(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
09 January 2025 (09.01.2025)

WIPO | PCT

(10) International Publication Number
WO 2025/008428 A1

(51) International Patent Classification:
G01N 33/00 (2006.01)

(21) International Application Number:
PCT/EP2024/068781

(22) International Filing Date:
03 July 2024 (03.07.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
23183428.4 04 July 2023 (04.07.2023) EP

(71) Applicant: **AB MAURI (UK) LTD** [GB/GB]; Weston Centre, 10 Grosvenor Street, London W1K 4QY (GB).

(72) Inventors: **BAIPAS, Sergio Gabriel**; c/o Weston Centre, 10 Grosvenor Street, London Greater, London W1K 4QY (GB). **BALZAN, Tony Paul**; c/o Weston Centre, 10 Grosvenor Street, London Greater, London W1K 4QY (GB).

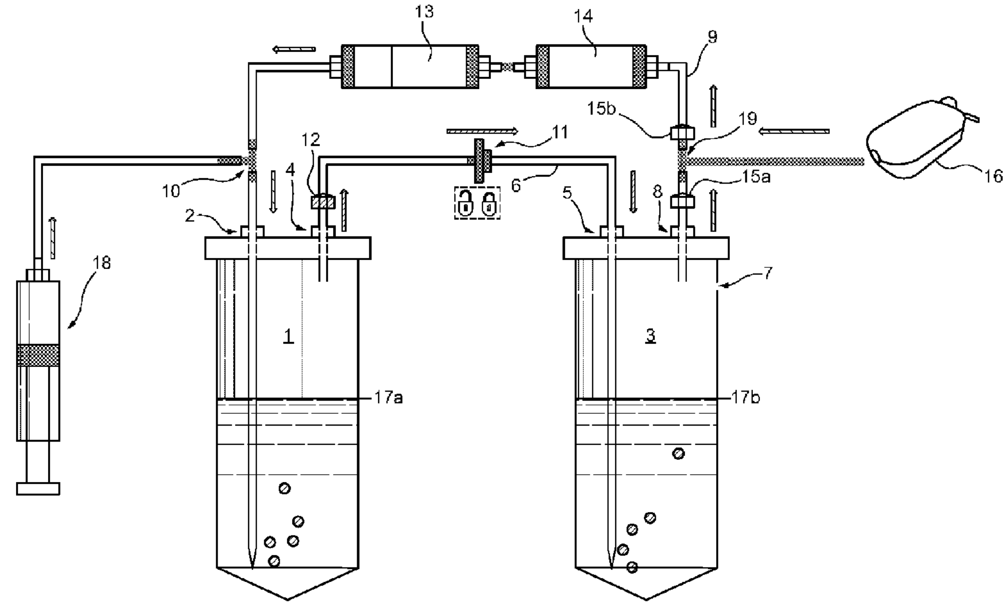
(74) Agent: **WITMANS, H.A.**; V.O., P.O. Box 87930, 2508 DH Den Haag (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,

(54) Title: MINIATURISED RAPID SO2 INSTRUMENT

Figure 1



(57) **Abstract:** The invention relates to a portable sulfur dioxide (SO2) detection installation, said installation comprising a reaction cell and a collection cell, said reaction cell comprising an outlet for SO2 which is connected via a conduit to an inlet for sulfur dioxide into the collection cell, and an inlet for air connected via a conduit to an outlet for air of the collection cell, wherein said conduit is arranged with a device for introducing ambient air into the installation, wherein said reaction cell comprises an inlet for acid and wherein said collection cell comprises, in an upper portion, an outlet for air.

WO 2025/008428 A1

[Continued on next page]

LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

Title: Miniaturised Rapid SO_2 Instrument

The invention relates to a portable SO_2 detection installation and to a process for capturing and detecting SO_2 in an aqueous mixture.

Molasses, such as sugarcane molasses, represent an excellent medium for growth of yeast. However, at certain levels, free and loosely bound SO_2 present in molasses can inhibit yeast production, thereby rendering the yeast manufacturing process inefficient, reducing profitability and increasing waste. It is thus beneficial to assess the sulphite content of substrates (such as molasses) prior to use in yeast production, such that sub-standard substrates that are high in sulphite can be treated or blended with other substrates to prevent inhibition of yeast growth.

Current installations for SO_2 quantification of substrates generally applied are the Rankin Aspiration Instrument and Monier-Williams Instruments. These instruments have been optimized for the quantification of sulphite content in wine, and generally assess the total content of SO_2 present in the substrate.

In the Rankin Aspiration Method, addition of acid occurs in an open system, potentially allowing a significant loss of SO_2 on addition of the acid prior to attachment of the condenser to the reaction cell. Further, in the Rankin Aspiration method presence of air results in at least partial oxidation of free SO_2 and SO_3 to SO_4. Accordingly, due to these inaccuracies, the Rankin Aspiration Instrument typically underestimates the content of SO_2 in the substrate to be assessed.

The Monier-Williams Instrument provides an improvement to the Rankin Aspiration Instrument. The system is essentially closed and can be operated under an inert atmosphere. This significantly reduces the risk of oxidation of free SO_2 and SO_3 to SO_4 and therefore total SO_2 content is assessed more accurately. However, the use of inert gases such as nitrogen is expensive requiring a fixed-location installation and typically requires housing for gas cylinders. This makes the instrument more complex and unsuitable for on-site use where there is a need for test location flexibility.

Further, both the Rankin Aspiration Instrument and the Monier-Williams Instrument require expensive equipment typically prepared from glass, which is required to withstand harsh conditions typically required to assess the total sulphite content of the substrate.

There is thus a need for a novel installation that enables rapid capturing and detection of free and loosely bound SO_2 in sufficient accuracy that overcomes one or more of the above-mentioned drawbacks. In particular, there is a need for an SO_2 capturing and detection installation for use in yeast production with adequate accuracy and which is simple, cost efficient, portable and suitable for on-site use.

Accordingly, the invention relates to a portable sulfur dioxide (SO_2) detection installation, said installation comprising a reaction cell and a collection cell, said reaction cell comprising an outlet for SO_2 which is connected via a conduit to an inlet for sulfur dioxide into the collection cell, and an inlet for air connected via a conduit to an outlet for air of the collection cell, wherein said conduit is arranged with a device for introducing ambient air into the installation, wherein said reaction cell comprises an inlet for acid and wherein said collection cell comprises, in an upper portion, an outlet for air. Said installation is for (use in a process for) capturing and detecting SO_2 in an aqueous mixture.

Advantageously, the installation according to the invention is suitable for detecting SO_2 by capturing of SO_2 during a process for capturing or detecting SO_2 in an aqueous mixture, without requiring detection equipment integrated into the installation. This makes the installation lightweight, portable and suitable for on-site use.

The invention further relates to a process for capturing or detecting SO_2 in an aqueous mixture in an installation according to any one of the preceding claims, the process comprising addition of an acid into the reaction cell, said reaction cell containing an aqueous mixture comprising sulphite, thereby forming SO_2; allowing said SO_2 to move from the reaction cell to the collection cell, said collection cell containing hydrogen peroxide, thereby forming sulfuric acid.

The installation (for use in a process) according to the invention can be advantageously operated under air atmosphere, whilst the risk of oxidation of SO_2 and SO_3 to SO_4 is reduced compared to the Rankin Aspiration Instrument. The SO_2 and SO_3 detection installation (for use in a process) according to the invention, is arranged such that, during use, the inlet of fresh ambient air is minimized and that the total volume of air typically containing oxygen (in particular present in the headspaces of the reaction cell and collection cell) is much lower compared to the Rankin Aspiration instrument. With an installation (for use in a process) according to the invention a high accuracy of assessment of SO_2 may be obtained, typically about 90% or higher, whilst the use of an inert atmosphere is not required.

Further, the installation (for use in a process) according to the invention can be advantageously prepared from disposable materials, such as centrifuge tubes, whereas the Rankin Aspiration Instrument and Monier-Williams Instrument require more advanced glass equipment. This is because the Rankin Aspiration and Monier-Williams methods require high temperatures to release strongly bound SO_2 from the substrate, whereas the process according to the invention may be operated at relatively low temperature.

Further, the installation (for use in a process) can advantageously operate on small scale, thereby requiring lower sample sizes and producing less waste.

Summary of the invention

The invention relates to a portable sulfur dioxide (SO_2) detection installation, said installation comprising a reaction cell and a collection cell, preferably wherein said collection cell comprises hydrogen peroxide, more preferably wherein at least 50 vol% of the volume of the collection cell is filled with a hydrogen peroxide solution, said reaction cell comprising an outlet for SO_2 which is connected via a conduit to an inlet for sulfur dioxide into the collection cell, and an inlet for air connected via a conduit to an outlet for air of the collection cell, wherein said conduit is arranged with a device for introducing ambient air into the installation, wherein said reaction cell comprises an inlet for acid and wherein said collection cell comprises, in an upper portion, an outlet for air, preferably wherein said outlet for air is arranged to allow about 70 to about 80 vol.% of air introduced into the installation by said device to exit the collection cell.

Preferably, said inlet for acid and/or said inlet for air is arranged to direct acid and/or air into a lower part of the reaction cell and/or said outlet for SO_2 is arranged to direct said SO_2 into a lower part of the collection cell.

In a preferred aspect, said conduit connecting said outlet for SO_2 of the reaction cell to said inlet for SO_2 of said collection cell contains a filter and/or one or more flow check valve(s) for preventing liquid or foam to translocate between the reaction cell and the collection cell.

