

# THE CONTROL OF OXYGEN IN BEER PROCESSING\*

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The content of reducing substances in wort and beer at different stages of production can be estimated by measuring Redox Titration Values; dissolved oxygen is satisfactorily determined by means of the Hays Oxygen Meter. Taken in conjunction, these two figures can be used to indicate stages where oxidation is likely to occur and where particular care must be taken during processing in the brewery. Procedures are suggested for minimizing oxygen pick-up and the use of anti-oxidants is briefly discussed. The efficiency of yeast as an anti-oxidant during secondary fermentation is emphasized.

Key words: *anti-oxidant, beer, oxygen, wort, yeast.*

mainly this aspect of the problem with which the present paper is concerned.

## INTRODUCTION

OXIDATION is without doubt the most widespread of the common faults in beer and it may be estimated that from about a third to a half of all beer consumed in the world today is more or less oxidized. Since the bread-like taste of oxidized beer is both unpleasant and easily recognized, there can be no doubt the brewers owe it to their customers to improve their beers greatly in this respect. It is a fact, of course, that since Thomson reviewed the problem twenty years ago,<sup>14</sup> considerable improvements have taken place, especially as regards less enclosure of air during packaging; whereas in the 1950s air contents of 15 ml per litre were common in packaged beer, average figures of about 5 ml/litre are now usual.

However, a low content of air in the sealed package, desirable as it is for the quality of beer, is by no means the whole story since quality can be adversely affected by oxidation at earlier stages of processing and it is

## REDUCING SUBSTANCES IN BREWING

Normal wort contains substantial amounts of reducing substances, some of which are of great value in protecting beer against later oxidation and should be preserved as far as possible throughout the brewing process. A determination which is useful for checking the content of reducing substances, and thus the state of oxidation of wort or beer at any stage of the process is the Redox Titration Value (RTV) of Klopffer<sup>11</sup> which represents the content (in microvals/litre) of reducing components which react with 2·6 dichlorophenol-indophenol in 20 seconds at 20°C and pH 3-5. The most important stages at which the RTV is increased or decreased are:

1. Towards the end of malt kilning the content of reductones increases; with relatively high cured pilsner malt mainly enediols, or sugar reductones, are formed; with darker malts mainly melanoidins are produced.

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2. In wort at temperatures greater than 80° C, carbohydrate and proteins or amino acids react to form enediols and melanoidins and thus increase the reducing substances.
3. During wort boiling the reactions of (2) continue to produce rapidly reducing compounds, but there is simultaneously a loss through oxidation and coagulation; the direct contribution of reducing substances by hops, however, is quite marked. The net result is an increase of RTV.
4. During wort cooling, aeration and at the start of fermentation there is a temporary decrease of RTV.
5. During the first 12 hours of bottom fermentation, the RTV rises again to a level which is maintained during the rest of the fermentation.
6. Oxygen which is picked up by the beer during transfers, in storage, during filtering and bottling will react to give a fall in RTV.
7. Addition of antioxidants, e.g. ascorbic acids and bisulphites, will increase RTV.

Table I shows some typical values for RTV in samples drawn at different stages of the brewing process.

In the first two columns are shown the amounts of instantaneously reacting and

rapid reacting reducing components, analysed according to Klopper<sup>11</sup> and to de Clerck & van Cauwenberge<sup>3</sup> respectively. In the third column are shown dissolved oxygen contents measured by a Hays D.O. analyser, for comparison. In the final column a balance is drawn, and as a working hypothesis we take it that there is a certain correlation between this figure and the susceptibility of the beer to oxidation. In other words, low figures in this column indicate a stage in the process where oxidation is likely to occur and where care must be taken.

Table II shows how the reserve of reducing components may be augmented or decreased by certain operations. As will be seen, air pick-up at bottling weighs very heavily, although it may be a little pessimistic to fear a pick-up of 1.4 ppm O<sub>2</sub> from 5 ml of air.

For control within a brewery, where it is desirable to follow the ups and downs of the "pool" of fast reducing substances and to balance these with dissolved oxygen contents, the RTV-method does in fact work very well and is quite widely used.

