

Automated Measurement of Total Oxygen in Beer Packages¹

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ABSTRACT

An instrument has been developed to provide accurate, reliable analyses of total oxygen levels in filled beer packages. It is readily adaptable to all sizes of cans and bottles, and analysis cycle time is about 5 min. By utilizing the Hersch galvanic cell to analyze only the headspace gas and then determining the total oxygen by automatic calculation, many process problems have been avoided. The method is non-destructive of the sample, and the same beer can later be used for chemical and organoleptic analyses. Automatic sequencing and direct digital readout make the analyzer insensitive to operator skill level and provide a reliable means to relate $\mu\text{g}/\text{kg}$ oxygen levels in the packaging operation to levels obtained in the cellaring operation.

Key words: *Automatic sampling, Dissolved oxygen, Gas/liquid equilibrium, Headspace oxygen, Hersch cell.*

The measurement and control of dissolved oxygen during all phases of the brewing process continues to be a major problem for most brewers. Instruments and analytical methods are readily available for the determination of oxygen in beer during processing (1,6,8). However, the Zahm gasometric air shakeout device (9) still remains as the only commonly accepted method of analyzing "total air" in the container after packaging. Difficulties arise when comparisons are attempted between the ml air/package readings and the $\mu\text{g}/\text{kg}$ dissolved oxygen readings obtained at the final beer filtration. The Zahm gasometric values oftentimes do not have a normal 20% oxygen composition, and the method itself is not noted for its accuracy and reliability. Due to the necessity to measure and control oxygen at a very low level in the package, developmental research was conducted to construct an accurate and reliable package beer analyzer.

Various papers had been written about the use of the Hersch galvanic cell to accomplish this measurement (2,3,4). Additional research indicated that, for various reasons, none of this work has resulted in practical testing equipment for the routine measurement of package beer oxygen content. It was thought that, with a few innovations, a practical analyzer for the measurement of package beer oxygen content could be built, using as the oxygen measurement device the extremely sensitive and reliable Hersch galvanic cell. A brief description of this oxygen sensor follows:

The electrochemical cell consists of two couples:

An oxygen couple:



and a cadmium couple:



The overall redox reaction of the electrochemical cell is:



Two molecules of cadmium are oxidized (anode) releasing four electrons for the reduction of one molecule of oxygen (cathode) and the voltage produced is:

$$E_{\text{cell}} = 0.0402 \text{ volts} - (-0.401 \text{ volts}) \\ = 0.803 \text{ volts}$$

Applying Faraday's Law, one can calculate that the reduction of one microgram of oxygen will cause 1.206×10^{-2} amp-sec or coulombs of current to flow. If the cell is 95% efficient, then 1.146×10^{-2} amp-sec of current will flow. When all of the cadmium in the cell has been oxidized to $\text{Cd}(\text{OH})_2$, the cell is easily regenerated by applying a reverse current which causes the decomposition of the hydroxide to cadmium, oxygen, and water.

The design criteria established for the analyzer were as follows:

1. Measure only the headspace oxygen and determine the dissolved oxygen by calculation.
2. A digital readout in wt parts per billion ($\mu\text{g}/\text{kg}$).
3. Limit the sample size to the minimum practical level.
4. Replace the headspace gas removed during the analyzing cycle by applying ultrasonic agitation to the bottom of the container.
5. Completely automate the analyzing cycle except for placement and removal of the container.
6. Calibration with a known gas sample.

EXPERIMENTAL

System Design

The block diagram of the analyzer is shown in Fig. 1. Labeled photographs are included in Figs. 2 and 3. Hydrogen is used as the carrier gas and for purging the sampling chamber and the piercing device. Nitrogen is used for purging the valve stem areas of the miniature air-operated valves of the sample valve complex. The sample is injected into the carrier gas stream and transported through the potassium hydroxide scrubber where the carbon dioxide is removed and the carrier gas is humidified. The oxygen in the sample is carried into the Hersch cell where it is reduced, causing an electrical current to flow. This current passes through an adjustable resistor and the resulting voltage drop is amplified, converted to pulses per sec and then to a digital readout by a counter. The count is a representation of the total oxygen in the sample and through special calculations and calibration reads out the total package oxygen content.