The invention further preferably relates to a portable SO_2 detection installation, wherein said conduit for connecting an outlet for air of the collection cell to an inlet for air of the reaction cell comprises an oxygen trap filter for removing O_2, preferably a zinc, aluminum, iron, tin, copper or combinations thereof and optionally a moisture trap filter for removing water, preferably comprising silica gel.

The portable SO_2 detection installation according to the invention is preferably prepared from disposable materials, more preferably plastic, such as polystyrene, polypropylene, polyethylene terephthalate, polypropylene copolymer or polycarbonate.

Preferably, the invention pertains to a portable SO_2 detection installation, wherein the reaction cell comprises a marking for indicating the level of aqueous mixture in the reaction cell, preferably wherein said marking is located in an upper half of the reaction cell and/or wherein the collection cell comprises a marking for indicating the level of hydrogen peroxide solution in the collection cell, preferably wherein said marking is located in an upper half of the collection cell.

The invention further pertains to a process for detecting SO_2 in an aqueous mixture in an installation according to the invention, the process comprising addition of an acid into the reaction cell, said reaction cell containing an aqueous mixture comprising sulphite, preferably comprising molasses, preferably sugarcane molasses, beet molasses or a combination thereof, thereby forming SO_2; allowing said SO_2 to move from the reaction cell to the collection cell, said collection cell containing hydrogen peroxide, thereby forming sulfuric acid.

Preferably, the process according to the invention, further comprises recovering said sulfuric acid from the collection cell; and titrating said sulfuric acid with a base, preferably sodium hydroxide.

Preferably, in a process according to the invention, the reaction cell is heated to about 40 °C to about 70 °C, preferably about 60 °C.

In a preferred aspect, the (v/v) ratio between liquid and gas in the installation is between 1:0.5 and 1:0.8, preferably between 1:0.5 and 1:0.9.

Preferably in a process according to the invention, free SO_2, loosely bound SO_2 or both free SO_2 and loosely bound SO_2 is/are detected.

Figures

Figure 1 schematically shows a preferred set-up of a portable SO_2 detection installation (for use in a process) according to the invention. It schematically shows how a substrate, such as molasses, in a reaction cell (1) may be treated with an acid, which is introduced into the reaction cell (1) via an inlet for acid and air (2). Said inlet for acid and air (2) is arranged to direct the acid into a lower part of the reaction cell (1).

The installation further comprises a collection cell (3) which is in fluid communication with said reaction cell (1). In Figure 1, said reaction cell (1) comprises an outlet (4) for SO_2 connected to an inlet for SO_2 (5) of the collection cell (3) via a conduit (6). Said inlet for SO_2 (5) is arranged to direct said SO_2 into a lower part of the collection cell.

The collection cell (3) further contains an outlet for air (7) in an upper part of the collection cell. Said outlet for air (7) allows, during use, exit of air from the collection cell (3) to the atmosphere.

Said collection cell further comprises an outlet for air (8) connected via a conduit (9) to the inlet for acid and air (2) of the reaction cell (1). The conduit (9) for connecting the inlet for acid and air (2) to the outlet for air (8) of the collection cell (3) is adapted with a first three-way branch, known as a Y-connector (10) such that, during use, acid is introduced into the conduit (9) and, eventually, via the inlet for acid and air (2) into the lower part of the reaction cell (1). In Figure 1, Y-connector (10) is connected to syringe (18) for introducing acid into the conduit (9).

Said conduit (9) for connecting the inlet for acid and air (2) to the outlet for air (8) of the collection cell (3) is adapted with a second three-way branch, known as Y-connector (19) such that, during use, atmospheric air is introduced into the conduit (9) using a pump (16).

The conduit (6) for connecting the outlet for SO_2 (4) of the reaction cell (1) with the inlet for SO_2 (5) of the collection cell (3) is equipped with a filter (11) and/or one or more flow check valves (12). Said filter (11) and/or flow check valve(s)

(12) are adapted to prevent liquid or foam to translocate between the reaction cell (1) and the collection cell (3). In particular, said filter (11) and/or flow check valve(s) (12) are adapted to prevent cross-contamination from the reaction cell (1) to the collection cell (3).

The conduit (9) for connecting an outlet for air (8) to an inlet for acid and air (2) is preferably equipped with a filter for removing O_2 (13) from atmospheric air.

Additionally, said conduit (9) for connecting an outlet for air (8) to an inlet for acid and air (2) is further equipped with a water filter (14) for removing water from atmospheric air. Such water filter (14) is preferably located upstream of the filter for removing O_2 (13) from atmospheric air.

Alternatively or additionally, said conduit (9) for connecting an outlet for air (8) to an inlet for acid and air (2) is equipped with one or more flow check valves (15a,b). Said flow check valve(s) (15a,b) prevent reversal of air-flow in the direction of the collection cell (3), directing flow towards the reaction cell (1).

Figure 2 shows the results of a SO_2 recovery when using a solution of 0.1 g of Na_2SO_3 in 100 mL preboiled water using an installation according to the invention. It is shown that at least 88.7% of SO_2 was recovered using an installation according to the invention. This recovery rate could be improved to about 93.3% by using a Zinc oxygen trap filter, as shown in Figure 1 (first two bars).

Figure 3 shows a general setup for determining the air flow exiting the collection cell. As shown, a tube is connected to the outlet for air at the collection cell and feeds into a burette. The burette is filled with water above the 0-mark. The pump is switched on and the time is recorded when the water reaches the 50 mL mark near the bottom of the 50 mL burette. The exiting water flows through a tube feeding into a beaker.

Detailed description

The term “or” as used herein is defined as “and/or” unless specified otherwise.

The term “a” or “ an” as used herein is defined as “at least one” unless specified otherwise.

The term “substantial(ly)” or “essential(ly)” is generally used herein to indicate that it has the general character or function of that which is specified.

When referring to a quantifiable feature, these terms are in particular used to indicate that it is for at least 75 %, more in particular at least 90 %, even more in particular at least 95 % of the indicated feature.

In the context of the present application, the term “about” means generally a deviation of 15% or less from the given value, in particular a deviation of 10% or less, more in particular a deviation of 5% or less.

When referring to a noun in the singular, the plural is meant to be included, unless it follows from the context that it should refer to the singular only.

With the term “free SO_2” as used herein is meant SO_2 that is released from a substrate containing SO_3 or related forms therein, such as molasses, upon addition of an acid at ambient temperature. Typically, free SO_2 is released from SO_3 present in the substrate and as depicted by the following reaction: $3Na_2SO_3 + 2H_3PO_4 \rightarrow 3SO_2\uparrow + 3H_2O + 2Na_3PO_4$.

“Loosely bound SO_2” as used herein, refers to SO_3 that is captured by a compound, such as an aldehyde to form a complex, which may be released as free SO_2 under acidic conditions and under mild heating, i.e. a temperature not exceeding 80 °C, typically around 60 °C, at atmospheric pressure.

“Strongly bound SO_2” as used herein, refers to SO_3 that is firmly bound in a substrate in a compound like sodium hydroxymethylsulphonate (NaHMS) only to be released as SO_2 under acidic conditions combined with heating at elevated temperature of 100 °C or more.

The skilled person is familiar with terms like ‘upper’, ‘lower’ , ‘middle’ , ‘at bottom’, ‘near bottom’ , ‘at top’ and ‘near top’. Generally these are read in relation to another, and the skilled person will be able to reduce implementation thereof to practice, based on common general knowledge, the information and citation disclosed herein, and the specifics of a unit (such as reaction cell, collection cell, or a volume of matter contained in these cells) of the installation.

As a rule of thumb, unless follows differently from the context, ‘near’ a certain reference point (such as ‘bottom’ or ‘top’) usually means ‘at a relative height of up to +/-20% from the reference point’, in particular ‘at a relative height of up to +/-15% from the reference point’ more in particular ‘at a relative height of up to +/-10%’ from the reference point. The relative height is the distance from the bottom divided between the total height of the unit (height difference between bottom and top).

As a rule of thumb, unless follows differently from the context, an ‘upper’ part generally means in the upper 1/2, and in particular in the upper 1/3 of the unit, a ‘lower’ part generally means the lower 1/2 of the unit and in particular the lower 1/3 of the unit. When referring to a middle part, this in particular means the middle 1/3 of the unit (from 1/3 of the bottom to 1/3 from the top).

The aqueous mixture to be subjected to a process according to the invention may in principle be any aqueous mixture in which SO_2 is to be detected, provided it is compatible with acid. That is, the aqueous mixture preferably does not comprise substantial amounts of components that react with acid, such as a base.

Preferably, said aqueous mixture comprises a substrate for yeast production, more preferably molasses. Examples of molasses that are suitable as substrate for yeast production include sugarcane molasses and sugar beet molasses. Preferably, said molasses is sugarcane molasses.

Optionally said molasses is sulphured molasses. Sulphured molasses refers to molasses prepared from young sugar cane that has been treated with SO_2 for preservation. Such molasses typically contains a higher content of SO_2 than unsulphured molasses.

Optionally, said substrate may be diluted in an aqueous medium prior to charging in the reaction vessel of the installation (for use in a process) according to the invention, to reduce viscosity and increase processability.

As the skilled person will appreciate, the dilution rate in said aqueous medium depends on the viscosity of the substrate. Viscous substrates typically require a higher dilution rate than less viscous types of substrates. The skilled person is capable of selecting a suitable dilution rate, based on common general knowledge and the information provided herein.

Typically, said substrate, preferably molasses, is diluted in an aqueous medium, preferably water, in a wt. ratio of molasses to water of between about 5:1 and about 1:5, preferably between about 4:1 and about 1:4, more preferably between about 2:1 and about 1:2.

Said aqueous medium is preferably water, more preferably pre-boiled water.