Several other laboratory methods are available to determine the content of reducing substances in beer. These include:

- (a) The Indicator Time Test (ITT) of Gray & Stone.<sup>7</sup>
- (b) The similar method of de Clerck & van Cauwenberge<sup>4</sup> which, like the

TABLE I  
TYPICAL FIGURES FOR REDOX TITRATION VALUE AND DISSOLVED OXYGEN IN A TRIAL BREW  
(Results in Microval per litre)

Operation	Reducing components		Dissolved oxygen	Balance of Redox Titration Value
	Instantaneously reacting (<20 sec)	Rapidly reacting (20 sec-5 min)		
Mashing-in .. ..	60	90	700	-550
Mashing-off				
Light malt ..	10	70	125	- 45
Dark malt ..	80	120	125	+ 75
Wort boiled for 1 h..	80	120	0	+200
Aerated cold wort ..	40	110	900	-750
Fermenting wort 12 h	30	80	50	+ 60
Green beer .. ..	30	90	40	+ 80

TABLE II  
EFFECT OF VARIOUS OPERATIONS ON REDOX TITRATION VALUE AND DISSOLVED OXYGEN CONTENT  
(Results in Microval per litre)

Operation	Reducing components		Dissolved oxygen	Balance of Redox Titration Value
	Instantaneously reacting (<20 sec)	Rapidly reacting (20 sec-5 min)		
Transfer and pick-up of 0.1 ppm D.O. . .			+ 13	- 13
Dilution with 1% cold water containing 10 ppm D.O. . . . .			+ 13	- 13
Addition of ascorbic acid, 10 ppm . .	+35	+35		+ 70
Addition of KMS, 10 ppm = 5.3 ppm SO <sub>2</sub>	+80	+80		+160
Bottling with pick-up of 5 ml air/litre = 1.4 ppm O <sub>2</sub> . .			+180	-180

Klopper method, measures the rapid reducers while the ITT records the content of more slowly oxidizable compounds.

- (c) The method of Case & Thompson<sup>2</sup> which, especially in its logarithmic form, offers certain practical advantages.

#### MEASUREMENT OF OXYGEN IN BEER

The determination of air or oxygen in beer has been carried out for many years by a variety of methods. The most widely used of these for routine control are the method of Mendlik<sup>12</sup> and the "shake-out" methods using Zahm-Nagel and similar types of equipment which are based on absorption of CO<sub>2</sub> by caustic solution and measurement of the insoluble gases as "air." These have the disadvantages that it is not possible to assay worts or beers with low CO<sub>2</sub> contents and that beers with apparently low "air contents" may be already severely oxidized.

Measurement of dissolved oxygen in beer by the indigo carmine method of Rothchild & Stone<sup>13</sup> and by modifications of this method, particularly those of van Cauwenberge & de Clerck<sup>16</sup> and of Jenkinson & Compton<sup>9</sup>, are more reliable than absorption methods but to exclude access of air requires

great care, and such methods are so time-consuming that they have been used more for trouble-shooting and special investigations than for routine control in the plant.

A polarographic method was introduced by Ekström & Sandegren<sup>5</sup> but it was with the development of the oxygen electrode and the solution to the problem of electrode poisoning, as well as the adaptation to measure dissolved oxygen in beer, that the possibilities of controlling the level of oxidation in post-fermentation beer began to look like realities and it became possible to look forward to being able to control flavour deterioration from oxidation to an extent never before considered possible.

Although Ward & Dageford in 1966 describe the use in the brewery of a portable oxygen analyser,<sup>17</sup> it was in the following year that the breakthrough came with publication by Galloway *et al.*<sup>6</sup> of their experience with the Hays D.O. (Dissolved Oxygen) Analyser at the Pearl Brewery in San Antonio, and by Brenner<sup>1</sup> of the results of his work with the Delta-Schwarz D.O. Analyser which uses a dropping mercury electrode.

In 1968 Hunt<sup>8</sup> described some modifications to increase the flexibility and accuracy of the Hays instrument, and last year Klimovitz<sup>10</sup> gave a very interesting practical account of how this meter, coupled to a strip

recorder, may be used to monitor dissolved oxygen contents continuously during processing and how the results thus obtained can be used to lower D.O. contents in beer significantly.

While other D.O. analysers are used in breweries, especially the German W.T.W. Digitalmeter (DIGI 610), described by Ullmann<sup>15</sup> and the Radiometer Digital Analyser (Type PHM 72), our main experience has been with the Hays instrument and most of the following remarks are based upon practical results using this in the plant.