Equilibrium Relations

The Hersch cell produces a current directly proportional to the amount of oxygen reduced in the cell, regardless of the amount of total pressure being exerted in the beer package. This reading is a direct measurement of the grams of oxygen per sample volume removed from the headspace of the container. Consequently, the weight of oxygen contained in the headspace can be determined from the cell reading and, with close filler control, the average headspace volume.

In-plant tests have indicated that physical equilibrium between the gas and liquid phases is obtained within 15 min after packaging and the immersion in an ultrasonic water bath.² By controlling this bath temperature and equilibrating the container at 25°C, one can derive theoretical equilibrium relations to calculate the amount of oxygen dissolved in the beer. The mole fraction of oxygen dissolved is a direct function of the partial pressure of oxygen in the headspace gas and of Henry's Law Constant for oxygen in beer at 25°C. This partial pressure of oxygen is a measurement of the amount of oxygen in the headspace and can be determined directly from the Hersch cell reading, independent of total container

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²G. L. Jandreau, unpublished data.

pressure. Further details of this derivation are covered in Tables I and II.

Calculation of the total $\mu\text{g}/\text{kg}$ in the package assumes that all of the headspace oxygen is to be dissolved in the beer. This phenomena occurs fairly slowly and is a function of temperature and beer composition. However, the reaction is practically complete and given sufficient time, all oxygen will be removed from the headspace due to dissolution and resultant beer oxidation (7). Since the total calculated oxygen level has been shown to be a linear function of the Hersch cell reading ($\text{g O}_2/\text{sample volume}$), no complicated computer calculations are required. The simple adjustment of the variable resistance across the Hersch cell is sufficient to handle this linear calculation. Calibration is routinely accomplished by introducing a known carbon dioxide/oxygen mixture into the sampling chamber and adjusting the resistor so that the electronic counter reads out the calculated parts per billion.

The Hersch cell is highly specific for molecular free oxygen. It is not affected by other oxidizing agents or oxygen transfer agents (such as melanoidins and polyphenols). Consequently, close agreement can be obtained between this method and other methods employing polarigraphic membrane probes whose readout is a function of free oxygen partial pressure.

Operation Sequence

The sample valve complex and piercing device is the heart of the analyzer and is schematically shown in Fig. 4 and pictorially in Fig. 5. The dead space of the four valves and the connecting cross has sufficient volume for a sample chamber. The purge and operator lines for the valve stems are not shown in the schematic diagram but are identified as the plastic tubing in the photograph. The stainless steel tubing is the carrier gas line. The operation of the valves during the analyzing cycle is as follows:

1. Valves 1 and 2 are opened to purge the sample chamber.
2. Valve 2 is closed, valve 3 is opened and the piercing device is purged while the container is being pierced.
3. Valve 3 is closed at the moment the container is pierced.
4. Valve 1 is closed and valve 2 is opened, dumping the hydrogen under pressure to atmosphere.
5. Valve 2 is closed and valve 3 is opened, filling the sample chamber with headspace gas.
6. Valve 3 is closed and valve 2 is opened, dumping the headspace gas to atmosphere.
7. Valve 2 is closed and valve 3 is opened, filling the sample chamber with headspace gas.