Preferably, said aqueous medium is not a buffered aqueous solution or a basic aqueous medium.

Said aqueous mixture may optionally be subjected to one or more pre-treatment steps prior to subjecting it to a process according to the invention. For example, said aqueous mixture may be filtered to remove any solids from the feedstock.

The content of sulphite in said aqueous mixture to be assessed is typically in a range of between about 100 and about 3000 mg/Kg SO_2, preferably between about 200 and about 3000 mg/Kg SO_2, more preferably between about 500 and about 3000 mg/Kg SO_2.

The amount of aqueous mixture to be subjected to a process according to the invention typically depends on the scale of the process, the size of the installation to be used and the capturing, detection and/or quantification level of SO_2 required.

Typically, between about 15 mL and about 60 mL of aqueous mixture is charged in the reaction cell, preferably between about 18 mL and about 35 mL of aqueous mixture, in particular about 20 mL of aqueous mixture.

These amounts are particularly suitable if a reaction cell having a volume of between about 40 mL and about 80 mL is used, in particular if a reaction cell having a volume of about 50 to 60 mL is used. Particularly preferred is a reaction cell of about 50 mL, such as a 50 mL centrifuge tube.

As the skilled person will appreciate, the capturing, detection and/or quantification level of SO_2 may be increased by increasing the volume of the reaction cell to accommodate a larger content of aqueous fluid to be assessed. As a rule, this is not necessarily followed by an increase of the size of the collection cell, nor the amount of acid added into the reaction cell and hydrogen peroxide present in the collection cell during use.

As a rule of thumb, during use, it is advantageous to have as much aqueous mixture present in the reaction cell as possible, as this reduces the content of air present in the reaction cell and thus reduces the possibility of oxidation of SO_2 or SO_3 to SO_4. However, care should be taken not to overcharge the reaction cell. If too much aqueous mixture is present in the reaction cell, the risk of cross-contamination between the reaction cell and the collection cell is disadvantageously increased.

Accordingly, during use, said reaction cell preferably comprises at least 30 vol.%, more preferably at least 40 vol.%, in particular at least 50 vol.% of aqueous mixture. Preferably, during use, said reaction cell comprises at most 70 vol.% at most 60 vol.% of aqueous mixture. For example, in a process according to the invention said reaction cell is preferably filled for between about 30 and about 70 vol.% with aqueous mixture, more preferably between about 35 and about 65 vol.%, more preferably between about 40 and about 60 vol.% of the reaction cell is charged with aqueous mixture.

Said acid may in principle be any acid that is capable of reacting with sulphite at ambient temperature and atmospheric pressure to form gaseous SO_2. Upon addition of the acid into the reaction cell, said acid undergoes a chemical reaction with free sulphite present in the aqueous mixture, as shown by general reaction equation 1.

$$X_2SO_3 + 2HA \rightarrow SO_2\uparrow + H_2O + 2XA \qquad \textit{reaction equation 1}$$

Herein, HA represents an acid, and X represents a monovalent cation, typically Na^+, K^+ and Li^+. As the skilled person will appreciate, the reaction equation may differ slightly depending on the valency of counter ion present or the type of acid used. For example, when a polyprotic acid, such as H_3PO_4 is used, the reaction equation is adapted as shown in reaction equation 1a.

$$3X_2SO_3 + 2H_3PO_4 \rightarrow 3SO_2\uparrow + 3H_2O + 2X_3PO_4 \qquad \textit{reaction equation 1a}$$

Examples of acids that may be used include phosphoric acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, perchloric acid and nitric acid. Preferably, said acid is phosphoric acid or hydrochloric acid, more preferably said acid is phosphoric acid.

The amount and strength of acid to be used should be sufficient to produce a pH of 1 or less (as determinable with a pH meter) in the reaction cell. At such pH the release of substantially all free and loosely bound SO_2 from the substrate present in the aqueous mixture is typically envisaged.

Said acid may be a concentrated acid solution in water or may be a diluted solution. Preferably, said acid is a concentrated acid solution, such as a concentrated phosphoric acid solution (85 vol.% H_3PO_4 in water with a molarity of around 18 M).

Preferably, the concentration of acid in the aqueous mixture after addition of said acid is between about 8 N and about 15 N, more preferably between about 10 and about 13 N, in particular about 12 N.

A typical volume of acid, preferably concentrated phosphoric acid, to be used in a process according to the invention is between about 5 and about 20 mL. Preferably, said volume of acid, preferably concentrated phosphoric acid, is between about 8 and about 12 mL, such as around 10 mL. Such an amount of acid, preferably concentrated phosphoric acid, is typically sufficient to produce a pH of 1 or lower in the reaction cell.

Said acid is preferably introduced into the reaction cell using a syringe. Preferably, said syringe is connected to a conduit connecting an inlet for acid of the reaction cell to an outlet of air of the collection cell via a three-way branch.

The syringe, if present, typically plays a dual role in that it provides a means for introducing acid (specifically phosphoric acid) into the reaction cell and also performs as a visual signal to the detection of a significant blockage in the installation. Such a blockage can for example occur when a filter is used in the conduit connecting the reaction cell to the collection cell, which filter may become blocked by condensate or fluid travelling out of the reaction cell, towards the collection cell. If a blockage occurs, the plunger present in the syringe is pushed up to an upper part of the syringe. This, together with a lowering of the bubbling rate in the collection cell, provides evidence of a blockage starting to occur, caused by applied back-pressure onto the plunger.

Alternatively, another means for introducing acid into said reaction cell, such as an acid dispenser, may be used. Preferably, the inlet for acid should be properly sealed, such that, during use, the risk of leakages is minimized.

Preferably, in an installation (for use in a process) according to the invention said inlet for acid and/or said inlet for air is arranged to direct the acid and/or air into a lower part of the reaction cell, such that, during use, the acid or air is introduced under the surface of the aqueous mixture, thereby causing exo-thermic action on the aqueous mixture and simultaneous immediate mixing-agitation thereof. This is in particular beneficial when acid is added into the reaction cell as it promotes proper mixing of the acid with the aqueous mixture and accordingly promotes the reaction between acid and sulphite comprised in the aqueous mixture.

In an embodiment, said inlet is configured to direct said acid and/or air into a lower part of the reaction cell by extending the inlet from an upper to a lower part of the reaction cell, such that the acid and/or air is introduced directly under the surface of the aqueous mixture. Alternatively, or additionally, said inlet for acid and/or air is located in a lower part of the reaction cell, thereby directing said acid and/or air below the surface of the hydrogen peroxide solution, during use.

Preferably, said inlet comprises an inlet structure. Said inlet structure preferably comprises a conduit that is connected to an aperture in (an upper part of) the reaction cell, through which, during use, acid and/or air may be introduced into the reaction cell, preferably introduced in a lower part of the reaction cell.

Said acid and/or air is preferably air-flow directed. During use, air may be introduced into the installation by a device, preferably a pump. Said device typically promotes circularization of the air in one direction in the installation, as shown by the arrows in Figure 1. Such air flow promotes, during use, introduction of acid and/or air into a lower part of the reaction cell.

Stirring is further enhanced upon introduction of air into the reaction cell. This is advantageous, because it allows operation of the installation without the need for a mechanical stirring device. However, as the skilled person will appreciate, a mechanical stirrer may optionally be used to enhance stirring, if this is desired.

In the installation (for use in a process) according to the invention, the reaction cell and the collection cell are in fluid communication with one another. This is necessary to allow any SO_2, which is formed during the reaction, as shown by equation 1, to travel from the reaction cell to the collection cell.

Said reaction cell of the installation (for use in a process) according to the invention further comprises an inlet for air connected via a conduit to an outlet for air at the collection cell. During use, said conduit allows flow of air from the collection cell to the reaction cell, which is required to allow flow of the SO_2 from the reaction cell to the collection cell. Said conduit is typically configured such that, during use, SO_2 is at least substantially prevented to escape the installation and/or ambient air (other than ambient air introduced by a device for introducing ambient air into the installation, such as a pump) is essentially prevented from entering said conduit.

Advantageously, said inlet for air may be utilized both as inlet for acid and as an inlet for air into the reaction cell.

Said conduit connecting the inlet for air in the reaction cell with the outlet for air of the collection cell in the installation (for use in a process) according to the invention is arranged with a device for introducing ambient air into the installation. Said conduit is arranged to be connected to a device, which device may be used to, during use, introduce ambient air via a conduit into the reaction cell, thereby promoting the flow of air from the collection cell to the reaction cell, and indirectly the flow of SO_2 from the reaction cell to the collection cell. Preferably, said conduit is connected to said device.

Said conduit connecting the inlet for air in the reaction cell with the outlet for air of the collection cell typically comprises a three-way branch connected to a device for introducing ambient air into the installation.

Said device is preferably a pump, more preferably a mechanical pump, thereby advantageously allowing automatic operation of the process. Alternatively, said pump may be a manual pump, such as a syringe.

Said conduit is thus typically configured to receive, during use, ambient air from a device, such as a pump, to promote flow of air from the collection flask to the reaction flask.

As the skilled person will appreciate, during use, ambient air may be introduced into the installation at any suitable flow rate, depending in the scale of the installation and the configuration of the outlet for air exiting the installation. Typically, the flow rate is between about 1 L/hour and about 10 L/hour, more preferably between about 2 L/hour and about 6 L/hour, even more preferably between about 3 L/hour and about 4/L hour. The skilled person is capable of selecting an appropriate flow rate based on common general knowledge and the information provided herein.

Further, said installation (for use in a process) according to the invention comprises, in an upper portion of the collection cell, an outlet for air to exit the installation. The outlet conveniently permits circulation of a flow of air from the device for introducing air to the reaction cell, promoting a flow of SO_2 from the reaction cell to the collection cell.