The measuring cell of the Hays D.O. Analyser consists of two electrodes—the anode a combination of iron and zinc, and the cathode of silver—which are immersed in beer flowing through the cell to form a galvanic cell. When dissolved oxygen is present an oxidation-reduction reaction takes place, and an electric current is produced in the external load circuit; this current is proportional to the amount of dissolved oxygen present in the beer, and is measured in a span-adjusting potentiometer and meter scale calibrated in parts per billion (the American billion). The range of the scale is from zero to 1000 ppb (0–1.0 ppm). The unit, which is constructed in stainless steel, also includes a rotameter to adjust flow of sample and Tygon tubing with a standard clamp for connecting up to tank sample cocks, etc. It is sturdy, easily portable and can be operated by ordinary cellar workers.

However, the standardization and calibration of the meter can be a little tricky and this is best left to the laboratory staff. Some breweries prefer to standardize the Hays meter by measuring tanks of beer previously analysed by the Indigo Carmine (I.C.) method and setting the span adjustment to agree with I.C. readings. To avoid errors, it is desirable to sample several tanks and these should have neither too low D.O. contents (<0.20 ppm) nor too high figures (>0.50 ppm); to ensure uniformity the beer should have been in the tanks for 12–24 hours.

Since this is all rather cumbersome, most breweries we know prefer to calibrate by means of a special small tank containing tap water which is purged and carbonated to a suitable dissolved oxygen content, which is then measured by a modification of the Winkler method. The D.O. analyser is calibrated against this water, and it is a good

idea also to use this water for flushing the measuring cell at the end of the day, and even to allow it to stand full of water overnight. The frequency with which calibration is required is surprisingly variable between different breweries; it is usually about once or twice a week but cases are known of a meter holding its calibration without readjustment for six weeks of regular and frequent use.

From time to time the measuring cell and electrodes require to be cleaned to remove beerstone-like deposits and here again the actual frequency varies between different plants, being usually between four and twelve weeks. Cleaning is usually done by circulation of a very mild detergent and occasionally requires dis-assembling the cell, but newly cleaned measuring cells have a tendency to be unstable for a day or two afterwards. Breweries which own more than one D.O. Analyser generally prefer to clean them alternately, so that one is always available as stand-by and for calibration check.

To take a reading is simple and rapid. The calibrated D.O. Analyser, at cellar temperature, is connected to the sample cock of the tank or line by means of the clamp and tubing. The sample cock is opened, and then the inlet and outlet cocks of the analyser (this sequence is to avoid trapping air in the circuit) and the flow of beer is throttled back by adjustment of the needle valve on the rotameter until a flow rate of 12 gallons per hour is obtained. After a few seconds to stabilize the measuring cell, the value is read directly on the scale.

#### AIR PICK-UP DURING PROCESSING

Now that there is available a simple and precise method of measuring D.O. content in beer, intermittently or continuously, it may be of interest briefly to summarize some experiences with Hays D.O. Analysers and to suggest perhaps how this type of instrument can best be used in daily control.

The most important sources of air pick-up in processing are:

1. transfers between tanks;
2. carbonation;
3. filtration;
4. addition of stabilizers;
5. addition of recovered beer; and
6. at bottling and keggings.

These are discussed separately below.

1. *Tank transfers.*—The greatest pick-up of air in the process occurs at tanking and the general pattern is something like this:

There is a high initial pick-up which is due to turbulent entry to the tank; this gets smaller as transfer proceeds and tends to rise again towards the end of transfer. The final rise in D.O. content may be partly due to the presence of surface beer which has been in contact with air or to vortexing at the end of the transfer.

Actual figures (in ppb of dissolved oxygen) for a transfer from fermentor to storage tank were as follows:

Samples taken at the pump inlet at the start of the transfer showed 50 ppb D.O., falling to 20–30 as transfer proceeded and rising to 70 at the end, 3 hours later. At the tank inlet an initial 80 ppb rose and remained at 100 until the end when it fell to 80 ppb. The beer in the receiving tank showed an initial reading of 240 ppb which fell to 180 ppb at the end of the transfer.

The high initial D.O. in the receiving tank fell as the first beer was diluted by later low D.O. runnings. Within 24 hours, after assimilation of oxygen by the yeast, and probably some oxidation of beer reductones, the D.O. of the tank beer fell to 30 ppb, thereafter very slowly to about 10–20 ppb.

When yeast is present, the consequences of oxygen pick-up are not serious since the yeast will quickly absorb most of the added oxygen, and the content of reductones will be largely unchanged. When, however, the yeast has sedimented and clear beer is transferred to another tank, the oxygen picked up at the transfer (50–100 ppb) can only be taken up by the beer's reserve of natural reducing substances.

Pick-up of oxygen at transfer can be minimized when certain precautions are taken.

