

[54] **APPARATUS FOR AND METHOD OF DETERMINING OXYGEN AND CARBON DIOXIDE IN SEALED CONTAINERS**

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23/254 R, 73/421.5 R, 73/423 A

[51] Int. Cl. **G01n 1/16, G01n 1/26, G01n 33/14**

[58] Field of Search **23/230 R, 253 R, 232 R, 23/232 E, 254 R, 254 E, 259, 255 E; 73/421.5 R, 423 A**

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[57]

ABSTRACT

An apparatus and a method by means of which oxygen and carbon dioxide dissolved in a liquid in a sealed container and oxygen in the headspace of the same container can be determined. The apparatus can also be used to measure dissolved oxygen in liquids in open containers. A valve fitted with a syringe makes it possible to draw representative samples of known volume from both the headspace and the liquid within the container. The specimens thus obtained are directed into an oxygen-free stream of inert gas from which CO₂ is absorbed and the O₂ is transferred to an oxygen detector. Dissolved CO₂ is determined from a reading of the total gas pressure on a gauge and from measurements of the volume of liquid in the container and the volume of the container itself.

9 Claims, 5 Drawing Figures

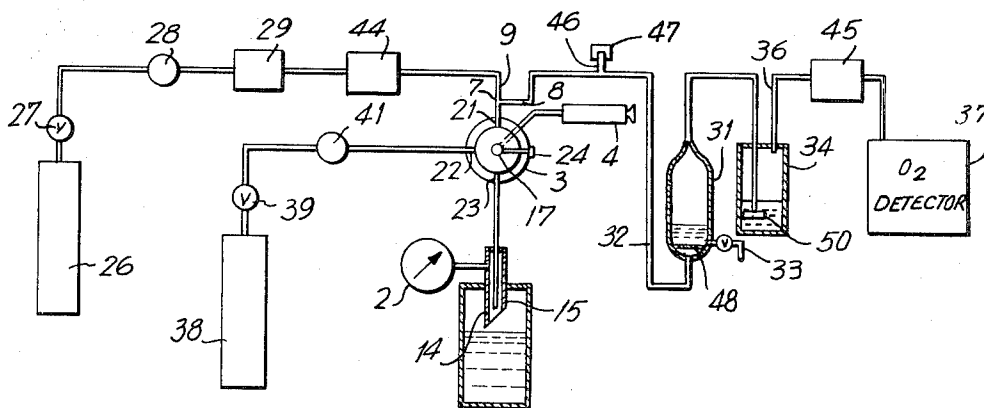


FIG. 1

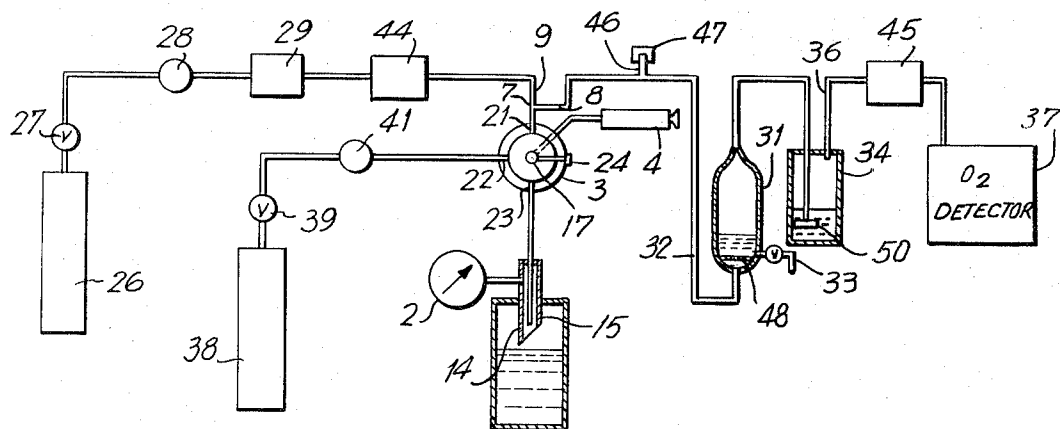


FIG. 2

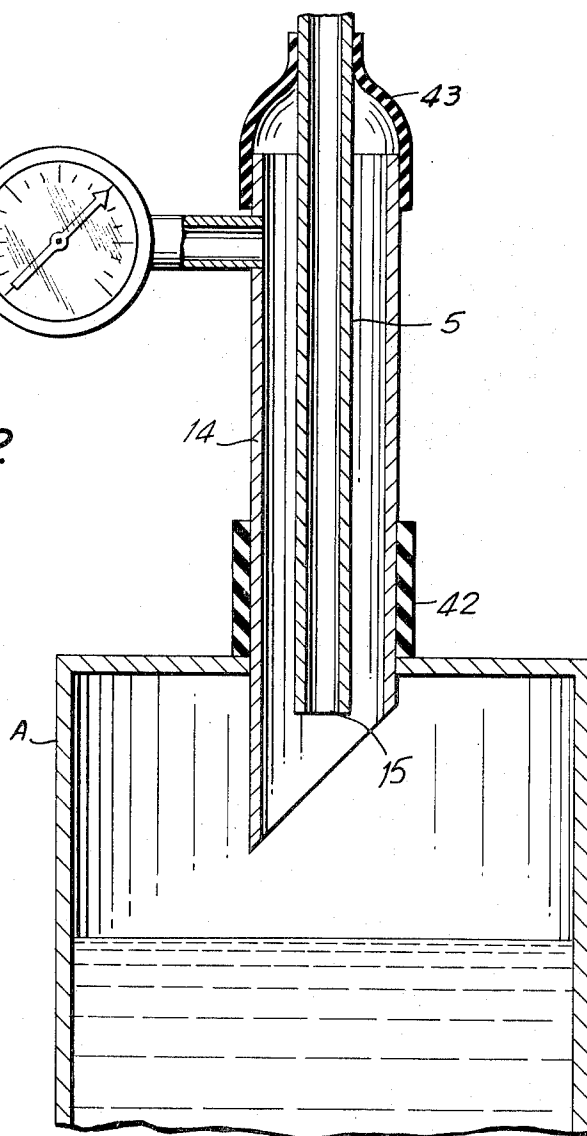


FIG. 3

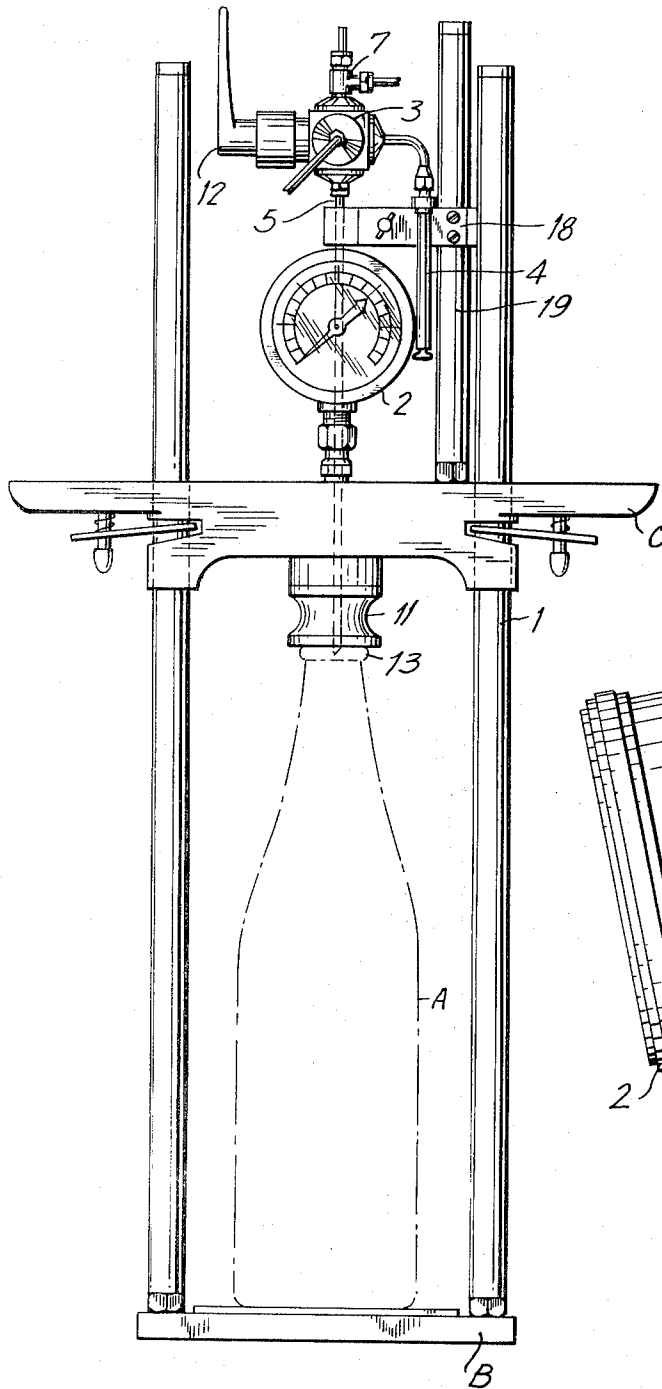


FIG. 4

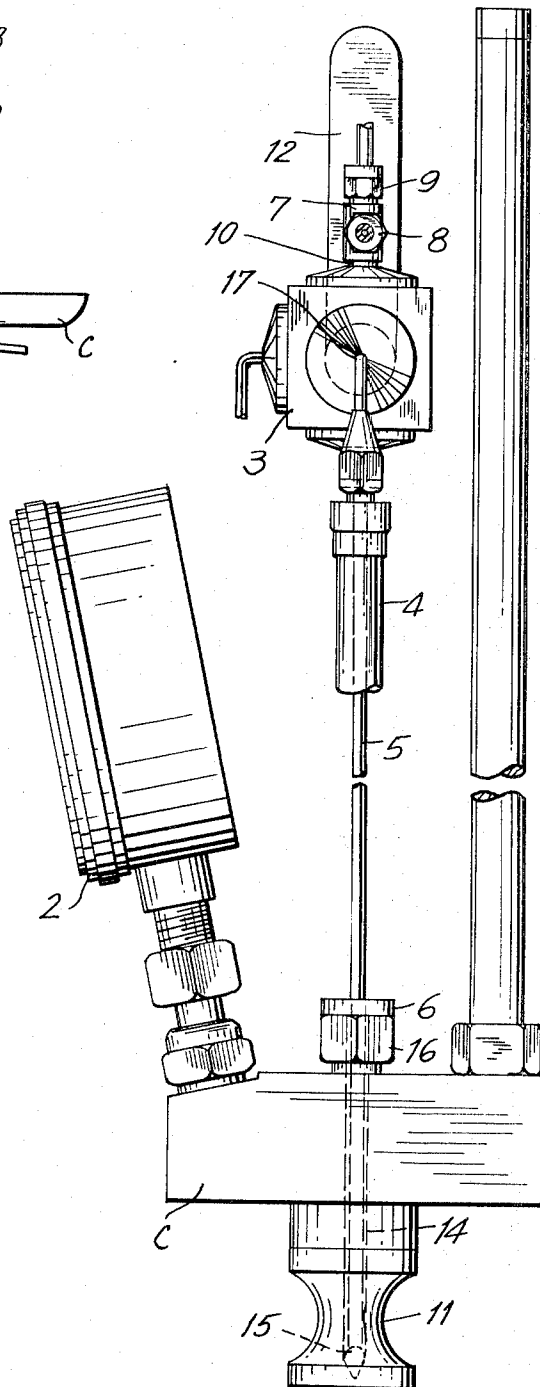
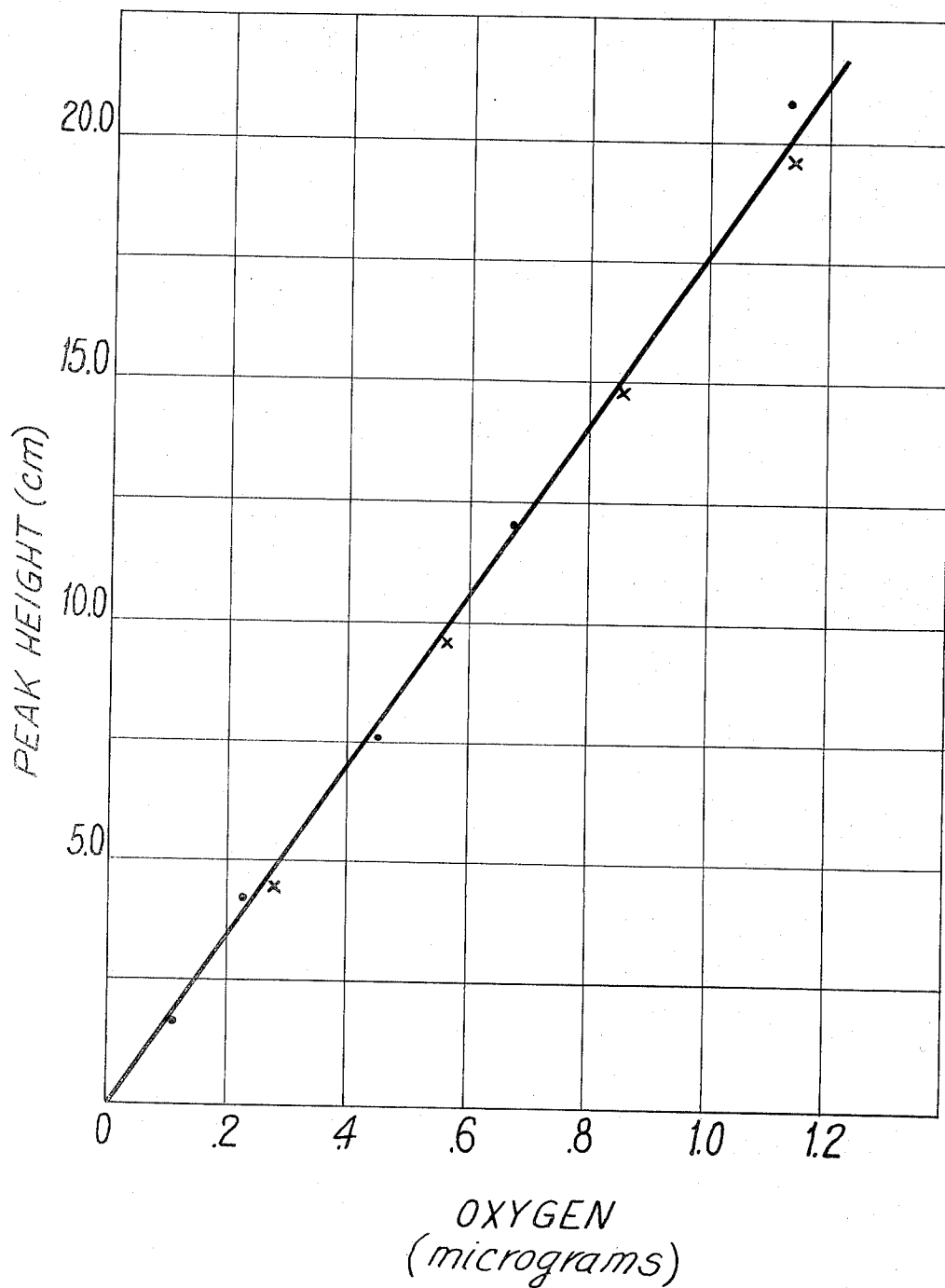