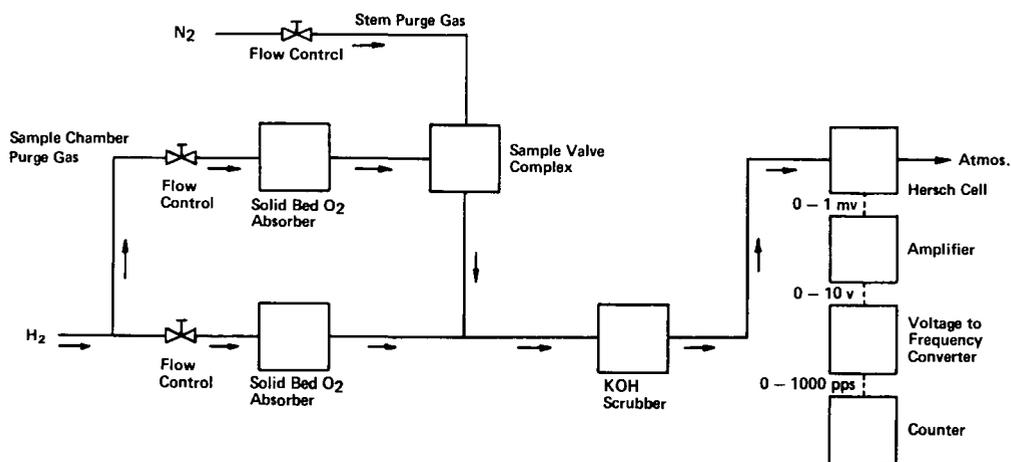


Fig. 1. Block diagram of oxygen analyzer.

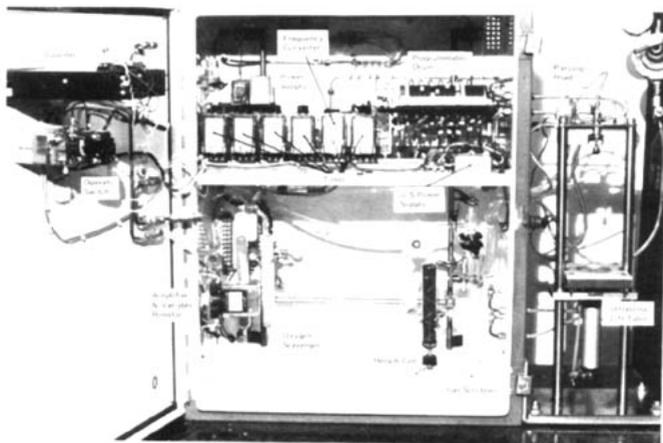


Fig. 2. Instrumental view of beer package oxygen analyzer.

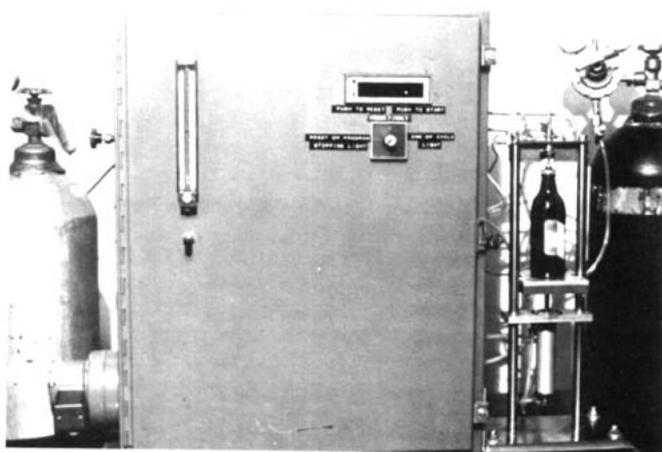


Fig. 3. Front view of beer package oxygen analyzer.

TABLE I
Headspace Gas/Dissolved Gas Equilibria—Classical Approach

A. Headspace Composition: H_2O , O_2 , N_2 , CO_2 , ethanol

Valid Assumption: mole fraction of $CO_2 = Y_{CO_2} = 1.00$

therefore, mole fraction of $O_2 = Y_{O_2} = \frac{\text{moles } O_2}{\text{moles } CO_2} = \frac{N_{O_2}}{N_{CO_2}}$

HCR = Hersch Cell Readout = $\frac{g \ O_2}{\text{volume of gas sample}}$

Using a 1 ml gas sample at T, P.

$$N_{CO_2} = \frac{P}{T} (8.30 \times 10^{-4}) \text{ and } N_{O_2} = \frac{HCR}{32}$$

then, $(Y_{O_2})_{T,P} = \frac{HCR(T)(37.6)}{P}$, or $(Y_{O_2})_{25^\circ C, P} = \frac{HCR(1.121 \times 10^{-4})}{P}$