- (a) All joints and couplings in the transfer line must be tight, and the line itself must be so designed that excessive beer flow velocities and turbulence are avoided.
- (b) Whenever possible, CO<sub>2</sub> should be used in place of air for top and back pressure.
- (c) A light carbonation (0.1–0.2 vol) may be given during the transfer and excess CO<sub>2</sub> blown off from the tank, carrying any air with it before it has time to

react. Too much carbonation should, however, be avoided, since it may lead to loss of desirable volatiles.

- (b) Beer should enter the receiving tank with a low velocity (<3 feet/sec) so that turbulence is prevented.

We recommend increasing the diameter of the tank inlet and bringing the inlet pipe in as a cone with a top angle of 6–10°. An increase of 50% in diameter gives an increase in cross-section of 125% which will reduce the inlet velocity to 45% and the hydraulic pressure, and thus the amount of splashing, to only 20% of the previous figures.

It can also be helpful to pump at lower velocities at the beginning and end of each transfer. The shape of the tank is not without influence on air pick-up and under normal working conditions horizontal tanks, particularly bright beer tanks, will generally give beers with D.O. contents 50% higher than vertical tanks. With horizontal tanks, the surface area to volume ratio is less favourable. Vertical tanks, too, can be filled completely whereas horizontal tanks, which usually fall and drain to the front, have an air pocket remaining at the rear end after filling.

- (e) Transfer lines should be filled with water before commencing any transfer and this water may be pressed out by CO<sub>2</sub> before beer enters the line. If there is to be any admixture of beer and water, the latter should preferably be carbonated or otherwise de-aerated since mains water contains about 8–10 ppm dissolved oxygen, or about one hundred times as much as can be accepted in beer.

2. *Carbonation.*—Increase in oxygen pick-up can frequently be traced to carbonation, and increases of 100 ppb D.O. are not unusual from this source. When it is realized that carbonation of beer by one volume of CO<sub>2</sub> containing 0.05% air can theoretically contribute (if all oxygen becomes dissolved in the beer) 0.2 mg/litre, or 200 ppb, the importance of carbonating with pure CO<sub>2</sub> becomes obvious.

3. *Filtration.*—Almost always dissolved

oxygen content increases greatly in the first beer passing a newly started filter; a typical increase would be from 10–20 ppb D.O. in the beer tank to about 120–150 ppb D.O. in the beer leaving the filter during the first 10–15 minutes of a cycle. This increase in D.O. gets less as filtration proceeds and the overall increase due to filtration can usually be kept down to 20–30 ppb with careful working.

The risk of oxygen pick-up at early stages of filtration can be diminished by pre-coating kieselguhr filters with beer rather than with tap water, or by using de-aerated water, or the water used to sterilize the filter. In some breweries which have experienced problems with oxidation, kieselguhr slurries for both precoat and bodyfeed are carbonated prior to addition, to wash out some of the air trapped in the spaces in the diatom cell structures.

4. *Additives and residual beer.*—A ready source of dissolved oxygen is the addition of stabilizing or foaming additives and we know of instances where a pick-up of 200 ppb D.O. could be traced to the addition of a foam stabilizer to a pre-filtered beer. Here, again, when additives are prepared in water suspension the use of de-aerated water can be recommended.

Residual beer commonly contains large quantities of dissolved oxygen, some derived from first and last filter runnings and some picked up by exposure of tank bottoms etc. to air in beer tanks or in sedimentation tank. D.O. figures of several thousand ppb have been recorded in untreated residual beer. Thus, the recovery plant should include provision for extensive washing of the beer by CO<sub>2</sub> prior to pasteurization and dosage.

5. *Kegging and bottling.*—It has been possible to use the Hays D.O. analyser to monitor keg filling in selected kegs, by means of a sample cock mounted directly on a keg-valve fitting, and surprisingly high figures were found for pick-up of oxygen. Increases of from 150 to more than 700 ppb D.O. were recorded, with an average of more than 500 ppb. It is difficult to see how such large increases in D.O. at kegging can be avoided, except when provision for pre-evacuation is made.

The Hays Analyser cannot, at least at present, be adapted to measure D.O. in

bottled or canned beer, for which the Indigo Carmine method and shake-out methods for air determination are still used. However, within each brewery it is possible by running a series of duplicate determinations on beer in bottling tanks or at the filler base, to establish a correlation between D.O. content by Analyser and air content by shake-out. The exact relationship will depend upon the percentage of oxygen in the shake-out "air," and a typical conversion for a brewery with 16–17% oxygen in shake-out "air" will be:

ppb D.O.  $\times$  0.0044 = "air value" as ml/litre

Thus it is convenient to use the D.O. Analyser for control of oxidation throughout the brewing process up to the bottling tank, and thereafter to continue to use gasometric methods as routine, and perhaps Indigo Carmine determinations of D.O. for trouble shooting.