FIG. 5



APPARATUS FOR AND METHOD OF DETERMINING OXYGEN AND CARBON DIOXIDE IN SEALED CONTAINERS

BACKGROUND OF THE INVENTION

To date, the determination of CO₂ content or the dissolved oxygen or headspace oxygen in packaged products is not a routine practice. Also, the determination of O₂ dissolved in liquids in open containers is generally not a routine practice in the brewing industry. Following are examples of products which could benefit from such determination:

brewery wort, non-alcoholic beverages (carbonated and non-carbonated), wines (carbonated and non-carbonated), cocktails, cordials, products in flexible packages, any food or beverage product where oxygen and possibly carbon dioxide is of importance, any non-food product where dissolved oxygen or headspace oxygen is important; for example, pharmaceutical products, aerosol products.

Occasionally, this measurement is accomplished in beer by gasometric or colorimetric methods. The colorimetric method is accurate to approximately 0.1 ppm but it is only applicable to the liquid phase and not to the headspace. In addition, the procedure is long and tedious and requires considerable skill on the part of the analyst.

For determination of oxygen in the headspace of a sealed container, the only methods available are gasometric. These methods, in addition to being lengthy and tedious, suffer in sensitivity and at best give only an approximation of the oxygen content. The brewing industry has been particularly concerned with the problem of dissolved oxygen and oxygen in the headspace of sealed containers due to the deleterious effect of such oxygen on the flavor and physical stability of the beer. Recently, several types of oxygen analyzers have been evaluated by the brewing industry for measurement of dissolved oxygen in beer. Most of these instruments are geared toward the measurement of dissolved oxygen in process streams and not in a packaged product. Two of these instruments are the Beckman Oxygen Analyzer and the Hays Oxygen Meter. The Hays instrument is a portable unit and is designed for spot checking beer in process. This analyzer has good sensitivity and can detect and measure oxygen in parts per billion level. However, the method is electrochemical and the electrodes necessary for the process are exposed to the beer medium; as a result, they are easily poisoned or corroded and require frequent cleaning and replacement.

The Beckman Oxygen Analyzer is adaptable for monitoring dissolved oxygen in process streams, but its sensitivity leaves much to be desired. Again, the readings obtained with this instrument are normally only an approximation of the dissolved oxygen content in process beer.

Such laboratory models as are commercially available for the examination of packaged beer normally require that the container's closure be physically removed and the contents either measured in the container or transferred to a different vessel for measurement of the oxygen content. This procedure presents obvious serious problems since transfer introduces the possibility of contamination by atmospheric oxygen. Furthermore, these instruments are not sufficiently sensitive for measuring the trace amounts of oxygen

normally found in beer. The typical measurement range on most of these instruments is 0-5 percent oxygen on the most sensitive setting. Presently, there are no commercial instruments available for measuring dissolved carbon dioxide, dissolved oxygen and headspace oxygen in a single sealed container.

SUMMARY OF THE INVENTION

The present invention takes advantage of the fact that devices are commercially available for measuring trace quantities of oxygen in a gas stream and for piercing the top of a container with a hollow needle under conditions such that there is no risk of loss of gas or of leakage of oxygen. Using a special 5-ported valve having a central port which can be connected selectively to any one of the other four ports, one of which four ports is sealed, it is possible to draw samples of headspace gas or a liquid from a container sealed except for having been pierced by said piercing device and to transfer said known volumes to an inert gas stream. The apparatus is adapted for achieving equilibration of gas and liquid phases in a sealed container. Where the sample withdrawn is liquid, the gas stream first transfers the liquid to a gas scrubber which retains the liquid while permitting oxygen, CO₂ and trace volatile organic components to be flushed therefrom by means of said gas stream and carried into a carbon dioxide absorber which removes carbon dioxide and other acidic components from said gas stream. The gas stream then flows through an activated carbon filter which removes traces of organic components. The gas stream is then carried to the oxygen detector, a device which gives a signal proportional to the instantaneous oxygen content of the gas stream. The signal is recorded and integration of the area under the curve gives the total O₂ quantity.

When the tip of the sample probe is positioned in the headspace, the syringe can draw a known volume of headspace gas from the container, and the gas can be transferred to the inert gas stream to pass in turn through the gas scrubber, the carbon dioxide absorber and the carbon filter to the oxygen detector for determining oxygen in a known volume of headspace gas.

A gauge of a suitable range is connected to the probe for determining the total gas pressure in the system. As is evident, for high CO₂ contents the total gas pressure and the CO₂ pressure are essentially identical.

Combination of the data thus obtained with measurements of the volume of liquid and internal volume of the container makes it possible to calculate the content of carbon dioxide.

The process is carried out with the container and the contents thereof at a known temperature, preferably 25°C. Tables are available which give the quantity of dissolved carbon dioxide as a function of the gauge pressure reading and measured temperature.