B. Dissolved Oxygen in Beer in Equilibrium with Y_{O_2}

Mole fraction of O_2 dissolved = $X_{O_2} = \frac{P_{O_2}}{H_{O_2}}$

where, P_{O_2} = partial pressure of $O_2 = Y_{O_2} P$
in headspace gas

H_{O_2} = Henry's Law Constant for O_2 at T
 $H_{O_2} = 6.84 \times 10^5$ PSIA at $25^\circ C$

$$\text{then, } (X_{O_2})_{25^\circ C, P} = \frac{Y_{O_2} P}{H_{O_2}} = \frac{(HCR)(T)(37.6)P}{H_{O_2} P}$$

$$= (HCR)(1.64 \times 10^{-2})$$

$$\begin{aligned} \frac{\text{Amt. of } O_2 \text{ dissolved}}{12 \text{ oz beer}} &= (X_{O_2}) (N_T) (32 \text{ g/mole})(\text{wt. of beer, g}) \\ &= (HCR)(1.64 \times 10^{-2})(5.44 \times 10^{-2})(32)(3.577 \times 10^2 \text{ g}) \\ &= (HCR)(10.2) \end{aligned}$$

C. Total Oxygen in the Package

$$\begin{aligned} \text{Total g } O_2 &= \text{g } O_2 \text{ in headspace} + \text{g } O_2 \text{ dissolved} \\ &= (HCR)(\text{headspace volume}) + (HCR)(10.2) \\ &= HCR(19.8) + HCR(10.2) \\ &= HCR(30.0) \end{aligned}$$

then,

$$\begin{aligned} \text{ug/kg} &= \frac{\text{total g } O_2}{\text{wt. beer, g}} (\text{ug/kg} \times 10^9) \\ &= \frac{HCR(30.0)}{357.7} \times 10^9 = HCR(8.40 \times 10^7) \end{aligned}$$

where,

$$HCR = \frac{g \ O_2}{1 \text{ cc headspace}} \text{ at } 25^\circ C \text{ and any container pressure.}$$

The actual sample size going to the Hersch cell is not critical, just as long as it remains constant.

Definition of Terms: Y_A = mole fraction of compound A in the gas phase, N_A = moles of compound A, X_A = mole fraction of compound A in the liquid phase, P_A = partial pressure of compound A, P = total system pressure, PSIA, T = temperature, $^\circ C$, H_A = Henry's Law Constant for compound A at specified temperature, T, and HCR = Hersch Cell Readout = $\frac{g \ O_2}{\text{volume of gas sample}}$.

8. Valve 3 is closed and valve 4 is opened to inject the headspace sample into the carrier gas stream.
9. Valve 4 is closed and valve 1 is opened, pressurizing the sample chamber with hydrogen.
10. Valve 1 is closed and valve 4 is opened to flush out the last of the headspace sample into the carrier gas stream.
11. Valve 4 is closed and the pierced container is removed, ending the analyzing cycle.

The miniature air-operated valves are operated by air switches on a programmable drum controller. To limit the dead space, each of the valves was threaded onto a single cross and the entire valve assembly threaded directly onto the carrier gas line. The miniaturized piercing device was threaded directly onto the sample valve.

Prior to analysis, the beer package is brought to physical equilibrium by a 15 min treatment at 25°C in an ultrasonic water bath. This container is then placed on the instrument platform, and the piercing is accomplished by an air-operated cylinder moving the platform and container to the piercing device. After the analyzing cycle is complete, the cylinder returns the platform and container to the rest position. An ultrasonic transducer was designed as a part of the platform to agitate the beer and ensure replacement of the headspace gas removed during sampling.

RESULTS AND DISCUSSION

Initial tests were conducted to determine the precision of oxygen values obtained. Employing the small gas sample container used for instrument calibration, repetitive analyses were conducted on the calibration gas. In seven consecutive tests, the standard deviation was less than ±1 µg/kg around a mean of 200 µg/kg. Replicate analyses were also conducted on various beer bottles as recorded in Table III. Even with time intervals between the same sample of over several hours (pierced container left in the analyzer), only 3–4% deviations were shown in the final oxygen levels. These data also confirm the establishment of complete physical gas/liquid

TABLE III
Replicate Analyses by Package Analyzer

Container Number		Total Oxygen µg/kg
1	5 min between tests	183 175
2	17 hr between tests	214 206
3	1 hr, 15 min between tests	209 204
4	5 min between tests	239 235
5	10 min between tests	131 129
6	5 min between tests	471 445
7	10 min between tests	130 125
8	2 hr between tests	219 221
Average % drop between replicate analysis		-3.1%

TABLE II
Headspace Gas/Dissolved Gas Equilibria—Practical Approach

Saturation curves relating µg/g dissolved oxygen in beer to temperature are available in the literature (1, 8). At equilibrium, 8 µg/g (8000 µg/kg) of oxygen is dissolved in the beer under standard atmospheric pressure (1 atm) and 25°C.