Aeration of beer during filling and in the filled container occurs in two different ways—absorption which takes place as the beer is filled and absorption from air left in the head space, and the amount of oxygen pick-up from each of these sources is about equal. Although it is very variable, the total pick-up of oxygen in a well-run plant is usually found to be about 1 ml O<sub>2</sub>/litre, corresponding to about 6 ml "air"/litre, or about 1,300 ppb D.O. This amount of oxygen is enough to react with 125 microvals of reducing substances per litre of beer, or more than the normal content of reducers in a beer to which antioxidants have not been added.

To achieve low figures for head space air is not too difficult nowadays. It is our experience that the most effective and uniform foaming up of bottles on high speed filling lines is obtained by a high pressure water jet which, at a pressure of about 400 psi, shoots about a fifth of a millilitre of water down through the surface of the beer in the neck of the bottle.

The maintenance and running of the filler has, of course, a profound influence on air pick-up during bottling, and this is really a subject for a separate paper.

It is as important here as anywhere else that beer lines should be adequately dimensioned to avoid excessive velocities and turbulence; they should be as short as possible and preferably insulated against rise of temperature. Fillers should not be run at higher speeds than they have been designed for,

since this will give great turbulence leading to higher air pick-up, even when CO<sub>2</sub> or another inert gas is used for counter-pressure in the filler. The longer the filling tube, the less, generally, is the pick-up of air, when other conditions are equal, and tubeless fillers nearly always give higher air contents when the bottles are not pre-evacuated.

Regular inspection and cleaning of filling valves is essential, especially when these incorporate mesh screens which can retain sharp particles of beerstone, copper oxide etc. or glass chips; anything that can obstruct the smooth flow of beer in the filler or damage the valve surface may lead to turbulence which will entrap headspace air that cannot be removed by overfoaming after filling.

The filling operation should be carried out as uniformly as possible in respect of filling rate, filling levels and counter-pressure conditions since variations in any of these caused by stop-and-start operations usually lead to high air contents. Thus, there must be adequate accumulation of bottles both before and after the filler, and the bottle lifts and the conveyor between filler and crowner must operate smoothly to avoid jerks and knocks. In no part of the brewery does close attention to design engineering, maintenance and correct running pay greater dividends than in the bottling hall. It is, of course, absolutely essential that the bottles are very uniform in size and shape.

#### ANTIOXIDANTS

Finally, a brief word on antioxidants. These became very popular 20–25 years ago when the ascorbates, particularly, were hailed as a universal remedy. It became too easy to throw in to the filtered beer a little ascorbic acid and expect it to compensate for processing faults and to take the place of careful process control. Unfortunately, this dream did not come true; indeed it was found that if insufficient ascorbic acid were added to the beer, the dehydroascorbic molecule could actually act as an oxygen carrier and catalyse oxidation of beer, making things worse instead of better.

Sulphites and dithionites have the disadvantage that they have a tendency to impart a sulphury aroma and taste to some light beers even at levels at which they are not very effective as antioxidants. However,

SO<sub>2</sub> does seem to have a slight improving effect on flavour stability, probably by blocking some carbonyl groups and preventing them from taking part in browning reactions.

Probably the most unobjectionable procedure for removing oxygen from beer is an enzymic method using glucose oxidase in the presence of catalase; the former oxidizes glucose in the presence of oxygen to gluconic acid and hydrogen peroxide, which is decomposed by catalase to water and oxygen, used to oxidise more glucose.

However, all these antioxidants have side-effects and it is likely that in the near future we shall have to reconsider their addition to beer.

It is appropriate therefore to finish by recommending the best of all antioxidants—a brewer's aid which will never be questioned by food and drug authorities, namely Brewer's Yeast!

The role of yeast as an antioxidant and stabilizing agent during an active secondary fermentation or conditioning has been curiously neglected when one considers the strong reducing powers which it possesses and the large surface area, which in a secondary fermentation may amount to as much as 250 square metres per hectolitre of beer, or about 2700 sq. ft./U.K. barrel.

It is the experience of our laboratory that when beers are given a vigorous secondary fermentation or conditioning in storage tank, they are much less liable to oxidation and are more stable.

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