Said outlet for air is preferably configured to allow, during use, about 70 to about 80 vol% of the volume of air introduced by the pump to exit the cell.

Preferably, said outlet for air is configured such that, during use, a portion, preferably about 20 to about 30 vol%, of the air is recycled into the installation, and that about 70 to about 80 vol% exits the installation, based on the total volume of air introduced by the pump. Advantageously, such configuration promotes the maintenance of a positive back pressure on the device for introducing air into the installation, while allowing said device to continue to promote flow-through the cell.

This can e.g. be achieved by selecting the diameter of the outlet for air present in an upper part of the collection cell such that it is sufficiently small to allow only about 50 to about 90 vol%, preferably about 60 to about 85 vol%, in particular about 70 to about 80 vol.% of introduced air to exit the installation. As a result, the remaining about 10 to about 50 vol.%, preferably about 15 to about 40 vol.%, in particular about 20 to about 30 vol% of introduced air is forced to re-enter the reaction cell via the conduit connecting the outlet for air of the collection cell with the inlet for air of the reaction cell.

The volume percentage of air exiting the installation can be determined by measuring the air flow exiting the installation (from the outlet for air located in an upper part of the collection cell) and divide said air flow by the total air flow provided by the pump. The method described in Example 3 may be suitably used to assess the vol.% of air exiting the installation.

The skilled person is capable of selecting an appropriate size for the outlet for air to regulate the flow, based on common general knowledge and the information provided herein. Preferably, the outlet for air is about 2 mm or less in diameter, preferably about 1 mm or less in diameter, such as about 0.9 mm or less, more preferably about 0.8 mm or less, more preferably about 0.7 mm or less, more preferably about 0.6 mm or less, in particular about 0.5 mm or less in diameter.

Preferably, the outlet for air has a diameter of between about 0.5 mm and about 2 mm, more preferably between about 0.6 mm and about 1 mm.

Preferably, the outlet for air has a surface of about 15 mm^2 or less, more preferably about 12 mm^2 or less, more preferably about 10 mm^2 or less, even more preferably about 5 mm^2 or less, in particular about 3 mm^2 or less, more in particular 1 mm^2 or less, such as 0.8 mm^2 or less. Preferably, the outlet for air has a surface of between about 0.5 mm^2 and about 15 mm^2, more preferably between about 1 mm^2 and about 12 mm^2, in particular between about 3 mm^2 and about 10 mm^2.

By re-introducing a fraction of air introduced into the installation by the pump, preferably about 20 to about 30 vol. %, from the collection cell back into the reaction cell, the inflow of fresh ambient air into the installation is advantageously reduced. This is in contrast with the Rankin Aspiration instrument, wherein air is allowed to freely enter the instrument during operation. The installation according to the invention is thus typically configured to essentially restrict the inflow of ambient air into the installation and/or to essentially prevent loss of gaseous SO_2 from the installation. The installation is usually configured to, during use, essentially prevent ambient air to enter the installation, other than ambient air introduced by a device into the conduit connecting an outlet for air of the collection flask with an inlet for air of the reaction flask and/or to substantially prevent loss of gaseous SO_2 from the installation.

This is in particular advantageous in embodiments wherein oxygen from the air present in the installation (for use in a process) according to the invention is removed, thereby lowering the oxygen content in the installation and thus decreasing the risk of oxidation of SO_2 or SO_3 to SO_4.

Accordingly, said conduit connecting the inlet for air with the outlet for air in the installation (for use in a process) according to the invention is preferably equipped with an oxygen trap filter for removing O_2 from air. Removing O_2 from atmospheric air advantageously further improves accuracy of SO_2 capture and detection, as it reduces the risk of oxidation of SO_2 to SO_4.

Said oxygen trap filter preferably comprises a metal selected from aluminum, zinc, iron, tin, copper or combinations thereof. Most preferably said filter comprises aluminum or zinc. The presence of such a filter thus enhances the accuracy of the installation (for use in a process) according to the invention to >90% capture and detection of SO_2 (see Examples).

Optionally, said conduit connecting the inlet for air with the outlet for air in the installation (for use in a process) according to the invention further comprises a moisture trap filter for removing moisture from air present in the installation. Such a moisture trap filter may significantly enhance the life-time of the oxygen trap filter for removing O_2 from air, this can occur by preventing corrosion of the filter for removing O_2, especially when the filter comprises metal. The metal is typically oxidized on exposure to the oxygen in the introduced air, capturing it chemically on the surface, for this reason the metal preferably has a high surface area. To achieve a high surface area, the metal may be made into wool-like strands or alternatively be comprised of small flakes. Metallic powder is preferably avoided to prevent blockages.

Said moisture trap filter for removing moisture is thus preferably located upstream of the oxygen trap filter for removing O_2 from air, such that, during use, air moves from the collection cell through the moisture trap filter for removing moisture from air to obtain a dewatered air flow, which subsequently passes through the oxygen trap filter for removing O_2 from air, to obtain a dewatered and deoxygenized air flow, which enters the reaction cell through the inlet for air.

Said moisture trap filter for removing moisture may comprise any moisture-absorbing agent, but preferably comprises silica gel. With silica gel it is possible to determine when it no longer effectively absorbs moisture, through a dye-indicator.

A major advantage of the installation, (for use in a process) according to the invention, is that the installation is arranged such that, during use, the total amount of air in the installation is relatively low (typically about 10x less than reference installations such as the Monier Williams Installation or Rankins Aspiration Installation), due to relatively small headspaces of the reaction cell and the collection cell.

As a result of this inventive installation, the risk of oxidation of SO_2 to SO_4, thereby decreasing accuracy of the capture and detection process is drastically reduced. Advantageously, good efficacy of SO_2 assessment was achieved (typically at least 90%), whilst the requirement for the use of an inert gas was abolished, thereby making the process less cumbersome, more cost efficient and portable, without the need to wash the reaction or collection cells as they can be easily swapped. An advantage of the installation being portable is that it is suitable for on-site use, away from a specialized laboratory or factory.

Accordingly, the reaction cell and/or collection cell of the installation (for use in a process) according to the invention preferably comprise(s) a marking for indicating the liquid level in the reaction cell and/or collection cell, preferably wherein said marking is located in an upper half of the reaction cell. Preferably said marking is located at least at 30% of the total height of the reaction cell and/or the collection cell, more preferably at least at 40%, even more preferably at least at 50%, most preferably at least at 60 of the total height of the reaction and/or collection cell, when measured from the bottom to the top of the cell.

Such a marking indicates the level of liquid, e.g. aqueous mixture and/or hydrogen peroxide solution to be filled – during use - inside the reaction cell and/or collection cell, such that, during use, the (v/v) ratio between liquid (e.g. hydrogen peroxide solution or aqueous mixture optionally already mixed with acid) and gas in the installation (for use in a process) according to the invention is between about 1:1 and about 3:1, preferably between about 1.1:1 and about 2:1, more preferably between about 1.3:1 and about 1.5:1.

To minimize the risk of cross-contamination of fluid from the reaction cell to the collection cell (and vice-versa), the conduit connecting the outlet for SO_2 of the reaction cell with the inlet for SO_2 of the collection cell is preferably equipped with a flow check valve, that is present in the conduit connecting an outlet for SO_2 of the reaction cell with an inlet for SO_2 of the collection cell. Said flow check valve is preferably present near the outlet for SO_2 of the reaction cell to aid condensate collect and return to the reaction cell. This is due to the increased internal diameter of the flow check valve compared to the conduit, allowing condensation to occur and aiding breakup of bubbles that may originate from the reaction cell towards the collection cell. Said conduit connecting the outlet for SO_2 of the reaction cell with the inlet for SO_2 of the collection cell is typically configured such that, during use, ambient air is essentially prevented from entering said conduit. Thereby, oxidation of SO_2 is advantageously minimized.

Additionally or alternatively, said conduit connecting an outlet for SO_2 of the reaction cell with an inlet for SO_2 of the collection cell is further preferably equipped with a filter. Said filter is preferably present about half way of the conduit and typically blocks flow if moisture enters the filter housing and connects to a membrane.

Said filter is arranged such that the flow is automatically stopped if condensate wets the filter. Preferably, said filter is a microfilter, preferably a microfilter having a pore size of between about 0.1 and about 10 µM, such as between about 0.2 and about 5 µM, in particular around 0.45 µM.

If a syringe is used as a means for introducing acid in the reaction cell, advantageously, the filter, while offering a low back pressure that is sufficient to cause the plunger present in the syringe to be pushed back to the maximum extension, but not expelled, does not have the capacity to cause the ejection of the plunger. Rather, should sufficient pressure build-up between the pump and the blocked filter, the liquid held in the filter, forms a full blockage, causing back pressure, pushing the acid syringe backwards. Thus, the syringe can be further used as a means to detect a blockage in the device.

Accordingly, said filter thus substantially prevents aqueous liquid or foam to travel between the reaction cell and the collection cell.

To further reduce the risk of cross-contamination, the installation (for use in a process) according to the invention preferably comprises, during use, one or more anti-foaming agent(s) in the aqueous medium to suppress development of foam and potential cross-contamination between cells. Such an anti-foaming agent may prevent the formation of foam or break up foam that has already formed. In principle any anti-foaming agent may be used that is at least substantially stable at low pH, meaning that it does not decompose under acidic conditions.

Examples of suitable anti-foaming agents include silicones such as polydimethylsiloxanes, stearates, such as polyoxyethylene stearate and glycols. Preferably, said antifoaming agent is SILFAX L6010A Defoam2403.