The amount of oxygen dissolved is directly related to the partial pressure or the concentration of the oxygen in the gas.

Calculate weight of oxygen in 1 ml of air under test conditions:

$$g O_2 = 1 \text{ ml air} \left(.2094 \frac{O_2}{\text{air}} \right) \left(\frac{32 \text{ g}}{\text{g mole}} \right) \left(\frac{\text{g mole}}{22.4 \times 10^3 \text{ ml}} \right) \left(\frac{273^\circ \text{ K}}{298^\circ \text{ K}} \right)$$

$$= 2.739 \times 10^{-4}$$

Since partial pressure of O₂ is zero when O₂ concentration is zero, a linear equation can be written in the form: y = mx + b.

$$8000 \text{ µg/kg} = 2.739 \times 10^{-4} m + 0$$

$$m = 2.921 \times 10^7$$

Therefore,
Dissolved O₂ in µg/kg = 2.921 × 10⁷ ($\frac{\text{g } O_2}{\text{ml headspace gas}}$)

Total µg/kg = Headspace µg/kg + Dissolved µg/kg

where,

$$\text{Headspace µg/kg} = \frac{\left(\frac{\text{g } O_2}{\text{ml}} \right) (\text{ml Headspace}) \times 10^9}{\text{g beer in the container}}$$

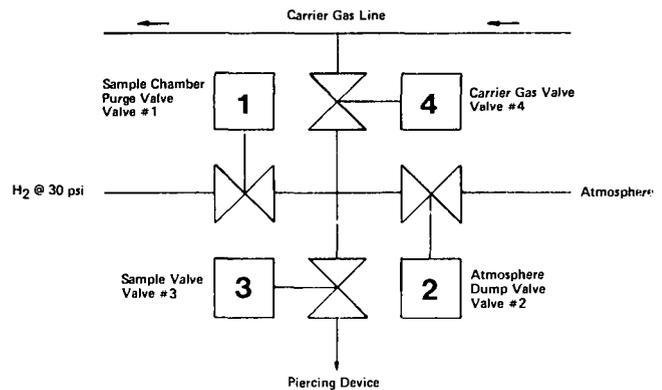


Fig. 4. Schematic sample valve complex and piercing device.

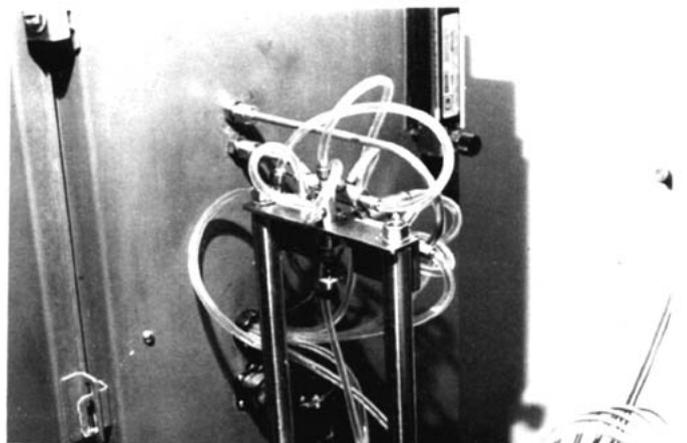


Fig. 5. Sample valve and piercing head assembly, showing all gas purge and sampling lines.

TABLE IV
Analysis of Comparison Testing: Gasometric Shakeout,^a New Package Analyzer, Gas Chromatograph

Sample Time	(1) Gasometric Shakeout		(2) New Package Analyzer		(3) Gas Chromatograph		Overall Line Av at Sample Time	Statistical Analyses Std. "T" Test Values		
	Av ^b	Std. Dev. ^c	Av	Std. Dev.	Av	Std. Dev.		(1) vs. (2)	(2) vs. (3)	(1) vs. (3)
1	229	25	284	36	113	46	288	5.93 ^d	11.93 ^d	8.44 ^d
2	343	33	360	63	201	63	415	1.15	8.14 ^d	9.36 ^d
3	333	28	330	54	295	123	315	0.24	1.25	1.44
4	326	39	276	63	584	136	345	3.24 ^d	9.86 ^d	8.75 ^d
5	337	21	352	51	407	80	328	1.30	2.74 ^d	4.06 ^d
Average	328	30	320	54	335	98	338	1.41	1.45	0.74

^aResults shown are the average equivalent oxygen levels in PPB ($\mu\text{g}/\text{kg}$) of 20–24 bottles taken from one filler station at one sample time and analyzed by the indicated method. The overall line average is the oxygen level indicated by routine quality control checks (gasometric shakeout) during the sample time.

^bAv = average.

^cStd. Dev. = Standard deviation.

^dDenotes significant difference at the 95% confidence level.

equilibria within the containers and the relative slow depletion of oxygen by beer oxidation.

The efficiency of the Hersch cell was checked by internally generating a known quantity of oxygen by electrolysis and measuring the current produced by the cell. Any slight calibration drift was easily compensated for by use of the calibration gas (primary gas standard) and the adjustment of the variable resistance across the cell. The real test of the new apparatus was a comparison against two other accepted methods for measurement of oxygen levels in the package: modified gasometric shakeout apparatus and a gas chromatographic method.

The modified gasometric shakeout method involves the removal of two separate, discrete volumes of gas from the package and the determination of the milliliters of air for each. Total milliliters of air is then calculated from a linear extrapolation out to the total gas shakeout volume known to exist from the package carbonation value. This value is then converted to total $\mu\text{g}/\text{kg}$ oxygen contained in the package, assuming that all oxygen contained in the headspace were to be dissolved in the beer. The assumption of approximately 20% oxygen in the "air bubble" for all freshly packaged samples has been validated by gas chromatographic analysis.³

The techniques employed for headspace gas analysis using gas chromatography were similar to those detailed by Jamieson *et al.* (5), except that no gas sample cooling was required since we were interested in only oxygen and nitrogen levels. The sampling method involved a manual piercing of the container with a Zahm piercing device and the removal of a headspace gas sample by a hypodermic syringe. The syringe sample was injected into a Baseline Model 1010B gas chromatograph with thermal conductivity detectors and a molecular sieve 5 \times column. The $\mu\text{g}/\text{kg}$ values for total package oxygen level were individually calculated from the molar percent of oxygen in the headspace gas by assuming Henry's Law of equilibrium relation and an average container pressure of 50 PSIA at 25°C.

Results from the comparison of the three methods are shown in Table IV. This analysis was not to determine the correctness of container oxygen levels but rather to compare the different measurement methods. Daily $\mu\text{g}/\text{kg}$ oxygen averages from the Hersch cell automatic analyzer (2) and the manual gasometric

method (1) compared favorably. The standard deviation is greater for the Hersch cell analyzer but this may be explained by the inherent greater equipment sensitivity. It has always been assumed that consecutive packages filled off the same filler station would have similar oxygen levels. This assumption may be invalid, since different averages and standard deviations resulted. The new package analyzer is capable of measuring minute sample differences, and the statistical analysis is based upon the assumption that all samples were taken from a single lot.

After the precision of the new package analyzer had been confirmed by the previous tests, experiments were conducted to determine the long term reliability of the Hersch cell-based automatic package analyzer. For a 2-mo test period, close comparison was maintained with the standard gasometric shakeout on all bottle samples from one packaging line.

Plans are being made to construct seven more analyzers to cover the analytical demands of all 12 can lines and five bottle lines. Estimated cost of each analyzer is \$3,500. One technician per shift will be able to operate all seven analyzers. Savings in quality control personnel and the attainment of more accurate and reliable oxygen analyses are sufficient cost justification for this expenditure.

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³C. W. Hahn, unpublished data.

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