The procedure is rapid and can be carried out by relatively unskilled technicians.

The procedure and apparatus are also suitable for determining dissolved oxygen in liquids in open containers, although no piercing of a container is required and the equilibration steps are omitted.

Accordingly, it is an object of the present invention to provide an apparatus for the determination of dissolved carbon dioxide and dissolved oxygen and headspace oxygen in a sealed container.

Another object of the present invention is to provide an apparatus for the determination of carbon dioxide and dissolved oxygen and headspace oxygen in a sealed container with high precision.

A further object of the present invention is to provide an apparatus for the determination of dissolved carbon dioxide and oxygen and headspace oxygen in a sealed container which can be carried out rapidly and by relatively unskilled technicians.

Still a further object of the present invention is to provide a method and apparatus for determining dissolved carbon dioxide and dissolved oxygen in process streams.

Yet a further object is to provide an apparatus for determining dissolved oxygen in an open container.

An important object is to provide a method of determining dissolved carbon dioxide, dissolved oxygen and headspace oxygen in sealed containers, and dissolved oxygen in a liquid in an open container with high precision.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the apparatus embodying features of construction, combination of elements and arrangement of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference is had to the following description taken in connection with the accompanying drawings, in which:

FIG. 1 shows diagrammatically the apparatus of the present invention;

FIG. 2 shows diagrammatically the position of a probe in a sealed container;

FIG. 3 is a front view of the means for piercing the top of a sealed container and the associated valve for withdrawing samples and directing them toward analytical apparatus;

FIG. 4 is a side view of the apparatus of FIG. 3; and

FIG. 5 is a graph showing oxygen-detector response as a function of known oxygen content in an inert gas stream.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A piercing device used for withdrawing samples from a sealed container is shown in front and side views in FIGS. 3 and 4. The device is a modified form of the Zahm model D-T piercing device manufactured by Zahm and Nagel Company, Incorporated, 74 Jewett Ave., Buffalo, N.Y. A container A shown as a capped bottle, but which also may be a sealed can, stands on a base B between upright rods 1. A movable cross bar C holds the container A firmly in position by means of rubber gasket 11. Entry through the cover 13 of container A is effected by means of piercing needle 14. Piercing needle 14 is hollow; probe 5 is positioned so that its lower end 15 is located proximate the tip of piercing needle 14. Probe 5 enters piercing needle 14 through septum 6 held in one-eighth inch Swage-Lok

nut available from Crawford Fitting Company, Salem, Ohio. Probe 5 slides through the septum 6 as held in nut 16 without entry of air or loss of gas. This sliding motion is needed so that tip 15 can be positioned either in the headspace in the container or in the liquid in the container.

Other components of the sampling device are pressure gauge 2 which is mounted directly above the piercing needle, and a micro 5-port distribution valve 3 which is attached to the piercing device. The distribution valve is a Hamilton chemically inert, 5 4-way distribution, model D4 TTTTTP, one-sixteenth inch OD tubing, Hamilton Company, Whittier, Calif. The sampling probe is stainless steel one-sixteenth inch O.D. tubing available from Analabs Inc., North Haven, Conn. The septum 6 is a gas chromatography silicone rubber septum cut to fit inside the one-eighth inch Swage-Lok nut, and is available from Applied Science Laboratory, P.O. Box 440, State College, Pa.

A gas-tight syringe 4 is connected to valve 3 at its central port 17. Syringe 4 is held firmly by clamp 18 to upright rod 19. Movement of the probe 5 in a vertical direction is effected by sliding clamp 18 on rod 19.

Central port 17 connects with an axial passage in the plug of valve 3. The plug of valve 3 also has therein a radial passage making connection with the axial passage. Rotation of the plug by means of handle 12 makes it possible to connect syringe 4 with any one of ports 21, 22, 23, or 24 (see FIG. 1). Port 24 is sealed with a cap, thus affording an off position to the valve. Port 21 has connected thereto a branched tube shown in FIGS. 3 and 4 as a T-tube 7. Inert gas, such as nitrogen, is passed through branched tube 7 and is used to transport samples withdrawn from container A to downstream separation and analytical apparatus. Port 22 (FIG. 1) is connected to a source 38 of gas containing a known quantity of oxygen which is used in calibrating and testing the apparatus.

The volume of the measuring device 4, i.e., gas-tight syringe, should be chosen according to the oxygen content of the sample. For low concentrations of oxygen a large volume is necessary; conversely, samples having a high concentration of oxygen require a much smaller volume measuring device. For example, a three milliliter syringe is very adequate for measuring beer samples. Air-saturated water samples high in oxygen concentration can best be measured with a syringe of less than 1.0 milliliter volume.