Said flow check valve, preferably present near the outlet for SO_2 of the reaction cell, also referred to in the art as a check valve, non-return valve, reflux valve, retention valve, foot valve or one-way valve, is a valve that allows a fluid to flow through it in only one direction. Such a valve, during use, thus promotes flow of SO_2 from the reaction cell to the collection cell by preventing flow of SO_2 back into the reaction cell. Said flow check valve, preferably present near the outlet for

SO_2 of the reaction cell, during use, further acts as a liquid return reservoir, returning condensate to the reaction cell due to build-up of condensate.

Further, said inlet for SO_2 of the collection cell is preferably arranged to direct said SO_2 into a lower part of the collection cell, such that, during use, said SO_2 is directed below the surface of the hydrogen peroxide solution. In an embodiment, said inlet for SO_2 is configured to direct SO_2 into a lower part of the collection cell by extending the inlet from an upper to a lower part of the collection cell, such that the SO_2 is allowed to be introduced directly under the surface of the hydrogen peroxide solution. Alternatively, or additionally, said inlet for SO_2 of the collection cell is located in a lower part of the collection cell, thereby directing said SO_2 below the surface of the hydrogen peroxide solution, during use.

Preferably, said inlet for SO_2 comprises an inlet structure. Said inlet structure preferably comprises a conduit that is connected to an aperture in (an upper part of) the collection cell, through which, during use SO_2 may be introduced in the collection cell, preferably introduced in a lower part of the reaction cell.

Said SO_2 is preferably directed into a lower part of the collection cell by air-flow. During use, air may be introduced into the installation by a device, preferably a pump. Said device typically promotes circularization of the air in one direction in the installation, as shown by the arrows in Figure 1. Such air flow promotes, during use, introduction of SO_2 into a lower part of the collection cell.

Such an advantageous setup ensures that gaseous SO_2 introduced into the collection cell is allowed to react directly with a capturing agent such as hydrogen peroxide (present in the hydrogen peroxide solution) to form sulfuric acid or another non-gaseous compound, thereby capturing SO_2, as shown by reaction equation 2 when hydrogen peroxide is used as capturing agent.

$$SO_2\uparrow + H_2O_2 \rightarrow H_2SO_4 \qquad \textit{reaction equation 2}$$

Said collection cell of the installation (for use in a process) according to the invention, during use, may in principle comprise any agent capable of capturing SO_2 by reacting with SO_2 to form a non-gaseous compound. Preferably, the collection cell comprises, during use, a solution of hydrogen peroxide in water, more preferably between about 0.1 and about 30 v/v% of hydrogen peroxide in water, even more preferably between about 0.2 and about 20 v/v%, such as between about 0.3 and about 10 v/v%, between about 0.4 and about 5 v/v%, in particular about 0.3 v/v% of hydrogen peroxide in water.

The amount of hydrogen peroxide solution preferably present in the collection cell of an installation (for use in a process) according to the invention typically depends the size of the collection cell to be used.

Typically, between about 10 mL and about 50 mL of hydrogen peroxide solution is present in the collection cell, preferably between about 15 mL and about 40 mL, in particular between about 20 mL and about 30 mL of collection. These amounts are particularly suitable if a collection cell having a volume of between about 40 mL and about 80 mL is used, in particular if a collection cell having a volume of about 50 to 60 mL is used. Particularly preferred is a collection cell of about 50 mL, such as a 50 mL centrifuge tube.

Preferably, during use, said collection cell comprises, based on the volume of the collection cell, at least 30 vol.%, more preferably at least 40 vol.%, at least 50 vol.% of hydrogen peroxide solution. Preferably, during use, said collection cell comprises at most 90 vol.%, at most 80 vol.%, at most 70 vol.% at most 60 vol.% of hydrogen peroxide solution, based on the volume of the collection cell.

Preferably, during use, the reaction cell and collection cell are filled to essentially the same level.

The installation according to the invention is suitable for detecting SO_2 without requiring equipment for detecting SO_2 integrated into the installation. For example, SO_2 which is, during use, captured in the collection flask by a capturing agent such as hydrogen peroxide, may be detected by the naked eye on the basis of detecting sulfuric acid. In an installation (for use in a process) according to the invention, said SO_2 may be detected by observing a change in color or turbidity caused by capturing of SO_2 by hydrogen peroxide to form sulfuric acid (during use), which change is visible by the naked eye in presence of a suitable indicator. Said suitable indicator is preferably a pH indicator. In an embodiment, a color indicator, such as screened methyl red may be present in the collection flask to affect a color change from light blue to pink-salmon (during use), indicating that SO_2 has been captured into sulfuric acid and thus detected. Alternatively or additionally, barium chloride may be present in the collection flask as indicator to affect, during use, formation of barium sulfate out of sulfuric acid which causes a change in turbidity.

Accordingly, said collection cell of the installation (for use in a process) according to the invention, during use, preferably comprises an indicator, more preferably screened methyl red indicator or barium chloride.

Alternatively or additionally, detection of SO_2 may be aided by using an additional detecting means, which need not be integrated into the installation. For example, sulfuric acid may be detected by colour matching, litmus or other acid sensitive paper. Further, photometric or electrochemical equipment, such as a pH meter, may be used to detect or quantify the amount of sulfuric acid that has been formed in the collection cell by capturing of SO_2. Detection of SO_2 using additional detection means may be done *in situ*, or by taking a sample for further analysis.

In an embodiment, if quantification of the amount of SO_2 is desired, the solution comprising the non-gaseous compound, preferably sulfuric acid, present in the collection cell, may be recovered and analyzed. For example, if the non-gaseous compound is sulfuric acid, a sample may be recovered from the collection cell and may be subjected to a step of titration with a suitable base, preferably sodium hydroxide, as visualized by general reaction equation 3.

$$2XOH + H_2SO_4 \rightarrow X_2SO_4 + 2H_2O \qquad \textit{reaction equation 3}$$

Herein, OH represents a base and X represents a monovalent cation, such as Na^+, K^+ or Li^+. As the skilled person will appreciate, the reaction equation may differ slightly depending on the valency of the cation present or the type of base used.

Any method may be used that is known in the art, for example titration using a burette or a graduated pipette. Alternatively, without the use of a volume measuring device, a molal or weight dispensed amount of titrant convertible to a volume using its density may be used.

The reaction changes from salmon pink to grey. The total amount of SO_2 detected can be calculated using formula 1.

$$SO_{2\,(mg/\,kg)} = \frac{32.03 \times N \times T \times 1000}{W_g}$$ formula 1

Wg = weight of undiluted aqueous substrate used

N = normality or molarity x2 of base used in titration

T = titration volume (mL) of base

In principle, any base may be used that is capable of neutralizing H_2SO_4 to induce a change of colour. Examples include a hydroxide, such as lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide or caesium hydroxide. Preferably, said base is sodium hydroxide.

Alternatively or additionally, said base may be a carbonate, such as sodium carbonate or potassium carbonate, a bicarbonate such as sodium bicarbonate or potassium carbonate, ammonia or ammonium hydroxide, as shown in reaction equation 4.

$$H_2SO_4 + X_2CO_3 \rightarrow X_2SO_4 + H_2O + CO_2\uparrow$$ *reaction equation 4*

Herein, CO_3^{2-} represents a base and X represents a monovalent cation, such as Na^+, K^+ or Li^+. As the skilled person will appreciate, the reaction equation may differ slightly depending on the valency of the cation present or the type of base used.

Alternatively, the amount of SO_2 may be assessed using gravimetric analysis. In this approach, a compound such as barium chloride is used to capture SO_4 to form insoluble barium sulphate as shown by reaction equation 5.

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$$ *reaction equation 5*

The insoluble precipitate (e.g. barium sulphate) may be collected and its weight may be assessed to determine the amount of SO_2 captured from the substrate.

A major advantage of the installation (for use in a process) according to the invention is that it can be prepared from low-cost, disposable materials. For example, for the reaction cell and the collection cell, centrifuge tubes may be advantageously used. After each process, the tubes may be removed and replaced by new tubes. Further, the conduits may be prepared from silicone tubing. The tubing and lids of the reaction cell and collection cell, and if present, the filters, syringe and flow check valves of the installation may be washed and re-used, advantageously be recycled or discarded if needed.

The materials are commercially available, typically at low cost. For example, centrifuge tubes are commercially available from Fisher Scientific or Merck.

This further advantageously reduces the amount of cleaning fluids required to clean the installation. Alternatively, it allows for quick-swapping between stages of an experiment.

Accordingly, the installation (for use in a process) according to the invention is preferably prepared from disposable materials, preferably plastic material, such as polystyrene, polypropylene, polyethylene terephthalate, polypropylene copolymer or polycarbonate. Advantageously, the use of centrifuge tubes allows to use vortex mixing to disperse viscous molasses samples in water prior to addition of acid to initiate a method according to the invention.

Preferably, said disposable material has a melting temperature of about at least 120 °C or more, more preferably at least 140 °C or more, even more preferably at least 160 °C or more. Such an installation is also advantageously suitable to detect loosely bound SO_2 as well as free SO_2, as will be described in more detail herein below.

The installation (for use in a process) according to the invention may in principle be executed with a wide flexibility in size or scale. It is an advantage however, that the process can be effectively carried out at small scale, reducing factors that can lead to inaccuracy of SO_2 assessment.

Typical volumes of an installation according to the invention are between about 50 cm^3 and about 150 cm^3, preferably between about 80 cm^3 and about 120 cm^3. Accordingly, typical volumes of the reaction cell and the collection cell are between about 20 cm^3 and about 70 cm^3, such as around 50 cm^3. The internal head-space volume of the installation design is approximately around 3 to 5 times smaller compared to other methods, advantageously introducing less air into the device.

