliliters of acid

into the enclosed volume **102**. When the acid dosage time has expired block **534** directs the microprocessor **354** to block **536**, which directs the microprocessor to generate control signals to deactivate the acid dosage pump **414**.

Block **538** then directs the microprocessor **354** to determine whether a beverage dosage time has elapsed. In one embodiment the beverage dosage pump **404** is operated for a time period sufficient to draw a quantity of about 15 milliliters of beverage from the container **402**. The beverage dosage time will thus generally extend beyond the acid dosage time. When the beverage dosage time has elapsed, block **538** directs the microprocessor **354** to block **540**. Block **540** directs the microprocessor **354** to generate control signals to deactivate the beverage dosage pump **404** and to close the beverage valve **410**. In this embodiment, block **540** also directs the microprocessor **354** to generate a control signal **380** to cause the push valve **426** to open to drain the liquid sample line. The pressurized gas from the pressurized gas supply **416** pushes out the remaining beverage in the liquid sample line through the liquid inlet **210** into the enclosed volume **102**. In this disclosed embodiment a first portion of the quantity of beverage is thus delivered to the enclosed volume **102** by operating the liquid dosage pump **404** followed by a second portion of the quantity of beverage being delivered to the enclosed volume by flushing the liquid dosage pump using a pressurized fluid to remove residual beverage from the liquid sample line. The removal of the residual from the liquid sample line reduces the likelihood of cross-contamination with a later beverage sample drawn from a different beverage container. In other embodiments the additional step of opening the push valve **426** to drain the sample line may be omitted. Block **542** then directs the microprocessor **354** to generate a control signal to close the push valve **426**. In one embodiment the push valve **426** is opened for about 4 seconds for the purpose of draining the liquid sample line. Block **542** then directs the microprocessor **354** to generate a control signal **380** to close the vent valve **454** in preparation for recirculation of the gaseous sample. At this time the optical subsystem **300** is sealed from the atmosphere to contain any released SO_2 within the headspace **106** or the interior volume **112** of the flow cell **110** and the flow lines between these volumes.

In the embodiment shown the size of the enclosed volume **102** and the quantity of beverage may be selected to fill the enclosed volume **102** such that the headspace **106** occupies a proportion of about 50% of the enclosed volume. Any entrained liquid that reaches the interior volume **112** of the flow cell **110** could deposit on the windows **310** and **312**, thus potentially obstructing the optical path **118**. As such, it is important to maintain separation between the liquid sample **104** and the headspace **106** to prevent liquid from being entrained in the gaseous sample drawn through the gas outlet **214** into the interior volume **112** of the flow cell **110**. Fermented beverages in particular are very susceptible to foaming, which may cause liquid to be

entrained in the gaseous sample. The proportion of the enclosed volume **102** occupied by the headspace **106** represents a trade-off in that a smaller headspace facilitates a more rapid release of free SO_2 from the liquid sample into the headspace, thus potentially reducing an overall measurement time. However, if the headspace **106** is too small, there is a greater risk of entrainment of liquid in the gaseous sample. In some embodiments the liquid sample **104** may occupy as much as 90% or 95% of the enclosed volume **102** and the headspace **106** proportion may thus be relatively small. In other embodiments, the liquid sample **104** may occupy as little as 15% of the enclosed volume **102**. For example, the ratio of the volume of the liquid sample **104** to the headspace **106** may be 20 mL/ 100 mL (e.g., the liquid sample **104** may occupy 20% of the volume occupied by the headspace **106**, which corresponds to 16.67% of the enclosed volume **102**).

In some embodiments where foaming or liquid entrainment is not problematic the headspace proportion may be reduced below 50% of the enclosed volume **102**. While in the embodiments disclosed above the gaseous sample is described as being taken from the headspace **106** and delivered to the flow cell **110**, in embodiments where foaming is not problematic the UV light may be directed through the gaseous sample while in-situ within the headspace **106**. In this case, the UV light may be delivered directly through the headspace **106** through windows (not shown) in the upper housing portion **202** of the reactor vessel **200**. As such the separate flow cell **110** may be eliminated and effectively incorporated within the reactor vessel **200**. The recirculation of gas from the headspace **106** may be maintained for purposes of sparging the liquid sample **104** or sparging may be accomplished using other mechanical or vibrational means as described above.

The process **520** then continues at block **544**, which directs the microprocessor **354** to generate a control signal **380** that activates the recirculation pump **450** to draw the gaseous sample from the headspace **106** through the gas outlet **214**. In this disclosed embodiment the gas conduit **222** and gas outlet **214** are at a location above the surface **108** of the liquid sample **104** and are spaced apart from the liquid sample surface to reduce the likelihood of liquid or foam entering the recirculated gaseous sample and reaching the flow cell **110**. The upwardly extending passage **220** provides for further separation between the surface **108** of the liquid sample **104** and the gas outlet **214**. Additionally, the gas conduit **222** being orientated at laterally (i.e. at an angle of about 90°) to the passage **220** further reduces the likelihood of any liquid or foam splashed upwardly within the enclosed volume **102** entering the gas conduit **222**.

The activation of the recirculation pump **450** causes the gaseous sample to be drawn from the headspace **106** and circulated through the inlet port **316** , through the interior volume **112** of the flow cell **110**, and out

through the outlet port **318**. The recirculated gaseous sample is returned to the reactor vessel **200** through the gas inlet **216** and the sparging tube **224** for sparging the liquid sample **104**. The opening **226** of the sparging tube **224** delivers the recirculated gaseous sample to the enclosed volume **102** at a location proximate a lower end of the enclosed volume **102**. The opening **226** is thus directed generally downwardly and with a component directed toward a lateral wall of the enclosed volume **102**, which has the effect of reducing the possibility of foaming and splashing of the liquid sample that may enter the passage **220** and gas conduit **222**. Furthermore, the recirculated gaseous sample has the effect of increased mass transfer between gas phase bubbles created by the recirculated gaseous sample and the liquid sample **104** during sparging due to the increased path for the bubbles to reach the surface **108** of the liquid sample. The conditioning of the liquid sample thus involves sparging the liquid sample **104** by drawing the gaseous sample from the headspace **106** and recirculating the gaseous sample back below the surface **108** of the liquid sample to cause free SO_2 in the liquid sample to be released into the headspace.

The measurement process **520** then continues at block **546**, which directs the microprocessor **354** to determine whether a recirculation time has elapsed. The recirculation should be maintained for a sufficient time to cause the free SO_2 in the liquid sample **104** to be released into the headspace **106**. In one embodiment the recirculation time may be about 30 seconds.

During the recirculation time, the signals generated by the photodetectors **120** and **334** are monitored and recorded as described above in connection with block **528**. When the recirculation time expires block **546** directs the microprocessor **354** to block **548**. Block **548** directs the microprocessor **354** to stop recording the signals generated by the photodetectors **120** and **334**. Block **548** also directs the microprocessor **354** to deactivate the recirculation pump **450**, completing the measurement process **520**. Block **548** then directs the microprocessor **354** to block **562** of the purge process **560** shown in Fig. **5C**.

Referring to Fig. **5C**, an embodiment of a purge process performed after the measurement process **520** is shown generally at **560**. The purge process **560** begins at block **562**, which directs the microprocessor **354** to generate control signals **380** to open the drain valve **236** and open the vent valve **454**. The vent **456** permits air to enter the enclosed volume **102** through the vent valve **454**, which facilitates draining the liquid sample **104** from the enclosed volume **102**. Block **564** then directs the microprocessor **354** to generate control signals to open the push valve **426** and the purge valve **428**. The open push valve **426** delivers the pressurized gas purge fluid **416** through the liquid inlet **210** to the enclosed volume **102**. The pressurized gas forces the liquid sample **104** through the open drain valve **236** and drain outlet **218** into the waste receptacle **458**. At the

same time the gas line between the gas outlet **214** and the vent **456** is flushed by the pressurized gas through the vent **456**. The open purge valve **428** also delivers pressurized gas via the outlet port **318** to the outlet port **318** of the flow cell **110**. Since the recirculation pump **450** is not activated the flow is effectively blocked by the pump. The pressurized gas thus flows through the outlet port **318**, purges the interior volume **112** of the flow cell **110**, and is vented through the vent **456**.

Block **566** then directs the microprocessor **354** to determine whether the purge time has expired. In one embodiment the purge time may be about 5 seconds. When the purge time has expired, the microprocessor **354** is directed to block **568**, which directs the microprocessor to generate control signals **380** to cause the vent valve **454** to close. When the vent valve **454** closes, a full flow of pressurized gas being delivered through the liquid inlet **210** and via the purge valve **428** through the flow cell **110** will be directed through the drain valve **236**, which causes a surge to drive a substantial remaining portion of the liquid sample **104** through the drain valve.

The purge process **560** then continues at block **570**, which directs the microprocessor **354** to generate control signals **380** to reverse the beverage dosage pump **404** and to activate the recirculation pump **450**. The reversing of the beverage dosage pump **404** draws pressurized gas through the beverage valve **410** which purges the liquid sample line **406** and dip tube **408**. The recirculation pump **450** also draws the pressurized gas through the gas line **424** and purge valve **428** to flush the recirculation pump **450** and the gas inlet **216** with the pressurized gas. The pressurized gas vents through the drain valve **236**. Block **572** then directs the microprocessor **354** to generate control signals **380** to deactivate the recirculation pump and beverage dosage pump.

Following completion of the purge process **560**, the enclosed volume **102** of the reactor vessel, interior volume **112** of the flow cell, the sparging tube **224**, the gas lines, liquid sample line, and the pumps **404** and **450** will all have all been flushed by the pressurized gas. The use of an inert gas such as nitrogen as the pressurized gas would effectively remove a substantial portion of the liquid sample **104** and beverage sample from the monitoring system **400** and reduce the likelihood of cross-contamination occurring in a subsequent SO_2 measurement performed for a different beverage. The drain valve **236** and vent valve **454** may remain open to prepare the beverage monitoring system **400** for a subsequent measurement, since the measurement process **520** starts out with these valves in this state.

The reference channel of the optical subsystem **300** may be used by the controller **350** to correct for any noise in the UV light beam **322** generated by the UV light source **116**. Small concentrations of SO_2 in the gaseous sample will typically result in small signal differences that can easily be obscured in the noise due to the UV light source **116** or other elements of the optical subsystem **300** and controller **350**. The reference channel and measurement channel would generally be subjected to the same noise sources and the reference signal may thus be used to attenuate the noise, thus increasing the signal to noise ratio for discriminating absorption effects due to SO_2 on the measurement signal produced by the measurement photodetector **120**.

Referring to Fig. **6**, a channel balancing process is shown generally at **600**. The process begins at block **602**, which directs the microprocessor **354** to select data sample values form the recorded photodetector signals for both the reference channel and measurement channel. These samples would typically be selected from the first samples recorded starting at block **568** of the measurement process **520** during a time t_i. At this time, the flow cell **110** remains in a purged state established by executing the purge process **560** after a previous measurement on a beverage had been completed. The signal level produced by the measurement photodetector **120** will thus be effectively unattenuated by its passage through the flow cell **110** since the interior volume **112** would have been flushed of SO_2 from the previous measurement by the purge fluid **416**.

Examples of signals generated by the measurement photodetector **120** and the reference photodetector **334** during the initial time t_i while the quantity of beverage is being delivered to the enclosed volume **102** are shown graphically in Fig. **7** at **700**. Referring to Fig. **7**, the measurement channel signal produced by the measurement photodetector **120** is shown at **702**. In this embodiment the UV light source **116** is sinusoidally modulated at about 1000 Hz and the symbols "♦" represent data sample values that are generated by the signal conditioner **370** of the controller **350** in response to receiving the signal produced by the measurement photodetector **120**. The reference channel signal produced by the reference photodetector **334** is shown at **704** and the symbols "●" represent data sample values that are generated by the signal conditioner **370** of the controller **350** in response to receiving the signal produced by the reference photodetector. Each data sample value is thus represented by a pair of values (y,t) including a photodetector voltage y and a sample time t. In this embodiment the data sample values **702** from the measurement channel are at a slightly higher level than the data sample values **704** from the reference channel due to a small imbalance between the channels.

The process then continues at block **604**, which directs the microprocessor **354** to fit a sinusoid to the data sample values **702** for the measurement channel. In one embodiment a linear regression may be performed using the following function:

$$y(t) = a\,sin(2\pi ft) + b\,cos(2\pi ft) + c. \qquad \text{Eqn } \mathbf{1}$$

Each data sample value *y* at a sample time *t* in the data sample values **702** may be substituted into Eqn **1** above to perform a linear regression that yields the parameters *a*, *b*, and *c*. The determined parameters *a*, *b*, and *c* may be used to define a sinusoid **706** for the measurement channel, written as:

$$y_M = A_M\,sin(2\pi ft + \phi_M) + c_M, \qquad \text{Eqn } \mathbf{2}$$

where:

y_M is the measured signal;

A_M is the amplitude of the sinusoid;

f is the frequency in Hz;

t is the time in seconds;

ϕ_M is the phase shift of the sinusoid; and

c_M is the dc offset of the photodetector signal (**0**.080 V).

The process then continues at block **606**, which directs the microprocessor **354** to repeat the above linear regression for the data samples to fit a sinusoid to the data sample values **704** for the reference channel:

$$y_R = A_R\,sin(2\pi ft + \phi_R) + c_R, \qquad \text{Eqn } \mathbf{3}$$

where:

y_R is the reference signal;

A_R is the amplitude of the sinusoid;

ϕ_R is the phase shift of the sinusoid; and

c_R is the DC offset of the photodetector signal.

Even if the measurement photodetector **120** and reference photodetector **334** are matched and the beam-splitter **324** is configured for a **50**:**50** split ratio, there may be slightly different gain and/or DC offset between the measurement and reference channels that cause the sinusoids **706** and **708** to be separated on the y axis and also have slightly differing amplitude A_M and A_R.

Block **608** then directs the microprocessor **354** to determine a balancing transformation for balancing the reference channel to the measurement channel. The balancing transformation may be applied to subsequent reference channel data sample values y_R to provide a balanced reference signal y_{RB}:

$$y_{RB} = \left[\frac{A_M}{A_R}[y_R(t - \phi_R + \phi_M) - c_R] + c_M\right]. \quad \text{Eqn } \mathbf{4}$$

In practice, the phase shifts ϕ_R and ϕ_M may be considered negligible for the optical subsystem **300** shown in Fig. **3** and may be ignored.

In the embodiment described above the UV light generated by the UV light source **116** is sinusoidally modulated in intensity. In other embodiments various other modulation techniques that place a modulation signature on the UV light, such as wavelength modulation, may be implemented with similar effect.

In one embodiment synchronous detection (lock-in amplification) may be performed on the reference signal y_{RB} and measurement signal y_M. The lock-in amplification further improves the signal to noise ratio of the absorption and reference signals. Referring to Fig. **9**, a digital signal process executed by the processor circuit **352** in accordance with one disclosed embodiment is shown generally at **900**. The process **900** is separately executed for each of the signals y_M and y_{RB}. Block **902** directs the microprocessor **354** to multiply each of the signals y_M and y_{RB} by the reference frequency υ_{REF}. The resulting signals thus become:

$$y'_M = \frac{1}{2} y_M \upsilon_{REF}[cos([2\pi(f_M - f_{REF})]t + \phi_M - \phi_{REF}) - cos([2\pi(f_M + f_{REF})]t + \phi_M + \phi_{REF})]$$

Eqn **5**

and

$$y'_{RB} = \frac{1}{2} y_{RB} \upsilon_{REF}[cos([2\pi(f_{RB} - f_{REF})]t + \phi_{RB} - \phi_{REF}) - cos([2\pi(f_{RB} + f_{REF})]t + \phi_{RB} + \phi_{REF})]$$

Eqn **6**

where:

f_M is the frequency of the measured signal y_M;

f_{RB} is the frequency of the balanced reference signal y_{RB};

f_{REF} is the frequency of the reference frequency υ_{REF};

ϕ_M is the phase of the measured signal y_M;

ϕ_{RB} is the phase of the reference signal y_{RB}; and

ϕ_{REF} is the phase of the reference frequency υ_{REF}.

The output signals in equations **5** and **6** thus each have two AC components, one at a difference frequency ($f_M - f_{REF}$) or ($f_{RB} - f_{REF}$) and the other at a sum frequency ($f_M + f_{REF}$) or ($f_{RB} + f_{REF}$). The process then continues at block **904**, which directs the microprocessor **354** to low pass filter the signals y'_M and y'_{RB} to remove the sum frequency component in equations **5** and **6**. Additionally, since the frequency f_M and f_{RB} are both derived from the reference frequency f_{REF} generated by the reference frequency generator **364** the difference frequencies ($f_M - f_{REF}$) and ($f_{RB} - f_{REF}$) will both be zero. For the optical subsystem **300** the phase shifts should also be negligible and thus the remaining cosine term in equations **5** and **6** will be unity and the output signals will be:

$$y'_M \approx \frac{1}{2} y_M v_{REF} \qquad \text{Eqn } \mathbf{7}$$

and

$$y'_{RB} = \frac{1}{2} y_{RB} v_{REF}, \qquad \text{Eqn } \mathbf{8}$$

which are both DC signals proportional to the amplitude of y_M and y_{RB}.

In the digital lock-in amplifier implementation shown in Fig. **9**, the signals and reference frequency are both represented by sequences of numbers and the multiplication and filtering are performed mathematically by using digital signal processing functions.

Block **906** of the process **900** then directs the microprocessor **354** to further process the signals y'_M and y'_{RB} to yield an output absorption signal y_A by taking a ratio of the data sample values:

$$y_A = \frac{y'_M}{y'_{RB}}. \qquad \text{Eqn } \mathbf{9}$$

A graphical depiction of y_A is shown graphically in Fig. **8** at **800**. As disclosed above in connection with block **528** of the measurement process **520**, recording of the signals generated by the photodetectors **120** and **334** begins after the enclosed volume **102** has been flushed with a quantity of the beverage for which the SO_2 concentration is being determined. The recording of the signals generated by the photodetectors **120** and **334** continues through the measurement process **520** up to block **548**, which directs the microprocessor **354** to stop recording the signals. During the initial time period t_i the processed signal y_a has a value close to unity due to the above ratio being taken between the measurement signal values and the reference signal values, which have been balanced by the channel balancing process **600**. During the time t_i, the measurement channel has negligible absorption since the gaseous sample has not yet been introduced into the interior volume **112** of the flow cell **110**. Toward the end of the time period t_i the quantity of beverage is introduced into the enclosed volume **102**.

During a second time period t_m the quantity of acid is introduced into the enclosed volume **102**, which will promote the release of free SO_2 from the liquid sample **104** into the headspace **106** through acid hydrolysis. The recirculation pump **450** is also activated and the gaseous sample will thus begin to be delivered to the interior volume **112** of the flow cell **110**. The SO_2 concentration in the interior volume **112** of the flow cell **110** will begin to increase due to the combination of the sparging action and acid hydrolysis. The SO_2 concentration will thus start to increase causing a corresponding increase in absorption and thus a decrease in the ratio signal y_a. At some point during the time t_m, the SO_2 concentration within the interior volume **112** reaches an equilibrium and the signal y_a thus approaches an asymptote. At the end of the time t_m recording of the signal generated by the measurement photodetector **120** may be discontinued.

The process **900** then continues at block **908**, which directs the microprocessor **354** to fit an exponential function to the absorption ratio signal y_a values that fall within the time period t_m. The optical absorption due to a gas such as SO_2 is given by the Beer–Lambert law, which may be written in the form:

$$A = \frac{P_O}{P} = e^{\epsilon b C}, \qquad \text{Eqn } \mathbf{10}$$

where:

A is the absorption within the gaseous sample due to a concentration C of SO_2;

ϵ is the molar absorption coefficient for SO_2; and

b is the length of the optical path **118**.

Fitting an exponential function to the y_a values during the time t_m thus yields a value for the exponent ϵbC. In other embodiments, another function may be fitted to the y_a values to yield a value for ϵbC. For example, a function with a larger number of degrees of freedom may be used. Block **910** then directs the microprocessor **354** to calculate the SO_2 concentration C using known values of the molar absorption coefficient ϵ and the length of the optical path **118**.

The above disclosed embodiments provide for a rapid and accurate determination of SO_2 concentration in the presence of CO_2. In one embodiment the elapsed time between executing block **528** and executing block **548** may be about **50** seconds. The purge process **560** adds about 10 seconds for a total measurement time of about **1** minute. This test time makes the SO_2 measurement system **100** particularly suitable for applications where SO_2 monitoring is to be done on a large number of beverage containers, such as in a winery using wooden barrels. The implementation of various anti-foaming features in both the reactor vessel

and the measurement process reduces the possibility of liquid fouling of the optical subsystem **300**, which generally would necessitate cleaning downtime.

While specific embodiments have been described and illustrated, such embodiments should be considered illustrative only and not as limiting the disclosed embodiments as construed in accordance with the accompanying claims.

What is claimed is:

1. A method for rapid determination of a concentration of free sulfur dioxide (SO_2) in a liquid, the method comprising:

receiving a liquid sample in an enclosed volume, the liquid sample including:

a quantity of the liquid; and

a quantity of acid to promote gasification of SO_2 within the liquid;

while a temperature of the liquid sample remains below 35°C, conditioning the liquid sample to cause gasified SO_2 to accumulate in a headspace of the enclosed volume above a surface of the liquid sample to provide a gaseous sample;

directing UV light through the gaseous sample, the UV light having a wavelength within a spectral range of between 250 nm and 320 nm;

measuring an attenuation of the UV light due to absorption within the gaseous sample; and

determining the concentration of gaseous SO_2 within the gaseous sample from the measured attenuation, the gaseous SO_2 concentration being indicative of the free SO_2 concentration within the liquid sample.

2. The method of claim **1** wherein the liquid comprises a beverage.

3. The method of claim **1** wherein the liquid includes dissolved or entrained carbon dioxide (CO_2) and wherein conditioning the liquid sample comprises causing at least some CO_2 within the liquid sample to accumulate in the headspace, and wherein determining the attenuation of the UV light comprises determining the attenuation of the UV light in the presence of CO_2 in the gaseous sample.

4. The method of claim **1** further comprising causing the liquid sample to have a temperature within a temperature range of between 18°C and 35°C.

5. The method of claim **4** wherein receiving the liquid sample comprises passing the liquid sample through a heat exchanger to heat the liquid sample to a temperature within the temperature range.

6. The method of claim **1** further comprising drawing the gaseous sample from the headspace and delivering the gaseous sample to a flow cell and wherein directing the UV light through the gaseous sample comprises directing UV light through the flow cell.

7. The method of claim **1** wherein conditioning the liquid sample comprises sparging the liquid sample by drawing the gaseous sample from the headspace and recirculating the gaseous sample back below the surface of the liquid sample to cause free SO_2 in the liquid sample to be released into the headspace.

8. The method of claim **7** wherein sparging the liquid sample comprises delivering the recirculated gaseous sample to the enclosed volume at a location proximate a lower end of the enclosed volume.

9. The method of claim **8** wherein delivering the recirculated gaseous sample comprises directing the recirculated gaseous sample generally downwardly in the enclosed volume and with a component directed toward a lateral wall of the enclosed volume.

10. The method of claim **7** wherein recirculating the gaseous sample comprises passing the gaseous sample through a flow cell having an optical path therethrough, and wherein directing UV light through a gaseous sample comprises directing UV light through the optical path of the flow cell.

11. The method of claim **10** wherein drawing the gaseous sample comprises drawing the gaseous sample from a location above and spaced apart from the surface of the liquid sample to reduce a likelihood of liquid or foam from the liquid sample entering the recirculated gaseous sample and reaching the flow cell.

12. The method of claim **11** wherein the enclosed volume comprises a passage that extends the headspace of the enclosed volume upwardly away from the surface of the liquid sample and wherein drawing the gaseous sample comprises drawing the gaseous sample from a location proximate an upper end of the passage.

13. The method of claim **12** wherein drawing the gaseous sample comprises drawing the gaseous sample from the passage in a lateral direction.

14. The method of claim **1** wherein receiving the liquid sample comprises causing a liquid dosage system to draw the quantity of liquid from a container, and wherein:

a first portion of the quantity of liquid is delivered to the enclosed volume by operating the liquid dosage system; and

a second portion of the quantity of liquid is delivered to the enclosed volume by flushing the liquid dosage system using a pressurized fluid.

15. The method of claim **14** further comprising opening a vent valve in fluid communication with the headspace of the enclosed volume while flushing the liquid dosage system to permit the pressurized fluid to escape.

16. The method of claim **1** wherein the enclosed volume comprises a drain port sealed by a drain valve at the bottom of the enclosed volume and wherein the method further comprises, after the concentration of gaseous SO_2 within the gaseous sample has been determined, causing the drain valve to open to permit the liquid sample to be drained from the enclosed volume.

17. The method of claim **16** wherein the drain valve has a frustoconical shape and is received in a frustoconical valve seat at the bottom of the enclosed volume and wherein the valve is configured to open by lifting upwardly out of the valve seat such that when being drained the liquid sample is completely drained to the bottom of the enclosed volume.

18. The method of claim **16** further comprising flushing the enclosed volume by delivering a fluid to the enclosed volume that causes any remnants of the liquid sample to be forced out of the drain.

19. The method of claim **1** wherein directing UV light comprises directing UV light produced by a UV light emitting diode through the gaseous sample.

20. The method of claim **1** wherein measuring the attenuation of the UV light comprises:

generating modulated UV light;

generating a measurement signal in response to receiving the UV light at a photodetector after passing through the gaseous sample;

processing the measurement signal to extract components that are synchronized with the modulated UV light to determine an attenuation of the UV light; and

determining the attenuation by comparing the level of attenuated UV light with a level of the generated modulated UV light.

21. The method of claim **20** wherein generating modulated light comprises generating UV light that is intensity modulated at a reference frequency and wherein processing the measurement signal comprises processing the measurement signal to extract components that are synchronized with the reference frequency to determine the attenuation of the UV light.

22. The method of claim **20** wherein the photodetector comprises a silicon carbide photodetector that is responsive to wavelengths of UV light in a narrow band including the 280 nanometer wavelength of the UV light.

23. The method of claim **20** further comprising converting the measurement signal produced by the photodetector into a digital representation for receipt by a processor circuit and wherein processing the measurement signal comprises mathematically processing the measurement signal in the processor circuit.

24. The method of claim **20** further comprising splitting the UV light into a first beam of UV light and a second beam of UV light and wherein directing UV light through the gaseous sample comprises directing the first beam of UV light along a measurement optical path through the gaseous sample in a measurement channel and further comprising directing the second beam of UV light through a reference optical path in a reference channel to generate a reference signal for extracting the measurement signal from noise.

25. The method of claim **24** further comprising balancing the measurement channel and the reference channel while no gaseous sample is present.

26. The method of claim **20** wherein determining the concentration of gaseous SO_2 comprises:

producing an output absorption signal by taking a ratio of the measurement signal values and the reference signal; and

determining the SO_2 concentration based on fitting an exponential function to the output absorption signal.

27. The method of claim **1** wherein the quantity of acid comprises a quantity of phosphoric acid to lower a pH of the liquid sample to below pH 3.

28. A system for rapid determination of a concentration of free sulfur dioxide (SO_2) in a liquid, the system comprising:

an enclosed volume operable to receive a liquid sample, the liquid sample including:

a quantity of the liquid; and

a quantity of acid to promote gasification of SO_2 within the liquid;

a liquid sample conditioner operably configured to condition the liquid sample to cause gasified SO_2 to accumulate in a headspace of the enclosed volume above a surface of the liquid sample while a temperature of the liquid sample remains below 35°C;

a flow cell in fluid communication with the headspace of the enclosed volume, the flow cell being operable to receive a gaseous sample taken from the headspace of the enclosed volume, the flow cell having an optical path therethrough;

a UV light source having a wavelength within a spectral range of between 250 nm and 320 nm, the UV light source being disposed to direct UV light through the optical path of the flow cell;

a photodetector disposed to receive UV light passing through the gaseous sample and to generate a measurement signal representing an attenuation of the UV light due to absorption within the gaseous sample; and

a processor operably configured to determine the concentration of gaseous SO_2 within the gaseous sample based on the attenuation signal, the gaseous SO_2 concentration being indicative of the free SO_2 concentration within the liquid sample.

29. The system of claim **28** wherein the liquid comprises a beverage.

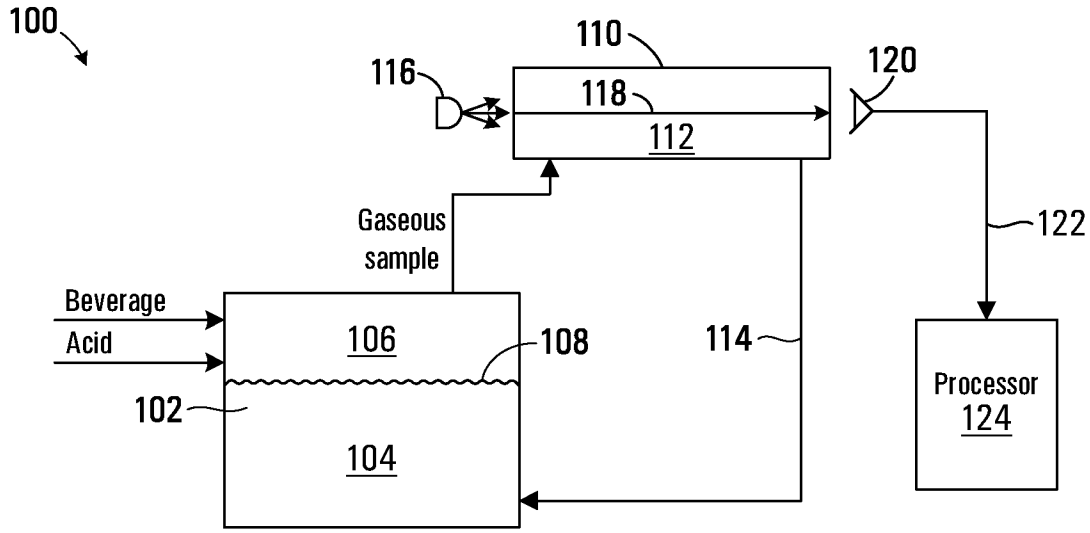


FIG. 1

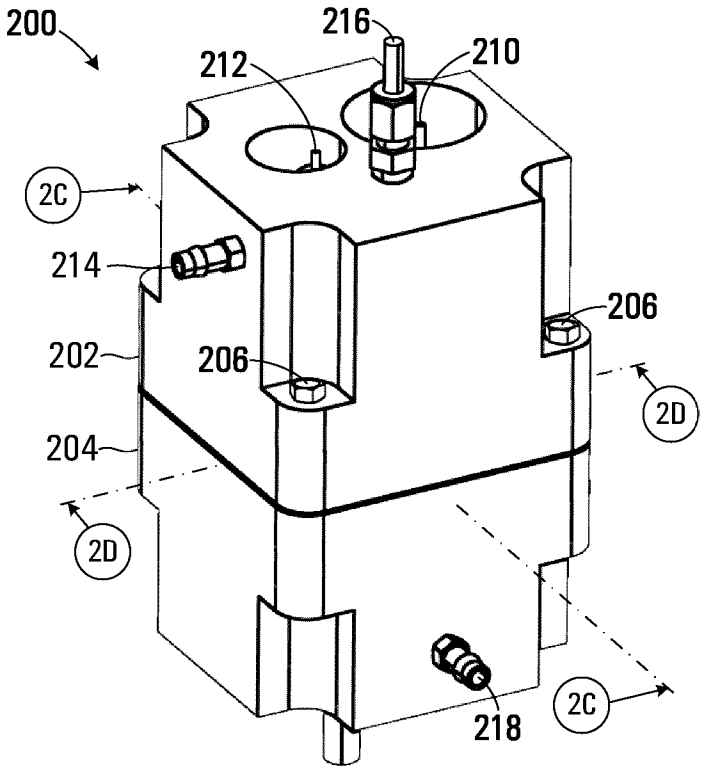


FIG. 2A

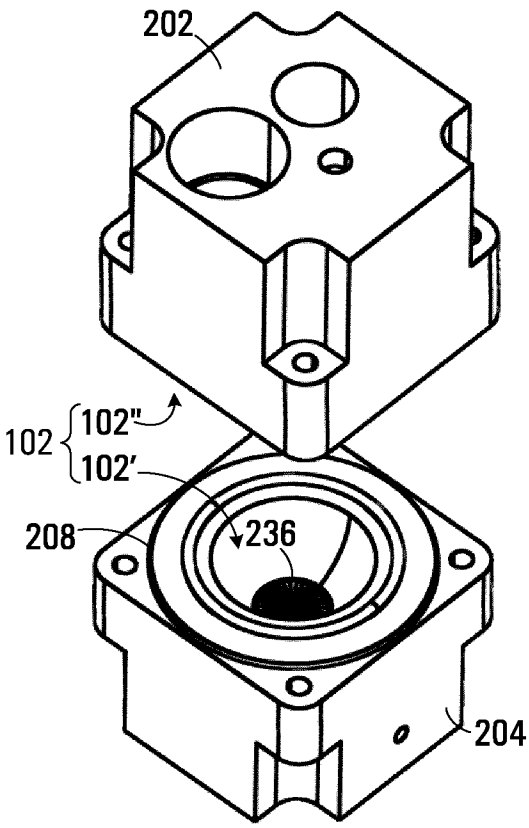


FIG. 2B

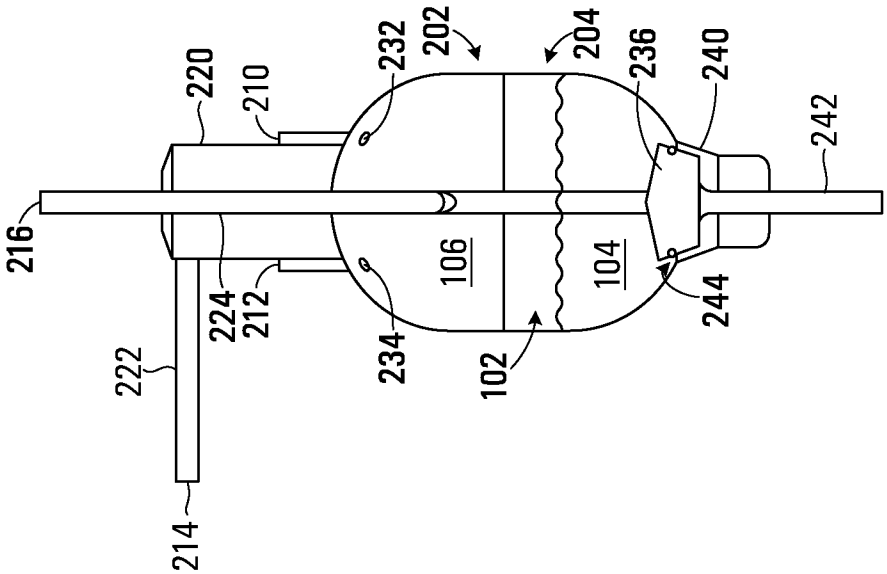

216
220
210
232
202
204
236
240
242
224
212
106
104
244
222
234
102
214

FIG. 2D

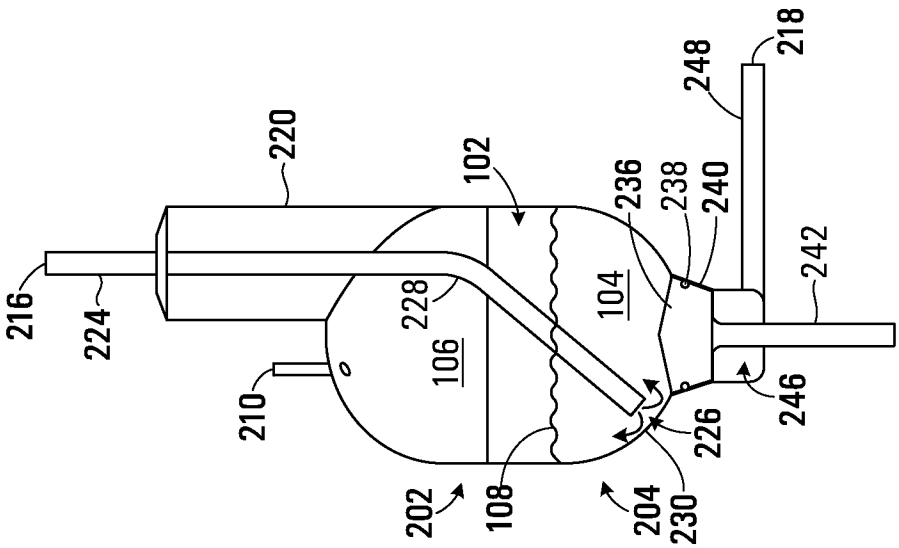

216
224
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102
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238
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248
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228
104
242
106
210
246
226
202
108
204
230

FIG. 2C

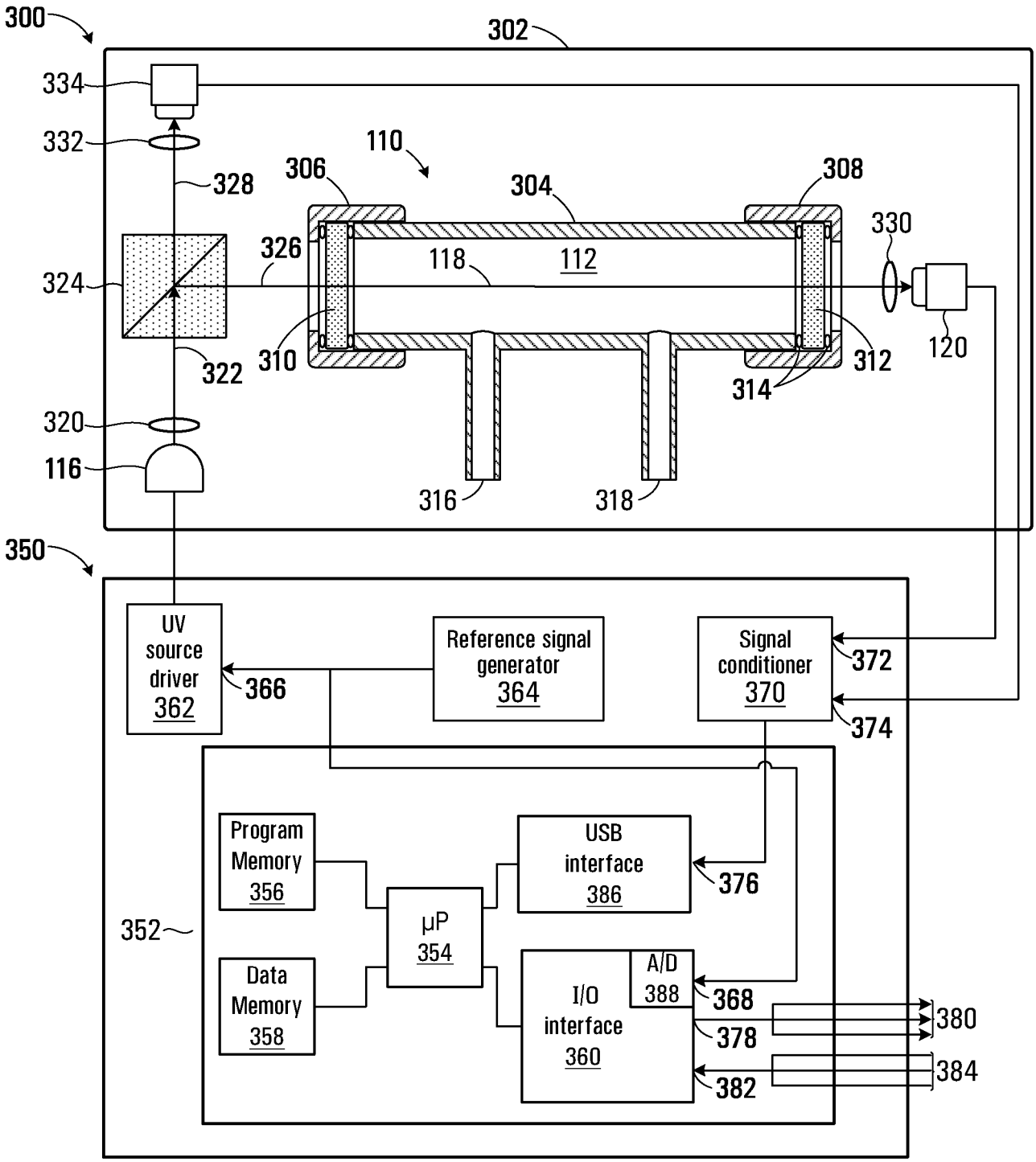

300
302
334
332
328
110
306
304
308
330
324
326
118
112
310
312
120
322
314
320
116
316
318
350
UV source driver 362
366
Reference signal generator 364
Signal conditioner 370
372
374
Program Memory 356
USB interface 386
376
352
µP 354
Data Memory 358
A/D 388
I/O interface 360
368
378
382
380
384

FIG. 3

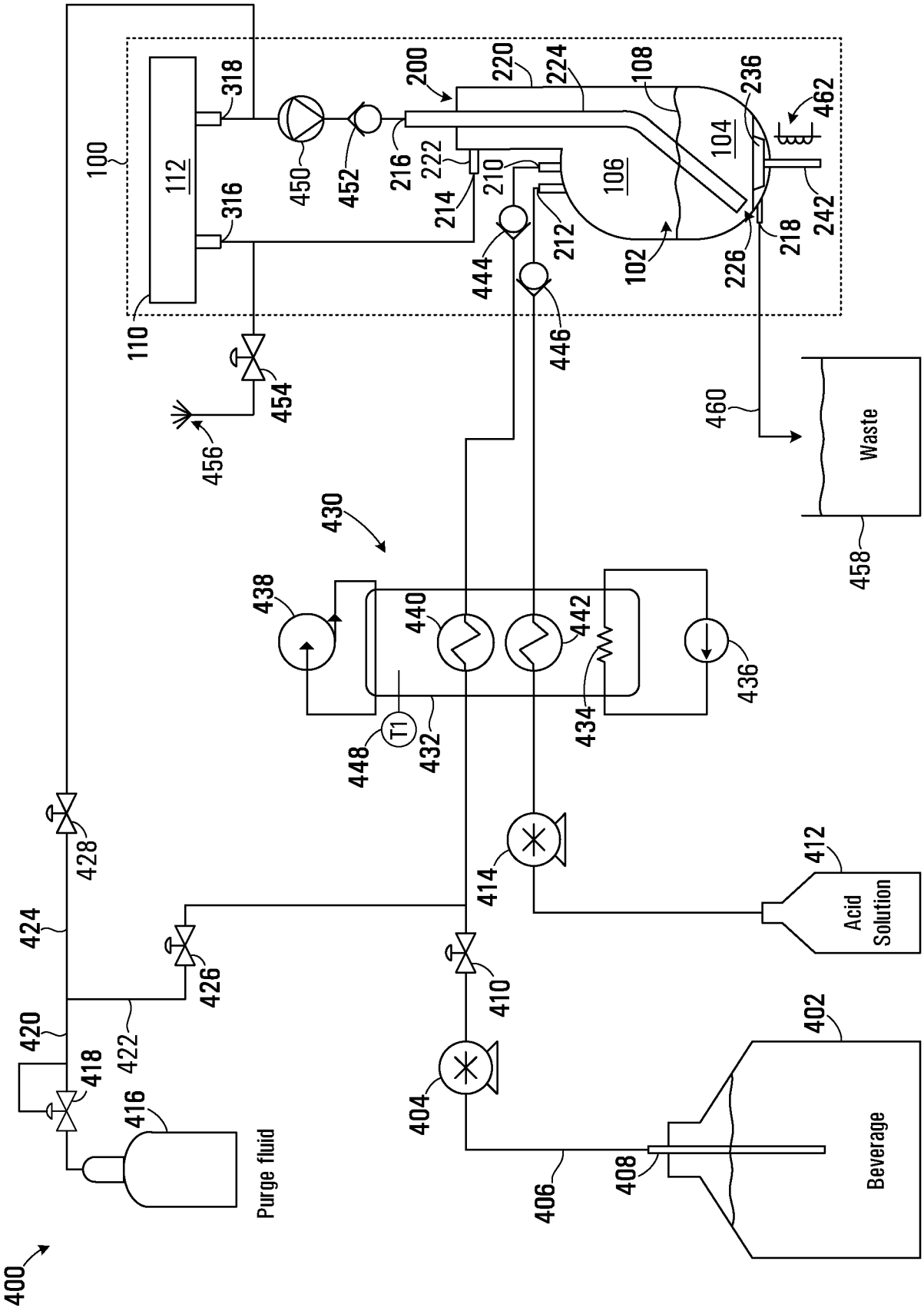

400
100
112
318
316
450
452
200
216
222
214
210
220
224
108
236
462
104
106
102
212
444
446
226
218
242
110
454
456
460
Waste
458
430
438
440
442
434
436
448
T1
432
428
424
426
420
422
418
416
Purge fluid
414
412
Acid Solution
410
404
406
408
402
Beverage

FIG. 4

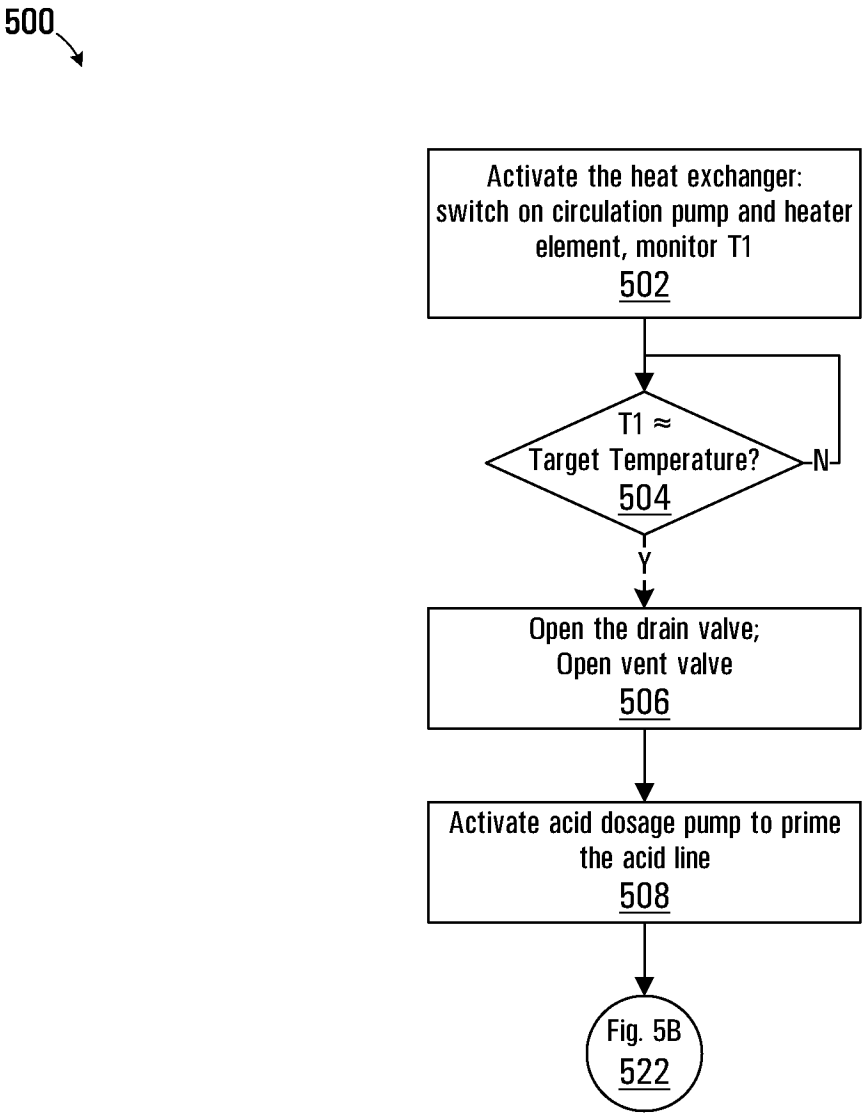

500
Activate the heat exchanger: switch on circulation pump and heater element, monitor T1
502
T1 ≈ Target Temperature?
504
N
Y
Open the drain valve; Open vent valve
506
Activate acid dosage pump to prime the acid line
508
Fig. 5B
522

FIG. 5A

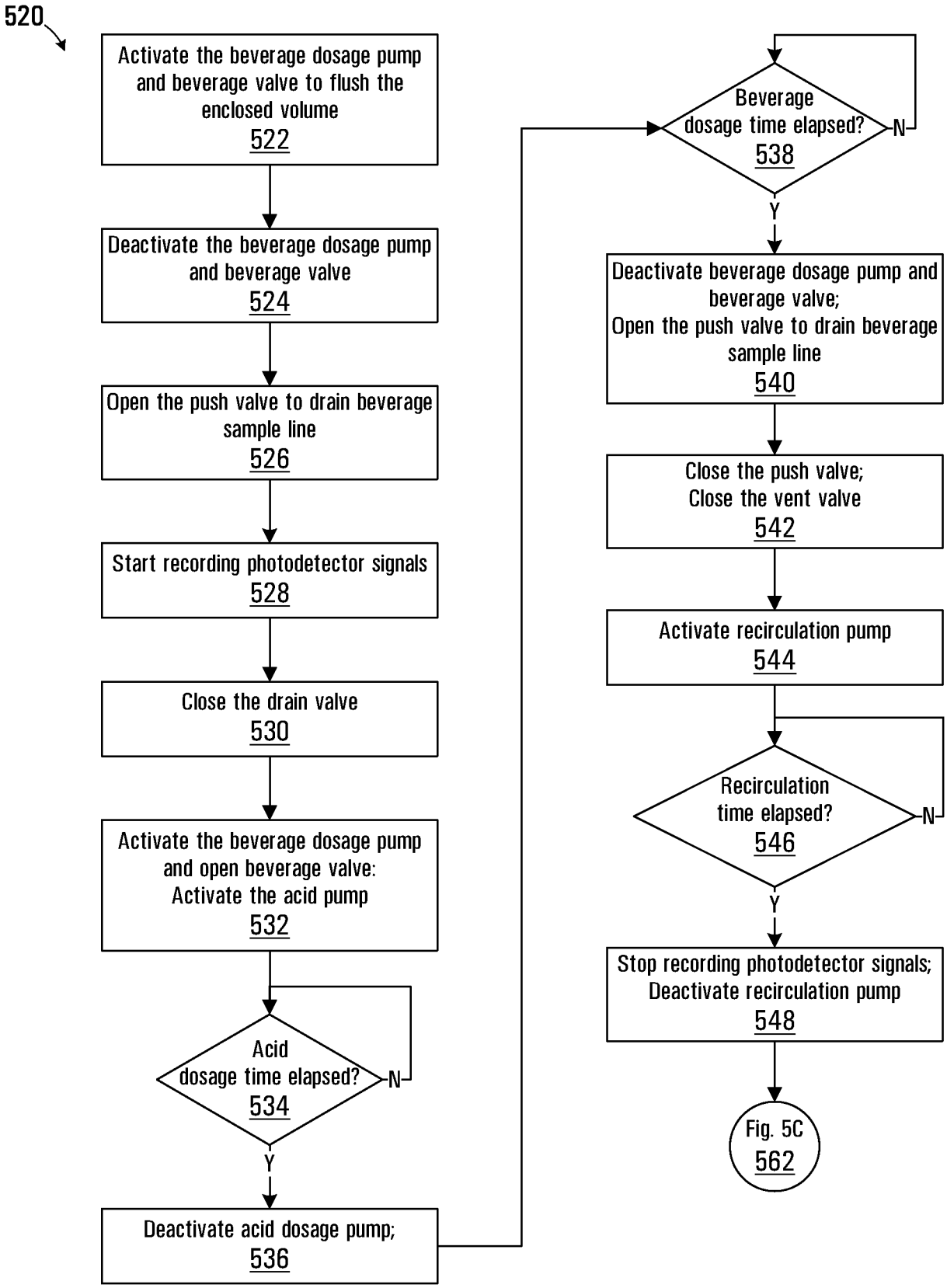

520
Activate the beverage dosage pump and beverage valve to flush the enclosed volume
522
Deactivate the beverage dosage pump and beverage valve
524
Open the push valve to drain beverage sample line
526
Start recording photodetector signals
528
Close the drain valve
530
Activate the beverage dosage pump and open beverage valve: Activate the acid pump
532
Acid dosage time elapsed?
534
N
Y
Deactivate acid dosage pump;
536
Beverage dosage time elapsed?
538
N
Y
Deactivate beverage dosage pump and beverage valve; Open the push valve to drain beverage sample line
540
Close the push valve; Close the vent valve
542
Activate recirculation pump
544
Recirculation time elapsed?
546
N
Y
Stop recording photodetector signals; Deactivate recirculation pump
548
Fig. 5C
562

FIG. 5B

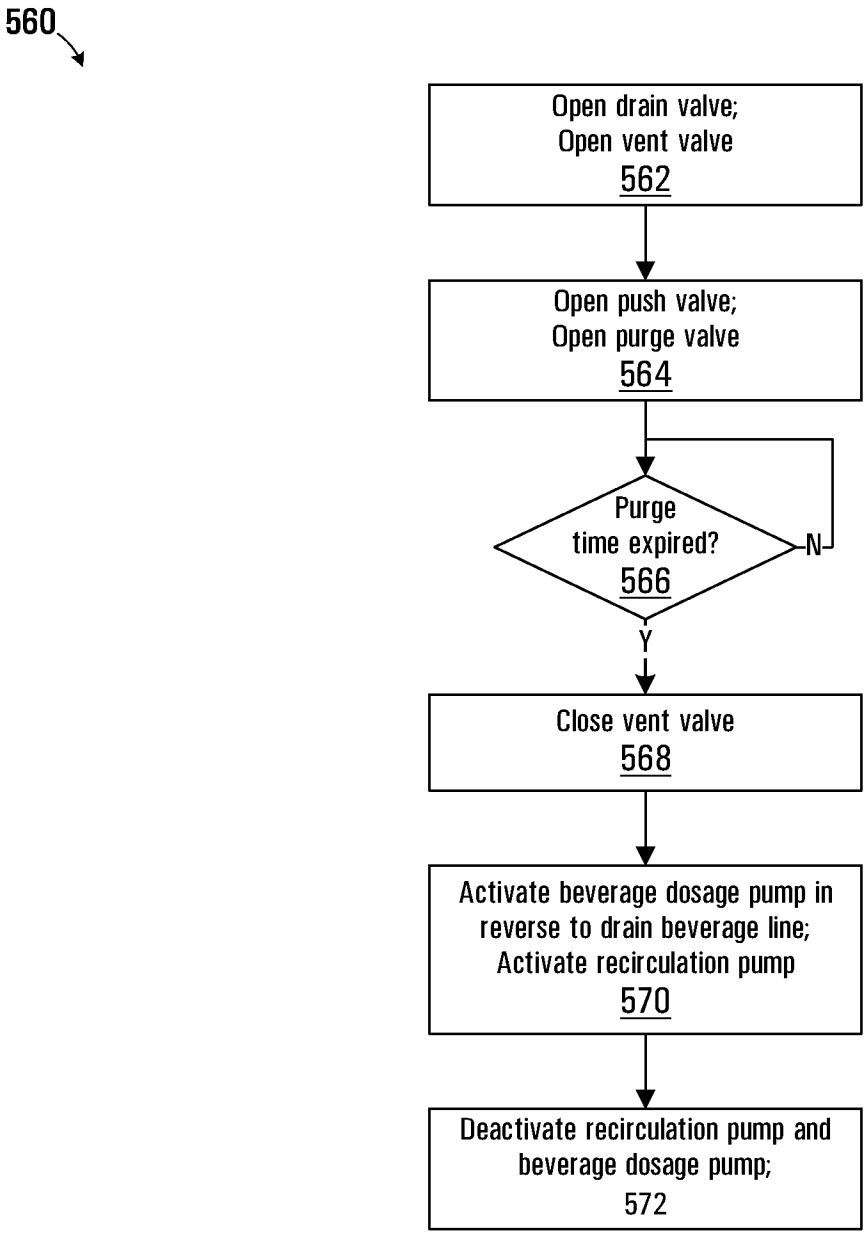

560
Open drain valve;
Open vent valve
562
Open push valve;
Open purge valve
564
Purge
time expired?
566
N
Y
Close vent valve
568
Activate beverage dosage pump in
reverse to drain beverage line;
Activate recirculation pump
570
Deactivate recirculation pump and
beverage dosage pump;
572

FIG. 5C

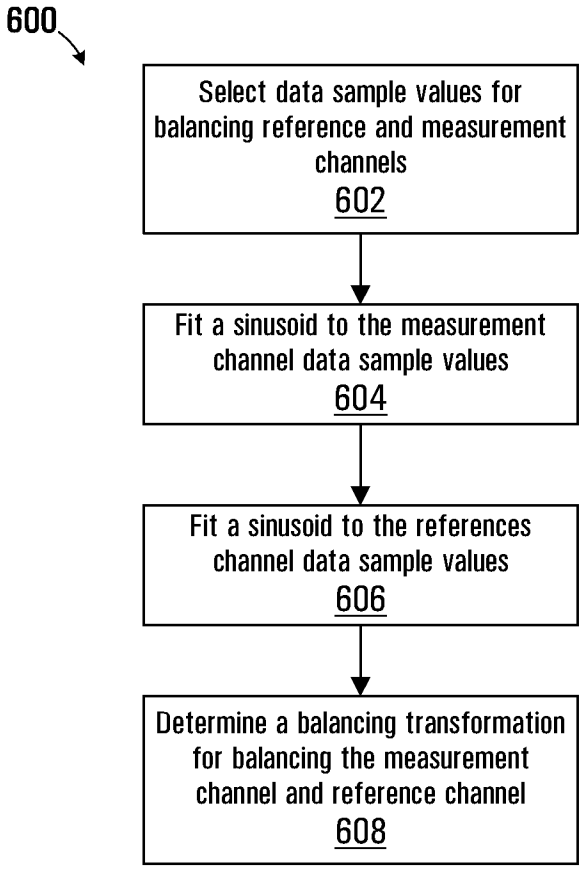

600
Select data sample values for balancing reference and measurement channels
602
Fit a sinusoid to the measurement channel data sample values
604
Fit a sinusoid to the references channel data sample values
606
Determine a balancing transformation for balancing the measurement channel and reference channel
608

FIG. 6

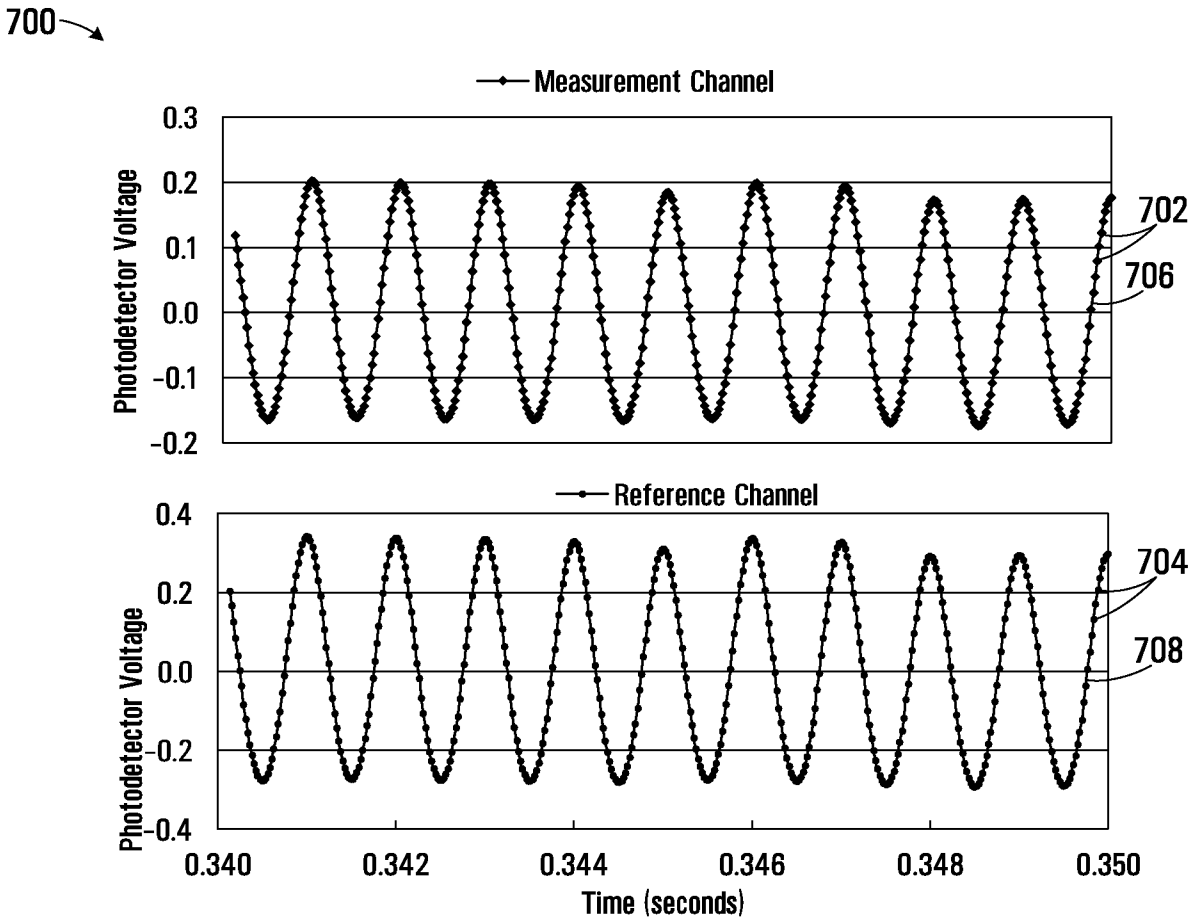

700
Measurement Channel
Photodetector Voltage
0.3
0.2
0.1
0.0
-0.1
-0.2
702
706
Reference Channel
Photodetector Voltage
0.4
0.2
0.0
-0.2
-0.4
704
708
0.340
0.342
0.344
0.346
0.348
0.350
Time (seconds)

FIG. 7

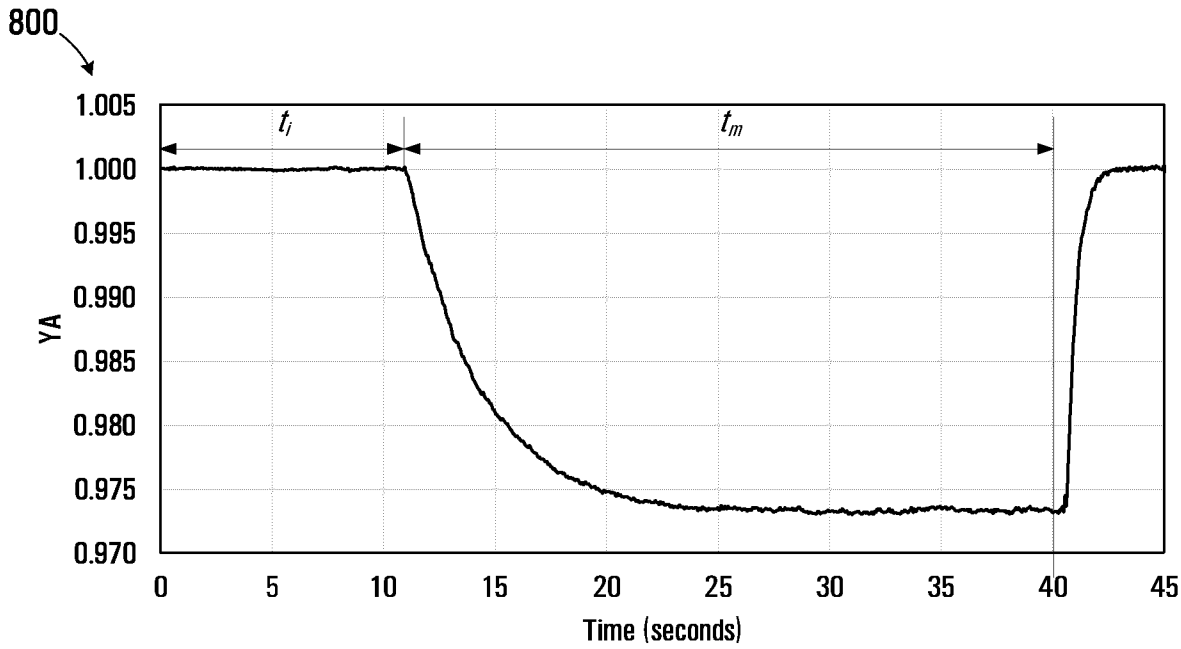

800
t_i
t_m
YA
1.005
1.000
0.995
0.990
0.985
0.980
0.975
0.970
0
5
10
15
20
25
30
35
40
45
Time (seconds)

FIG. 8

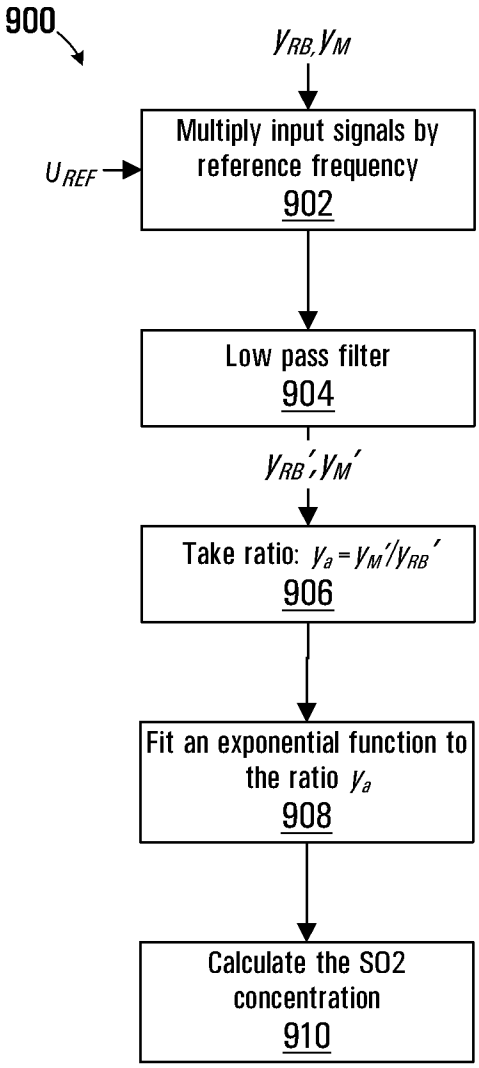

900
y_{RB}, y_M
Multiply input signals by reference frequency
902
U_{REF}
Low pass filter
904
y_{RB}', y_M'
Take ratio: $y_a = y_M'/y_{RB}'$
906
Fit an exponential function to the ratio y_a
908
Calculate the SO2 concentration
910

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2022/051497

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***G01N 21/61*** (2006.01) , *G01J 1/42* (2006.01)

CPC: **G01N 21/61** (2020.01) , G01J 1/429 (2020.01)

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)
Keywords searched across all of IPC.

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

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

Databases: Canadian Patents Database, Espacenet, Questel Orbit, Google, IEEExplore, Annual Reviews
Keywords : sulphites, sulphates, SO2, beverage, ferment, concentration, liquid, gas, UV, absorption, attenuation, conditioning, sparging, headspace, etc.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
[A]	US 20130236976 A1 (THOMSEN) 12 September 2013 (12-09-2013) *entire doc. esp. abstract, [004-5], [0009], [0017-18], [0020], [0026-27]*	1-29
[A]	US 20040238745 A1 (PEDERSEN et al.) 02 December 2004 (02-12-2004) *entire doc. esp. abstract*	1-29
[A]	EP 0603657 A2 (KURATLI) 29 June 1994 (29-06-1994) *abstract; p.9, line 35*	1-29

☐ 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
"D"	document cited by the applicant in the international application	"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
"E"	earlier application or patent but published on or after the international filing date	"&"	document member of the same patent family
"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)		
"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	Date of mailing of the international search report
16 December 2022 (16-12-2022)	19 January 2023 (19-01-2023)

Name and mailing address of the ISA/CA	Authorized officer
Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Anthony Glaser (819) 639-3193

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2022/051497

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US2013236976A1	12 September 2013 (12-09-2013)	US9212993B2	15 December 2015 (15-12-2015)
		AU2010364689A1	02 May 2013 (02-05-2013)
		AU2010364689B2	09 April 2015 (09-04-2015)
		CA2815400A1	07 June 2012 (07-06-2012)
		CA2815400C	24 October 2017 (24-10-2017)
		CN103210300A	17 July 2013 (17-07-2013)
		CN103210300B	23 September 2015 (23-09-2015)
		EP2646801A1	09 October 2013 (09-10-2013)
		EP2646801B1	03 September 2014 (03-09-2014)
		ES2503561T3	07 October 2014 (07-10-2014)
		NZ609194A	27 March 2015 (27-03-2015)
		PT2646801E	17 December 2014 (17-12-2014)
		WO2012072106A1	07 June 2012 (07-06-2012)
		ZA201303118B	30 July 2014 (30-07-2014)
US2004238745A1	02 December 2004 (02-12-2004)	CA2465544A1	08 May 2003 (08-05-2003)
		EP1308713A1	07 May 2003 (07-05-2003)
		EP1451555A1	01 September 2004 (01-09-2004)
		MXPA04004124A	29 October 2004 (29-10-2004)
		WO03038411A1	08 May 2003 (08-05-2003)
		ZA200403663B	31 May 2006 (31-05-2006)
EP0603657A2	29 June 1994 (29-06-1994)	EP0603657A3	28 September 1994 (28-09-1994)