Upstream of the valve 3 is a pressurized tank 26 of inert gas fitted with an ON-OFF valve 27 which leads to a regulator 28, a flow meter 29, and an oxygen trap 44 which removes traces of oxygen from the carrier gas stream. It is constructed from a stainless steel tube one-fourth inch diameter and 12 inches long, filled with "Ridox" oxygen scavenger. "Ridox" is available from Fisher Scientific Co., Fairlawn, N.J. These components supply a constant stream of oxygen-free inert gas to arm 9 of branched tube 7. The gas flowing through the branched tube 7 exits through arm 8 which leads the gas into gas scrubber 31. Scrubbing unit 31 is preferably a cylindrical glass vessel and may have a volume of about 30 milliliters. A coarse porosity fritted glass disc 48 is positioned at the end of inlet tube 32 to disperse the inert carrier gas and its contents into very fine bubbles for removing dissolved gases from liquid samples. Gas scrubber 31 is fitted with a drain line 33 for drainage of liquid samples transferred from container A. The

passage of inert gas through the liquid in gas scrubber removes all dissolved gases; (in the case of beer these gases are expected to be mainly carbon dioxide, small quantities of oxygen and possibly traces of volatile organic compounds), and sweeps these gases over into carbon dioxide scrubber 34. Scrubber 34 contains about 8 milliliters of a 15 to 25 percent potassium hydroxide solution. The scrubber itself is made from a 20 milliliter test tube. Inert gas carrying any oxygen present leaves scrubber 34 through outlet tube 36. Traces of organic compounds which may be present in the gas stream are removed by activated carbon filter 45. The gas stream then enters a standard Hersch Cell 37 which determines the oxygen content of the gas electrochemically. The Hersch Cell is available from Paul Hersch, 910 Franklin Ter., Minneapolis, Minn. Any recorder having a 1 millivolt input such as the Beckman model 100500 C 10-Inch Potentiometric Recorder (not shown) can be used. This recorder is available from Beckman Instruments, Inc. Incorporated of Fullerton, Calif.

For calibration of the device a tank 38 of pressurized gas containing a known fraction of oxygen supplies calibrating gas through valve 39 and regulator 41 at a known pressure to port 22 of micro-valve 3.

Alternatively, a known volume of oxygen can be inserted into inert gas stream leaving arm 8 by means of a microsyringe put through a rubber septum 47 (preferably of silicone rubber) capping T-tube 46.

Analysis of the contents of a sealed container starts with attemperation of the container and its contents to a known constant temperature, preferably 25°C. This may be effected by holding the container in a water bath for a long enough period. The cover of the container is to be pierced with piercing device 14 as indicated schematically in FIG. 2. Here the rubber gasket 11 is shown schematically as a rubber sleeve 42. Similarly, silicone rubber septum 6 is shown schematically as a second rubber sleeve 43. As is evident from FIG. 2, pressure gauge 2 is directly connected with piercing needle 14.

As the next step in the analysis, probe 5 is flushed with carrier nitrogen gas just prior to piercing the surface of the container by connecting port 21 with syringe 4. Carrier gas is drawn into the syringe and expelled through probe 5 by connecting port 23 with syringe 4. The procedure is repeated three or four times to insure removal of entrapped oxygen in probe 5. Immediately following, the surface of the container is pierced and probe 5 is lowered into the liquid in container A. By connecting port 23 with syringe 4, a sample may be drawn up into syringe 4. The plunger of syringe 4 is pumped out and in until the reading on gauge 2 is constant after each expulsion of sample from syringe 4. The reading on gauge 2 is then noted as the total gas pressure over the carbonated liquid. The purpose of the pumping action is to obtain equilibrium between the liquid and gas phase and to make certain that a homogeneous sample is taken. Generally, from two to five strokes are necessary. After taking the reading of gauge 2, a sample of the equilibrated liquid is drawn through port 23 into syringe 4, stop-cock 3 having been rotated to connect central port 17 with port 23. Equilibration can also be achieved by shaking the container or the water bath, either mechanically or by ultrasonic vibrator (not shown).

Syringe 4 is then connected to port 21 by rotation of handle 12. The sample in syringe 4 is injected into the inert gas stream coming from tank 26 through valve 27, regulator 28, flow meter 29 and O₂ trap 44 into branched tube 7. The gas stream, containing injected liquid sample passes through tubing 32 into scrubber 31 containing water. The gas stream continues to flow after the transfer of the sample into scrubber 31 is complete and serves to sweep out all traces of CO₂, O₂, and volatile organic components. These gases then pass into absorber 34 which removes CO₂ from the gas stream and thence to carbon filter 45 which removes volatile organic components from the gas stream. For effective scrubbing and absorption, the tubes leading into scrubber 31 and absorber 34 preferably have coarse porosity fritted glass discs positioned at the end of each of the inlet tubes to disperse the inert carrier gas into small bubbles. Scrubber 31 is fitted with a stop-cock 33 for drainage of the liquid sample after the analysis is complete.

The gas stream, now containing only oxygen, passes through tube 36 into oxygen detector 37 in which the oxygen content is determined electrochemically.

After determining the oxygen content of the liquid phase, probe 5 is raised so that its tip 15 is in the headspace of the container. A sample is taken as described above, injected into the gas stream through port 21 after which the oxygen detector 37 determines the total quantity of oxygen in the sample taken.