As a fully or partially portable configured device, the invention may comprise of a single unit as an assembly per Figure 1, as well as be applied in several units in parallel, but not joined. Alternatively, be added as a part of a larger serial combination of same units or devices allowing extractions of samples that can feed into this device serially.

Particularly good results have been obtained with an installation as shown in Figure 1. Accordingly, the invention preferably relates to a portable sulfur dioxide detection installation (for use in a process) according to the invention comprising a reaction cell and a collection cell, said reaction cell comprising an outlet for SO_2 which is connected via a first conduit to an inlet for sulfur dioxide into the collection cell, said first conduit containing a filter and one or more flow check valve(s) for preventing liquid or foam to translocate between the reaction cell and the collection cell and an inlet for air connected via a second conduit to an outlet for air of the collection cell, wherein said second conduit is arranged with a pump for introducing ambient air into the installation and wherein said second conduit comprises an oxygen trap filter for removing O_2, preferably a zinc filter and a moisture trap filter for removing water, preferably comprising silica gel, and wherein said moisture trap filter is located upstream of the oxygen trap filter, wherein said reaction cell comprises an inlet for acid and wherein said collection cell comprises, in an upper portion, an outlet for air, wherein said outlet for air is arranged to allow about 70 to about 80 vol.% of air introduced into the installation by said pump to exit the installation, in particular the collection cell.

An advantage of a process according to the invention is that it allows capture and detection of free SO_2, loosely bound SO_2 but not strongly bound SO_2. This is relevant in particular for the assessment of substrates for yeast production, because free and loosely bound SO_2, but not strongly bound SO_2 can inhibit yeast production.

Accordingly, in a process according to the invention, the aqueous mixture in the reaction cell is preferably left at a temperature of at least 20 °C, preferably at least 25 °C, at least 40 °C, more preferably at least 60 °C. In particular, the aqueous mixture in the reaction cell is preferably left at a temperature between about 20 °C and about 80 °C, preferably between about 25 °C and about 70 °C, more preferably between about 25 °C and about 60 °C, in particular at ambient temperature, e.g. between about 20 °C and about 25 °C. In the process, free SO_2 is typically released from the aqueous mixture upon acidification (specifically phosphoric acid) at ambient temperature, e.g. between about 20 °C and about 25 °C, whereas loosely bound SO_2 is typically released at a temperature of about 60 °C.

Heating may be achieved using any suitable method known in the art. For example, an ancillary device, such as a beaker with a magnetic bar and hotplate, is used to heat water to 60 °C, using a temperature feed-back control loop thermocouple, to control the bath temperature precisely. Said bath is used to hold the reaction cell suspended in the bath at 60 °C for the required time, while the collection cell may be held at ambient temperature, for example using a centrifuge tube holder next to the hotplate, to support the cell. Alternatively, a battery powered portable warming block or multiple warming block that can accommodate one or several reaction cells may also be used.

Typically, the installation is left to stand for at least 15 minutes, at least 30 minutes, at least 45 minutes, in particular at least 60 minutes after all acid has been introduced in the reaction vessel. Preferably, the installation is allowed to stand for between about 15 and about 60 minutes, more preferably between about 20 and about 55 minutes, in particular between about 25 and about 50 minutes after introduction of the acid in the reaction cell.

Advantageously, without significant loss of SO_2, it is possible to follow the amount of SO_2 being released over time by exchanging the collection cell for a fresh cell. If timed, then kinetics for the release of SO_2 could also be measured and the content of free SO_2 may be distinguished from loosely bound SO_2. Thus the installation (for use in a process) according to the invention could be customized for other reactions that may undergo similar mechanisms of reaction.

To aid exchanging of the collection cell between capture and/or detection of free and loosely bound SO_2, preferably the conduit connecting the outlet for SO_2 of the reaction cell and the inlet of SO_2 of the collection cell, and/or the conduit connecting the outlet of air of the collection cell and the inlet of air of the reaction valve is preferably equipped with one or more isolation or closable valve(s). During use, such one or more closable valve(s) may be closed to prevent leakage of SO_2 from the installation, whilst exchanging the collection cell for a fresh collection cell.

If it is desired to distinguish between free SO_2 and loosely bound SO_2 species, the collection cell is preferably exchanged before heating to a temperature of at least 40 °C, preferably at least 50 °C, more preferably at least 60 °C.

In such case, the process according to the invention is comprised of at least two stages, herein referred to as Stage I or Stage II, but that can exist in combination for substrate quality measurement, herein known as Stages (I+II).

In stage I, the installation is left to stand at a temperature of between about 20 °C and about 40 °C, preferably between about 25 °C and about 30 °C, such as around 22-25 °C. At these temperatures, free SO_2 is typically released from the aqueous mixture.

In stage I, the installation is preferably allowed to stand for at least 10 minutes, in particular at least 15 minutes, more preferably at least 20 minutes after introduction of acid in the reaction cell. Typically, the installation is allowed to stand for between about 5 minutes and about 30 minutes, in particular between about 10 minutes and about 20 minutes, such as about 15 minutes.

When stage I is completed, the collection cell is preferably exchanged for a fresh collection cell comprising a hydrogen peroxide solution, more preferably further containing screened methyl red indicator solution as defined earlier.

In stage II, the installation is left to stand at a temperature of between about 40 °C and about 80 °C, preferably between about 50 °C and about 70 °C, such as around 60 °C. At these temperatures, loosely bound SO_2 is typically released from the aqueous mixture.

In the stage II, the installation is preferably allowed to stand for at least 30 minutes, preferably at least 45 minutes, in particular at least 30 minutes after introduction of acid in the reaction cell. Typically, the installation is allowed to stand for between about 30 minutes and about 50 minutes, in particular between about 40 minutes and about 50 minutes.

The content of the one or more collected collection cells may optionally be analyzed to assess the content of SO_2 as described herein above.

It is an advantage of the process according to the invention that the process can be operated under air atmosphere, without compromising accuracy of capturing and detection of SO_2 (typically based on detection of sulfuric acid). This is because the risk of of oxidation of free SO_2 and SO_3 to SO_4 is significantly reduced in the installation according to the invention, because the amount of air present in the installation is reduced compared to known installations and because inflow of ambient air is restricted, as explained herein above and shown in Example 3. Therefore, the invention preferably relates to a process according to the invention, said process being carried out under non-inert atmosphere, preferably air-atmosphere. Preferably, said air atmosphere is an air atmosphere that comprises oxygen, in particular in an amount as present in the ambient atmosphere.

Preferably, in a process according to the invention, introduction of ambient air into the installation, other than ambient air introduced into a conduit connecting an outlet for air of the collection cell with an inlet for air of a reaction cell by a device for introducing ambient air, is substantially prevented. Preferably, in a process according to the invention, about 20 vol.% or more of air from the collection cell is reintroduced into the reaction cell, based on the total volume of the installation, more preferably about 30 vol.% or more, in particular between about 10 vol.% and about 50 vol.%, more in particular between about 20 vol.% and about 30 vol.%, based on the total volume of the installation.

Alternatively or additionally, the invention preferably relates to a process for capturing SO_2 in an aqueous mixture, wherein at most 80 vol.%, preferably at most 70 vol.% of ambient air, in particular between about 50 vol.% and about 90 vol.%, more in particular between about 70 vol.% and about 80 vol.% of ambient air is introduced into the installation, based on the total volume of the installation.

The skilled person is capable of achieving introduction of specific amounts of ambient air into the installation based on common general knowledge and the information provided herein, which amount can be determined with a method as described in Example 3.

For the purpose of clarity and a concise description, features are described herein as part of the same or separate embodiments, however, it will be appreciated that the scope of the invention may include embodiments having combinations of all or some of the features described.

The invention is demonstrated by the following examples.

Example 1: Determination of SO_2 content in molasses and wort

In an installation as depicted in Figure 1, about 25 mL of 0.3% v/v solution of hydrogen peroxide was charged in a 50 mL centrifuge tube which was used as a collection cell. The outlet for air was located just above the 45 mL mark and was approximately 1 mm in diameter. Three drops of screened methyl red solution R was added to the solution which turned blue-grey.

Diluted molasses prepared with pre-boiled water or wort were charged into another 50 mL centrifuge tube which was used as the reaction cell in the amounts as indicated in Table 1. Three drops of antifoaming agent SILFAX L6010A Defoam 2403 was added to the mixture.

In the combined assessment measuring free SO_2 and loosely bound SO_2 described as combined stages (I+II), the reaction cell was placed in a temperature-controlled water bath held at 60 °C. 10 mL of concentrated phosphoric acid was dispensed into the reaction cell using a syringe, before removing the collection cell for titration with dilute standardized sodium hydroxide solution to a blue end-point.

The mechanical pump is switched on immediately after addition of phosphoric acid.

The reaction cell was held for the period indicated in table 1 for the stage being tested.

Table 1; Reaction conditions of process for detecting SO_2 using an installation according to the invention

Sample type	mg/Kg SO2 in sample (x)	Mass of Wort or Molasses (g) (800 0/x)*	Approx. Diluent R (Pre-boiled Water) (mL)	Combined Extraction Stages 45min.,60°C	
				Stage 1 Added H3PO4 (mL)	Stage 2 Added H3PO4 (mL)
		Wsa	Dsa	Free SO2/SO3	Loosely Bound SO3
				Hold 15min./Amb.	Hold 30min./60°C
wort	100	20	0	10	0
molasses	500	16	4	10	0
molasses	1000	8	12	10	0
molasses	2000	4	16	10	0

When the experiment was finished, the collection cell was recovered and titrated with freshly prepared sodium hydroxide (0.025 N) using a 25 mL burette until the solution turned from blue-grey to salmon pink.

The amount of SO_2 was calculated in each test sample using the formula 1.

$$SO2\left(\frac{mg}{kg}\right) = \frac{T\ x\ M\ x\ F\ x\ 64.022\ x\ 1000}{Wsa\ x\ 2} \qquad \text{formula 1}$$

Wherein,
T =Sodium hydroxide titration (mL)
M = Molarity of NaOH titrant (typically *Dilute (0.025M) Sodium Hydroxide VS*)
F = factor of *1M Sodium Hydroxide VS* Section 5.13 (used to make *Dilute (0.025M) Sodium Hydroxide VS* freshly on day of use- step 5.16)
W =weight of standard (g)
Wsa = weight of sample (g)

Example 2: Determining recovery rate of SO_2 using installation according to the invention

The method described in example 1 was repeated, using a solution of 0.1 g of Na_2SO_3 in 100 mL of preboiled water.

In another experiment, the method was repeated using an installation as depicted in Figure 1, wherein the oxygen trap filter and moisture trap filters were not present unless indicated.

The sulfur dioxide recovery percentage was calculated using formula 2.

$$\%recovery = \frac{T\ x\ \ M\ x\ F\ x\ Vdil\ x\ MWx\ x\ 5}{W\ x\ P\ x\ Val} \qquad \text{formula 2}$$

Wherein , T, M and F are as defined herein above and wherein
Vdil. =dilution volume of standard solution (mL) (typically ***100mL***)
MWx = Molecular weight of standard applied (including water of hydration).
W = weight of standard (g)
P = % w/w purity ‘as is’ of standard
Val =aliquot volume taken into analysis (mL) (typically ***25.0mL***)

The results are shown in Figure 2. It can derived from Figure 2 that with the installation according to the invention a recovery rate of more than 88.7% was achieved (third and fourth bar from the top).

The recovery rate could be improved by about 4.6% when a zinc filter was used to capture oxygen from the air (comparison first and third bar from the top).

Recovery rates could be further improved by running the method for a longer amount of time (comparison third and fifth bar from the top).

Example 3: Air flow measurement

A 50mL burette was filled with liquid to the mark and connected via tube filled with water to the outlet for air located in an upper part of the collection cell of an installation according to the invention, as shown in Figure 3.

An aqua one stellar 50 aquarium pump for introducing air into the installation (as shown in Figure 1) was turned on and allowed to run until the water in the tube and burette reaches the 0-mark of the burette. The time was recorded. The pump flow was measured using formula 3.

$$\text{Air flow (mL/min.)} = (Ve - Vi) \times 60/(t) \qquad \text{formula 3}$$

Herein Ve = end volume (mL)
Vi = initial volume (mL)

t = time required until water reached the 0-mark in seconds.

The experiment was repeated using a set-up wherein the pump was directly connected to the burette replacing the installation according to the invention. The results are shown in Table 2.

Table 2; air flow of pump in absence and presence of the installation according to the invention

Condition	Time (s)	Air flow(ml/min.)	Av.	%rsd	L/h
pump	42.19	71.1			
pump	41.90	71.6			
pump	41.71	71.9	71.5	0.6	4.3
cell	55.22	54.3			
cell	55.15	54.4	54.4	0.1	3.3

As shown in Table 2, the total air flow of the pump in absence of the installation according to the invention is about 71.5 mL/min compared to 54.4 ml/min when the pump was arranged to pump air through the installation. It follows that about 76 vol.% of air exited the installation according to the invention, meaning that about 24 vol.% of air was recycled into the installation.

Figure legend:

1: reaction cell
2: inlet for acid and air
3: collection cell
4: outlet for SO2
5: inlet for SO2
6: conduit
7: outlet for air
8: outlet for air
9: conduit
10: first three-way branch
11: filter
12: flow check valve
13: oxygen removal filter
14: water filter
15a,b: flow check valves
16: mechanical pump
17a,b: markings

18: syringe
19: second three-way branch

Claims

1. A portable installation for capturing SO_2 in an aqueous mixture, said installation comprising a reaction cell (1) and a collection cell (3), said reaction cell (1) comprising an outlet for SO_2 (4) which is connected via a conduit (6) to an inlet for sulfur dioxide (5) into the collection cell (3), and an inlet for air connected via a conduit (9) to an outlet for air (8) of the collection cell (3), wherein said conduit (9) is arranged to be connected to a device (16) for introducing ambient air into the installation, wherein said reaction cell comprises an inlet for acid and wherein said collection cell (3) comprises, in an upper portion, an outlet for air to exit the installation (7).

2. The portable installation according to claim 1, wherein said inlet for acid and/or said inlet for air (10) is arranged to allow introduction of acid and/or air into a lower part of the reaction cell (1).

3. The portable installation according to any of the preceding claims, wherein said conduit (6) connecting said outlet for SO_2 (4) of the reaction cell (1) to said inlet for SO_2 (5) of said collection cell (3) contains a filter (11) and/or one or more flow check valve(s) (4) for preventing liquid or foam to translocate between the reaction cell (1) and the collection cell (3).

4. The portable installation according to any of the preceding claims, wherein said outlet for SO_2 (4) is arranged to direct said SO_2 into a lower part of the collection cell (3).

5. The portable installation according to any of the preceding claims, wherein said conduit (9) for connecting an outlet for air (8) of the collection cell (3) to an inlet for air of the reaction cell (1) comprises an oxygen trap filter for removing O_2 (13), preferably a zinc, aluminum, iron, tin, copper or combinations thereof and optionally a moisture trap filter (14) for removing water, preferably comprising silica gel.

6. The portable installation according to any of the preceding claims, wherein said outlet for air (7) is arranged to allow about 70 to about 80 vol.% of air introduced into the installation by said device (16) to exit the installation, based on the total volume of the installation.

7. The portable installation according to any of the preceding claims, wherein the installation is prepared from disposable materials, preferably plastic, such as polystyrene, polypropylene, polyethylene terephthalate, polypropylene copolymer or polycarbonate.

8. The portable installation according to any of the preceding claims, wherein the collection cell (3) comprises hydrogen peroxide, preferably wherein at least 50 vol% of the volume of the collection cell is filled with a hydrogen peroxide solution.

9. The portable installation according to any of the preceding claims, wherein the reaction cell (1) comprises a marking (17a) for indicating the level of aqueous mixture in the reaction cell (1), preferably wherein said marking (17a) is located in an upper half of the reaction cell and/or wherein the collection cell (3) comprises a marking (17b) for indicating the level of hydrogen peroxide solution in the collection cell (3), preferably wherein said marking is located in an upper half of the collection cell (3).

10. A process for capturing SO_2 in an aqueous mixture in a portable installation according to any of the preceding claims, the process comprising addition of an acid into the reaction cell (1), said reaction cell containing an aqueous mixture comprising sulphite, thereby forming SO_2; allowing said SO_2 to move from the reaction cell (1) to the collection cell (3), said collection cell (3) containing hydrogen peroxide, thereby forming sulfuric acid.

11. The process according to claim 10, further comprising recovering said sulfuric acid from the collection cell (3); and titrating said sulfuric acid with a base, preferably sodium hydroxide.

12. The process according to claim 10 or 11, further comprising heating of the reaction cell (1) to about 40 °C to about 70 °C, preferably about 60 °C.

13. The process according to any of claims 10 to 12, wherein said aqueous mixture comprises molasses, preferably sugarcane molasses, beet molasses or a combination thereof.

14. The process according to any of claims 10 to 13, wherein the (v/v) ratio between liquid and gas in the installation is between 1:0.5 and 1:0.8, preferably between 1:0.5 and 1:0.9.

15. The process according to any of claims 10 to 14, wherein free SO_2, loosely bound SO_2 or both free SO_2 and loosely bound SO_2 is/are captured.

16. The process according to any of claims 10 to 14, wherein ambient air is introduced into the installation in an amount of 80 vol.% or less, preferably 70 vol.% or less, based on the total volume of the installation.

17. The process according to any of claims 10 to 15, wherein the process is carried out under non-inert atmosphere, preferably air atmosphere.

Figure 1

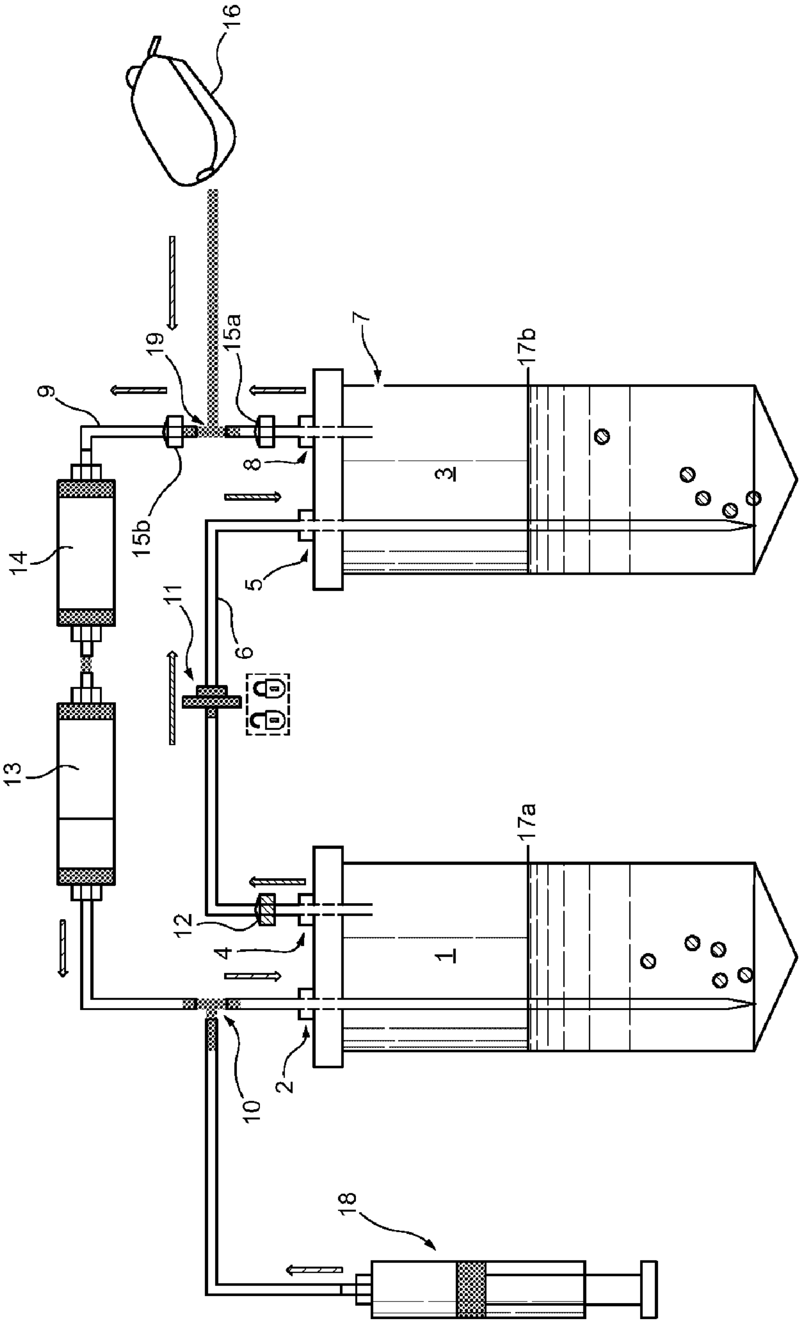


Figure 2

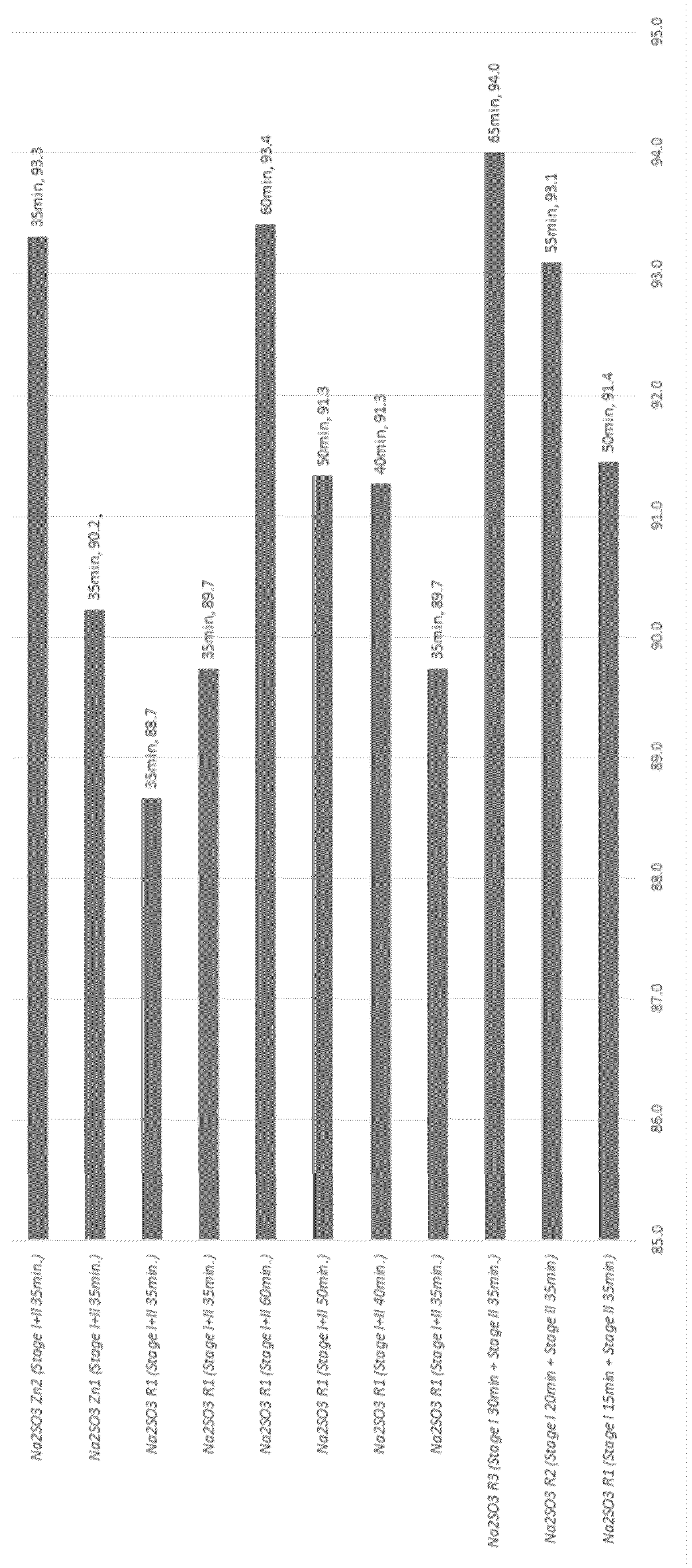
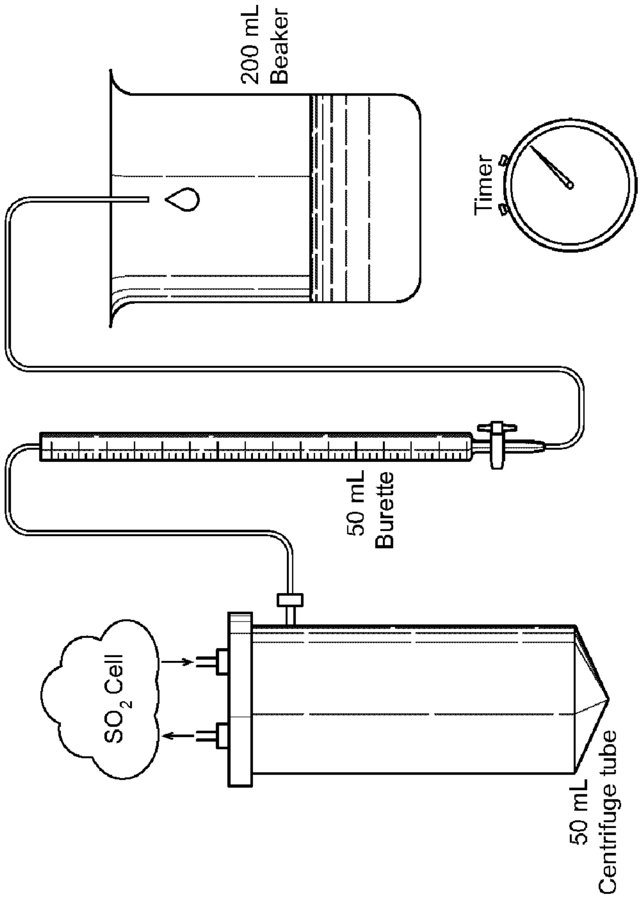

Na2SO3 Zn2 (Stage I+II 35min.)
35min, 93.3
Na2SO3 Zn1 (Stage I+II 35min.)
35min, 90.2
Na2SO3 R1 (Stage I+II 35min.)
35min, 88.7
Na2SO3 R1 (Stage I+II 35min.)
35min, 89.7
Na2SO3 R1 (Stage I+II 60min.)
60min, 93.4
Na2SO3 R1 (Stage I+II 50min.)
50min, 91.3
Na2SO3 R1 (Stage I+II 40min.)
40min, 91.3
Na2SO3 R1 (Stage I+II 35min.)
35min, 89.7
Na2SO3 R3 (Stage I 30min + Stage II 35min.)
65min, 94.0
Na2SO3 R2 (Stage I 20min + Stage II 35min)
55min, 93.1
Na2SO3 R1 (Stage I 15min + Stage II 35min)
50min, 91.4
85.0
86.0
87.0
88.0
89.0
90.0
91.0
92.0
93.0
94.0
95.0

Figure 3


200 mL
Beaker
Timer
50 mL
Burette
SO_2 Cell
50 mL
Centrifuge tube

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068781

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N33/00
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ISO: "ISO 5379 - Starches and derived products - Determination of sulfur dioxide content - Acidimetric method and nephelometric method" In: "ISO standards", 1 September 2013 (2013-09-01), ISO/TC93, XP009550075, vol. 5379, pages 1-13, the whole document ----- -/--	1-17

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

☐ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search
6 September 2024

Date of mailing of the international search report
16/09/2024

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Kraus, Leonie

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Honeywell: "SPM Flex Single Point Monitor Gas Detector", , 1 October 2016 (2016-10-01), pages 1-76, XP093105265, Retrieved from the Internet: URL:https://en.gazdetect.com/media/catalog/product/instruction/Manuel-technique-SPM-FLEX-Honeywell-EN.pdf [retrieved on 2023-11-24] the whole document -----	1-15
A	Chen Lillian ET AL: "Determination of Total and Free Sulfite in Foods and Beverages", , 1 August 2016 (2016-08-01), pages 1-8, XP093105311, Retrieved from the Internet: URL:https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-54-IEX-Sulfite-Food-Beverage-AN70379-EN.pdf [retrieved on 2023-11-24] the whole document -----	1-15

1