Periodically, the performance of the equipment is checked by taking a sample of gas containing a known quantity of oxygen from pressurized tank 38 through valve 39, regulator 41 and port 22. Syringe 4 is utilized to accept a sample of gas of known volume and pressure and the sample is then transferred into the inert gas stream from pressurized tank 26 in the usual manner. A low reading would indicate either that oxygen is being lost in the transfer from port 22 to the inert gas stream or that the Hersch cell is not operating properly. Conversely, a high reading would indicate that air is entering the system as, for instance, in the piercing of the container, or again, that the Hersch cell is operating improperly.

A particular advantage of the system described herein is that the syringe may be matched to the expected oxygen content of the sample to be analyzed. In this way, maximum accuracy in the measurement of the volume of the sample can be achieved. For instance, for beer headspace, normally a 0.20 ml sample is sufficient. For beer itself, sample volumes of from 0.50 to 2.00 ml are necessary.

Oxygen in the inert gas stream is reduced electrochemically in the Hersch cell, and the resultant current is proportional to the oxygen content of the sample. This current is measured by a recording device such as a millivolt strip chart recorder. A 10 ohm resistance decade box with a selection switch is conveniently set across the terminals of the Hersch cell. The millivolt strip chart recorder preferably has a span ranging from 1 to 100 millivolts. The selector switch on the resistance decade box can be set for any value of resistance from 1 to 10 ohms depending on the current produced by the cell and the amount of response required on the strip chart recorder. Likewise, the recorder's millivolt span range can be selected in accordance with the oxygen content of the gas stream and the size of the signal desired. For example, in beer analysis, a 5 ohm resistor

setting on the resistor decade box and a millivolt span range setting of 1 millivolt on the strip chart recorder produces a very acceptable signal on the recorder chart paper. For air-saturated water or atmospheric air where the oxygen concentrations are quite high, a setting on the resistance decade box of 1 ohm and 1 millivolt on the strip chart recorder are appropriate. FIG. 5 shows the response of the detector as a function of O₂ content in the stream.

Following are Tables showing test results which clearly show the excellent reproducibility of analyses achieved by the disclosed apparatus and process.

TABLE I

Reproducibility of Dissolved Oxygen Values In Beer (One Sample)	
Replicate No.	Dissolved Oxygen (ppm)
1	0.22
2	0.22
3	0.23
4	0.23
5	0.23
6	0.23
7	0.24
8	0.24
9	0.24
Mean	0.23
Std. Dev.	0.013
Rel. Std. Dev.	5.65

Note: All analyses run on a single bottle of beer

TABLE II

Reproducibility of Gaseous Oxygen Values (From Commercial Cylinder Nitrogen)	
Replicate No.	Oxygen (ppm)
1	4.20
2	4.30
3	4.30
4	4.30
5	4.30
6	4.20
Mean	4.30
Std. Dev.	0.063
Rel. Std. Dev.	1.47

TABLE III

Analysis of Beer Samples for Carbon Dioxide and Oxygen				
Brand	Approx. Age (Days)	Carbon Dioxide (Volume)	Headspace Oxygen (ppm)	Dissolved Oxygen (ppm)
A	1	2.61	0.93	0.18
B*	1	2.56	2.41	0.21
C	30	2.47	1.56	0.14
D	30	2.56	0.63	0.15
E	6	2.68	5.00	0.23
F	30	2.40	1.38	0.22
G	15	2.40	1.32	0.23

*Unpasteurized

TABLE IV

Analysis of Aerated Wort Samples for Dissolved Oxygen	
Sample	Dissolved Oxygen (ppm)
1	8.30
2	8.70
3	7.80
4	7.95

TABLE IV-Continued

Analysis of Aerated Wort Samples for Dissolved Oxygen	
Sample	Dissolved Oxygen (ppm)
5	8.50
6	8.25

It should be noted that the apparatus and method can with suitable and obvious modification be used for the detection of dissolved oxygen in liquids in open containers. The probe is inserted into the liquid as previously described, and a sample is withdrawn by the syringe and then transferred to the inert gas stream. No equilibration of gas and liquid phases by filling and emptying the syringe is needed.

As aforementioned, to standardize the apparatus a T-tube connection 46 is covered with a silicone rubber septum 47 through which a known quantity of oxygen can be inserted from a microliter hypodermic syringe. FIG. 5 shows the results obtained. The circles in FIG. 5 were obtained using the method described as used on beer samples. The crosses represent measurements of dissolved O₂ in water specimens. (O₂ in water determined by Winkler method.)

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in carrying out the above method and in the construction set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. An apparatus for determining dissolved O₂ and CO₂ in a liquid in a container and O₂ in the headspace of said container, wherein said apparatus includes a source of inert gas for providing a stream of gas at a chosen rate, a pressure gauge for measuring total gas pressure in said container, hollow tubular piercing means for penetrating a container without loss or leakage of gas at the region of penetration, said piercing means having a sharp tip, the tip of said piercing means being selectively positionable in the headspace or in the liquid after piercing said container, said pressure gauge being operatively connected with said piercing means, means for removing CO₂ and volatile organic components from a gas stream, and means for measuring the oxygen content of said gas stream, wherein said improvement comprises: valve means having first, second and third ports and an off position, and connecting means for connecting said first port to any of said second and third ports and said off position, a syringe detachably connected to said first port, a hollow probe tube lying within said hollow piercing means and having two ends, one of the ends of said hollow probe tube being proximate the tip of said piercing means and the other of its ends being connected to said second port of said valve means; and a branched tube having three ports, the first of said tube ports being connected to said third valve port, the second of said

tube ports being connected to said source of inert gas and the third of said tube ports being connected to said means for removing CO₂ and volatile organic components from said gas stream and to said oxygen-content measuring means for introduction of a sample taken by said syringe and from said syringe into said gas stream and flow in sequence through said means for removing CO₂ and volatile organic components and oxygen-content measuring means, thereby making it possible to determine the oxygen content of said sample, the CO₂ content of said sample being determinable from the reading of said pressure gauge.

2. An apparatus as defined in claim 1, wherein said inert gas source is a container of nitrogen, and further comprising means for controlling gas flow from said nitrogen container at a constant, selected rate.

3. An apparatus as defined in claim 1, further comprising a scrubber for receiving a quantity of liquid drawn from said container by said syringe and injected into said gas stream, said scrubber having a disperser for breaking said gas stream into fine bubbles to facilitate removal of dissolved gases from said liquid.

4. An apparatus as defined in claim 1, further comprising a T-tube connected between said valve means and said oxygen-content measuring means for transmitting said inert gas stream therebetween, said T-tube having a port covered with a rubber septum for introduction of a known quantity of oxygen from a micro-syringe into said inert gas stream for the purpose of calibrating said oxygen-content measuring means.

5. An apparatus as defined in claim 1, further comprising a fourth port on said valve means, said fourth port being connectable to said first port, and a source of gas with a known oxygen content connected to said fourth port.

6. An apparatus as defined in claim 5, wherein said gas source is a container of nitrogen having a known oxygen content, said gas source being intended for use in calibrating said apparatus.

7. A method of determining O₂ and CO₂ in a liquid in a container and O₂ in the headspace of said container by means of apparatus including a hollow piercing needle, said needle having a tip the position of which is vertically adjustable, a hollow probe within said needle and essentially concentric therewith, said probe having one end proximate the tip of said piercing needle, a pressure gauge for reading total gas pressure connected to said piercing needle, valve means having first, second and third ports and an off position, a syringe connected to said first port, the other end of said hollow probe being connected to said second port, a branched tube having three tube ports one of which is connected to said third valve means port, a second of said tube ports being connected to an oxygen-free gas source and the third of said tube ports being connected to a train comprising sequentially a gas scrubber, a CO₂ absorber, an activated carbon filter and an oxygen-content measuring means, said method comprising the steps of attempting said container and the contents

thereof, drawing a volume of inert gas into said syringe, expelling said volume of inert gas through said probe to flush any oxygen out of same, piercing said container and positioning the tip of said probe in said liquid, drawing a sample of liquid into said syringe and returning said liquid to said container a sufficient number of times to ensure equilibration of liquid and gas phases, said removal and return of liquid being continued until a constant reading is observed on said gas pressure gauge when all liquid is returned and said valve means is placed in said off position, noting said constant reading, drawing a known volume of liquid into said syringe, expelling said known volume of liquid through said branched tube into a stream of inert gas for transfer into said gas scrubber which retains said liquid while said inert-gas stream carries CO₂ and O₂ into said CO₂ absorber and carbon filter and said O₂ thence into said oxygen-content measuring means for determining the quantity of O₂ in said known volume of liquid, raising said probe into said headspace in said container, drawing a representative known volume of headspace gas into said syringe, and expelling said known volume of headspace gas into said gas stream for passage through said gas scrubber, CO₂ absorber, and carbon filter and thence to said oxygen-content measuring means for determining the O₂ content of said known volume headspace gas, all transfers to and from said syringe to and from selected ports being carried out by manipulation of said valve means, the combination of the data thus obtained with the measured volume of said liquid and the measured volume of said container making it possible to determine the CO₂ and O₂ content of said liquid and the O₂ content of said headspace.

8. The method as defined in claim 7, wherein said valve means has a fourth port connectable to said first port and further comprising the step of passing a known volume of a gas having a known content of O₂ through said apparatus by means of said fourth valve-means port to test and calibrate said apparatus.

9. A method of determining the dissolved O₂ content in a liquid in an open container comprising the steps of inserting a hollow probe into said liquid, said probe being connected to a first side port of a multi-ported valve means having a central port, connecting the central port of said valve means to said first side port, drawing a sample of known volume into a syringe connected to said central port, connecting said central port to a second side port, said second side port being connected in turn to a T-tube through which a stream of inert gas is flowing in sequence through a gas scrubber, a CO₂ absorber and an activated carbon filter to an oxygen-content determining means, and injecting the contents of said syringe into said gas stream through said second side port and said T-tube, whereby the O₂ in said sample is carried to said oxygen-content determining means for determining the quantity of dissolved O₂.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,849,070 Dated November 19, 1974

Inventor(s) Alan C. Garza & Vincent S. Bavisotto

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover page, the Assignee should read

--Theodore Hamm Company, St. Paul, Minnesota--.

Signed and sealed this 29th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks