

## REMOVAL OF DISSOLVED OXYGEN FROM WATER: A COMPARISON OF FOUR COMMON TECHNIQUES

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**Summary**—Four common techniques for the removal of dissolved oxygen from water have been examined: boiling at 1 atm, boiling under reduced pressure, purging with N<sub>2</sub> and sonication under reduced pressure. After treatment, the residual oxygen in solution was analysed by the Winkler method. Nitrogen purging for 20–40 min at flow rate of 25 mL/s was found to be the most effective oxygen removal method. Boiling at 1 atm was found to be the least effective. None of the techniques evaluated here lead to complete removal of oxygen. The concentration of residual dissolved oxygen after purging for 20–40 minutes with nitrogen is 0.2–0.4 ppm.

The removal of dissolved oxygen from water is important when experimenting with redox sensitive reagents. For example, it is vital when conducting experiments with metal sulphide systems.<sup>1</sup> Dissolved oxygen can be removed from solution by both chemical and physical means. Chemical methods can be extremely effective. For example, addition of titanium (III) citrate removes dissolved oxygen and poises the  $E_H(\text{pe})$  of a neutral solution anywhere between  $-480$  mV ( $\text{pe} = -8.11$ ) (equilibrium potential reported by Zehnder and Wuhrmann)<sup>2</sup> and  $-300$  mV ( $\text{pe} = -5.07$ ) (Rickard and Oldroyd, unpublished work). Addition of Ti(III) citrate has been used by Butler and Rickard<sup>3</sup> in the synthesis of framboidal pyrite, but it may not be suitable in experiments where titanium ions may catalyse reactions or sorb onto surfaces. In experiments where addition of a redox poise is undesirable, a physical method must be employed to remove oxygen. Although often used, the effectiveness of physical methods is rarely reported. The objective of this study is to evaluate the effectiveness of four physical methods that are in common usage. These are: purging with nitrogen, argon or a similar inert gas,<sup>4</sup> boiling at 1 atm,<sup>5,6</sup> sonication under “vacuum”<sup>7</sup> and boiling under “vacuum”. Other methods that have been used in a few studies, but that are not evaluated here are degassing by passing

water through a gas permeable plastic tube in a vacuum chamber<sup>8</sup> and boiling water while bubbling with nitrogen.<sup>9</sup>

### EXPERIMENTAL

Methods for dissolved oxygen removal were as follows.

#### *Nitrogen purging*

One litre of deionized water was placed in a PTFE stoppered pyrex reaction kettle. A glass bubbler was fitted and the water was bubbled with prepurified grade nitrogen for 5, 20, 40 and 60 min at room temperature. No stirring was used because the mixing caused by the passage of the nitrogen was considered sufficient to keep the water well mixed. Nitrogen was allowed to escape by means of a small vent hole. No air trap was fitted because the high N<sub>2</sub> flow rates made such a device obsolete. The water purged for 20 min with pre-purified grade nitrogen was used to make all analytical reagents for this study; these reagents were preserved under N<sub>2</sub> during the balance of the investigation. The oxygen content of the prepurified nitrogen, according to the distributor, is  $< 5$  ppm. In one set of experiments ultra high purity nitrogen with an oxygen content of  $< 0.5$  ppm was used to purge water for 30 min. The flow rate of the nitrogen was measured by timed collection of the expelled gas in an upturned measuring cylinder full of water. The flow rate used in these experiments was approximately 25 ml of gas

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(at 1 atm) per sec. The deionized water used in this study has a resistance of 18 MΩ.

#### Boiling at 1 atm

One litre of deionized water was placed in a conical flask and boiled for 30 min on a hot plate in open air. The boiling water was then poured into a plastic bottle and the remaining air in the bottle was squeezed out before tightly capping. The bottle was then cooled in running tap water.

#### Boiling under reduced pressure

Five hundred millilitres of deionized water were placed in a stoppered Buchner flask and attached to a hand vacuum pump. A trap was placed between the Buchner flask and the pump to prevent significant quantities of water getting into the pump. After boiling the water for 30 min, the flask was sealed and cooled in running water.

#### Sonication under reduced pressure

The procedure was the same as for boiling under vacuum except that the Buchner flask was placed in a sonic bath and sonicated for periods of both 30 min and 1 hr.

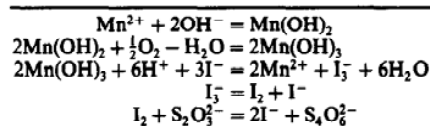
Trace oxygen in water was analysed by a Winkler titration as described by Clesceri *et al.*<sup>10</sup> Addition of Mn(II) sulphate solution plus a strongly alkaline solution of NaI to the system results in the precipitation of manganese hydroxides of higher oxidation states. Iodide in solution is in turn oxidized by the manganese hydroxides to iodine. The amount of iodine produced is in proportion to the amount of oxygen in solution. Iodine was then titrated against a solution of sodium thiosulphate which had been previously standardized against 0.0250N ± 0.0005N iodine solution. The overall reaction scheme for this method is summarized in Table 1.

All water samples for analysis were taken and treated in 250 ml conical flasks with ground glass stoppers. Analysis of the contents of each flask was carried out immediately after treatment.

### RESULTS

The results of this study are summarized in Table 2. The errors given with each oxygen concentration in Table 2 are the random errors due to uncertainties in the experimental

Table 1. Summary of the reaction scheme for the Winkler method. After Hitchman<sup>11</sup>



technique. Reagents were prepared using water purged with nitrogen; when water prepared by that method was analysed it was assumed that any oxygen in the reagents represented neither an addition to, or subtraction from, the system. Thus it is true that any error due to oxygen in the Mn(II) sulphate and NaI solutions is appreciably smaller than the random error and so is negligible.

There is a systematic error present due to oxidation of Mn(II) to higher oxidation states in the solid during storage. This error was found to

Table 2. Oxygen concentrations of deionized water after treatment to remove dissolved oxygen<sup>1</sup>

| Method                                                                    | Time    | Concentration O <sub>2</sub> |
|---------------------------------------------------------------------------|---------|------------------------------|
| N <sub>2</sub> purging<br>(pre-purified grade,<br><5 ppm O <sub>2</sub> ) | 5 mins  | 0.47 ppm ± 0.05 ppm          |
|                                                                           | 5 mins  | 0.56 ppm ± 0.05 ppm          |
|                                                                           | 5 mins  | 0.55 ppm ± 0.05 ppm          |
|                                                                           | 20 mins | 0.35 ppm ± 0.05 ppm          |
|                                                                           | 20 mins | 0.33 ppm ± 0.05 ppm          |
|                                                                           | 20 mins | 0.42 ppm ± 0.05 ppm          |
|                                                                           | 20 mins | 0.34 ppm ± 0.05 ppm          |
|                                                                           | 20 mins | 0.36 ppm ± 0.05 ppm          |
|                                                                           | 40 mins | 0.18 ppm ± 0.05 ppm          |
|                                                                           | 40 mins | 0.23 ppm ± 0.05 ppm          |
| (Ultra high purity<br>grade, <0.5 ppm O <sub>2</sub> )                    | 60 mins | 0.19 ppm ± 0.05 ppm          |
|                                                                           | 60 mins | 0.22 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.28 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.24 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.30 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.28 ppm ± 0.05 ppm          |
| Boiling at 1 atm                                                          | 30 mins | 1.20 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 1.21 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.87 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.93 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.77 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.75 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 1.00 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.85 ppm ± 0.05 ppm          |
| Boiling under<br>reduced pressure                                         | 30 mins | 0.34 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.31 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.31 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.28 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.28 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 0.26 ppm ± 0.05 ppm          |
| Sonication under<br>reduced pressure                                      | 30 mins | 6.92 ppm ± 0.05 ppm          |
|                                                                           | 60 mins | 0.67 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 2.38 ppm ± 0.05 ppm          |
|                                                                           | 30 mins | 1.18 ppm ± 0.05 ppm          |
|                                                                           | 60 mins | 0.55 ppm ± 0.05 ppm          |
|                                                                           | 60 mins | 0.49 ppm ± 0.05 ppm          |

<sup>1</sup>Concentrations derived from analysis of iodine produced directly from oxidation of manganese hydroxides by oxygen. Errors are the random errors due to uncertainty in experimental technique.

be  $+0.05$  ppm  $O_2$ . Hence this represents a systematic over estimation of the  $O_2$  content by  $+0.05$  ppm. The data in Table 2 have been corrected to take this error into account.

### DISCUSSION

Purging with nitrogen appears to be both a quick and effective procedure to scrub deionized water of dissolved oxygen. The optimum duration of the scrubbing at the flow rate used in these experiments is about 30–40 min (Fig. 1). Purging for longer periods, some workers bubble solutions for up to 1 day or more, will not further reduce the oxygen concentration. The kinetics of the degassing process depend upon the gas/liquid interface area, *i.e.* the removal of dissolved oxygen is faster when nitrogen is introduced as small bubbles. Therefore, a sintered glass bubbler to produce small  $N_2$  bubbles is a critical element in a purging setup. The data also seem to indicate that the use of expensive ultra high purity grade nitrogen ( $<0.5$  ppm  $O_2$ ) does not measurably aid the removal of dissolved oxygen from water (Fig. 1). In this investigation no difference was found between the concentration of residual oxygen expected using pre-purified nitrogen ( $<5$  ppm  $O_2$ ) and that observed using ultra high purity nitrogen as the purge gas.

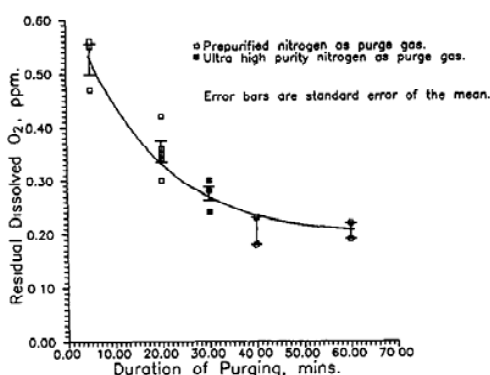


Fig. 1. Residual dissolved oxygen concentration after purging 1 l of distilled/deionized water with nitrogen at a flow rate of 25 ml/sec at 1 atm as a function of time. The initial oxygen concentration of the water was 8.5 ppm (measured with oxygen electrode) and the pH was near neutral. Most depletion occurred in the first 5 min. Further purging for 40 min to 1 hr resulted in a constant residual oxygen concentration of about 0.25 ppm. It is clear from this graph that extended durations of nitrogen purging do not noticeably further reduce the concentration of dissolved oxygen in solution. Purging with ultra high purity nitrogen is no more effective for the removal of dissolved oxygen than purging with purified grade nitrogen.

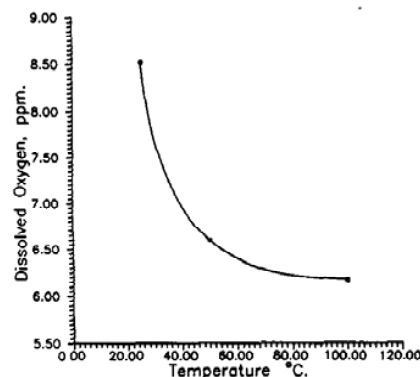


Fig. 2. Equilibrium dissolved  $O_2$  concentration vs temperature. The data are calculated using Henry's law constants taken from the SOLTHERM database.<sup>17</sup> In all calculations it is assumed that  $P_{O_2}$  equals 0.21 atm. At 25°C, the equilibrium  $[O_2]$  is 8.52 ppm, thus  $N_2$  purging for 40 min represents a greater than 40 times reduction in  $[O_2]$ .

Boiling water at 1 atm is probably the most common of the methods under investigation here. The equilibrium concentration of oxygen in water at 100°C in contact with air is 6.17 ppm (calculated using the Henry's law constant for  $O_2$  in water at 100°C<sup>12</sup> and assuming a  $P_{O_2}$  equal to 0.21 atm). This is significantly higher than the values found in this study. Therefore the removal of oxygen by this method clearly is not an equilibrium process. During the boiling process bubbles of water vapour, depleted in oxygen, are produced and it is with these that gas exchange takes place. Dissolved oxygen is entrained in the bubbles and then liberated to the atmosphere at the liquid surface. The liquid surface during vigorous boiling is extremely turbulent and so it is probable that a back reaction is taking place whereby atmospheric oxygen is able to redissolve in the water and is carried back into solution to be available once more for exchange at the liquid/bubble interface. This process may account for both the variability of the analytical results and the relative ineffectiveness of boiling at 1 atm as a method for the deoxygenation of water.

Boiling under reduced pressure is not only an effective method for removal of dissolved oxygen but it is also the most reproducible method studied here. Since oxygen is removed once liberated from the solution, the  $P_{O_2}$  of the gas phase in contact with the water is lower than for boiling at 1 atm. Hence the back reaction (uptake of  $O_2$ ) will be of less importance and removal of dissolved oxygen more effective. More complete deoxygenation could

probably be achieved by the use of a more efficient vacuum pump or aspirator. Water deoxygenated by this method needs relatively little cooling before it can be used and use of a stronger pump would reduce this factor still further.

Sonication was used as an aid to bubble nucleation by Schoonen *et al.*<sup>7</sup> but the present study indicates that the process has little virtue other than to warm the water. Indeed the initial experiment resulted in an oxygen concentration of almost 7 ppm after 30 min; significant deoxygenation was only achieved after the water had reached 45°C. The boiling process produced in the sonic bath is less vigorous than that produced by a hotplate and this may account for the longer duration required for deoxygenation of the water. Clearly the sonication itself is of little value and similar results could probably be obtained using a water bath to maintain an evenly distributed temperature.

It should be noted that the results of this study are in sharp contrast to statements made by Hungate.<sup>13</sup> Hungate has reported that boiling for 1 min results in almost complete deoxygenation and that purging with gas for 30 min to 1 hr is less effective than boiling for this brief period. No raw data was presented by Hungate<sup>13</sup> to back up these conclusions and no final O<sub>2</sub> concentrations were reported. Clearly, from the present study, significantly better removal of dissolved oxygen can be achieved by purging or boiling under vacuum than by boiling at 1 atm.

In summary, the authors recommend use of pre-purified grade nitrogen, a sintered glass bubbler, high gas flow rates and an air-tight container (with a small vent hole to let the purge gas out) for effective removal of oxygen by this method (Fig. 3). This method may be further improved if O<sub>2</sub> is removed from the N<sub>2</sub> gas before passing it through the water. For example, oxygen may be removed by passing nitrogen over hot copper turnings. Nitrogen purging does also have the virtue that the solution is cool and ready for use immediately after oxygen removal, in contrast to other techniques reviewed here. A possible drawback of purging with nitrogen is that there will be nitrogen in solution after oxygen removal. At low temperatures (perhaps <150°C) nitrogen is essentially inert and should not be a factor unless reactions involving nitrogen fixing bacteria occur. However, at higher temperatures (>150°C) dissolved nitrogen may be involved in

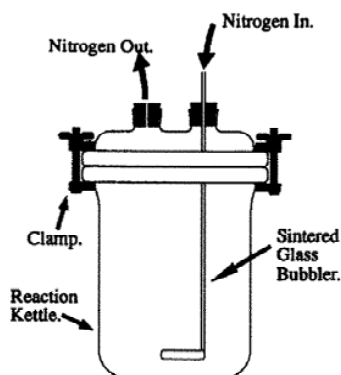


Fig. 3. Apparatus for N<sub>2</sub> purging of 1 l of deionized water. With this set-up it is possible to achieve [O<sub>2</sub>] equal to 0.2 ppm with N<sub>2</sub> purging for 40 min. The sintered glass bubbler is essential to obtain small bubbles, thus maximizing the surface area available for gas exchange. If a high N<sub>2</sub> flow rate is maintained then an O<sub>2</sub> trap is not needed at the gas outlet.

abiotic redox reactions. Thus for hydrothermal experiments, boiling under reduced pressure or perhaps nitrogen purging followed by boiling at reduced pressure should be employed.

It should be emphasized, however, that all the methods reviewed here leave some oxygen in solution and the complete elimination of oxygen from solution is not possible by any of the techniques evaluated in this study. In terms of the redox state of the water, the residual oxygen is significant. For example, 0.25 ppm residual O<sub>2</sub> at 25°C is equivalent to the equilibrium O<sub>2</sub> concentration in contact with an atmosphere with P<sub>O<sub>2</sub></sub> equal to 10<sup>-22</sup> atm. It is clear from Fig. 4 a pe/pH diagram, that even the best physical methods for the removal of dissolved oxygen cannot produce even a mildly reducing solution. Reduced conditions can only be obtained by using a redox poise, such as Ti(III) citrate. However, for some experiments it may be a challenge to find a redox poise that will only react with the dissolved oxygen and not with any other redox sensitive species or surface.

The inability to remove all dissolved oxygen with physical methods has important implications for the field of sulphide geochemistry. For example, the work by Sato<sup>15</sup> indicates that most sulphide minerals would be oxidized by the deoxygenated water produced in this study. Hence, exposure of most sulphide minerals to deoxygenated water is likely to lead to some change in their surface properties.<sup>1</sup> The residual dissolved oxygen becomes particularly important if the system under study has little or no

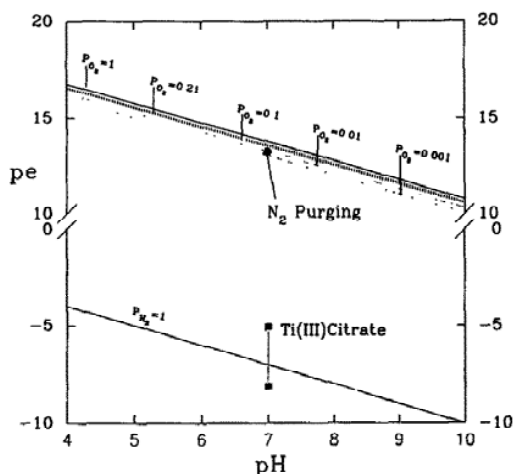


Fig. 4.  $pe$  ( $E_H$ ) vs  $pH$  diagram illustrating the redox state attained via nitrogen purging to remove dissolved oxygen. For comparison, the  $pe$  range obtained by adding a  $Ti(III)$  citrate solution is also shown. The four physical methods evaluated in this study lead to oxygen depleted, but still oxidizing water. Data from Drever<sup>14</sup> were used to calculate this diagram. The diagram was calculated for 298 K and a total pressure of 1 atm. The pressure contours for  $O_2$  and  $H_2$  are given in atm. At 298 K,  $E_H(mV) = 5.9 \cdot pe$ .

redox buffer capacity. For example, in very dilute  $H_2S$  solutions, the remaining  $O_2$  may react with a significant portion of the dissolved  $H_2S$  and radically change the solution  $pe$  ( $E_H$ ) and the sulfur speciation.

Finally it should be noted that although purging with  $N_2$  is an efficient method to remove dissolved oxygen from deionized water, it is a poor method to preserve solutions containing redox-sensitive species. Commercial grade nitrogen contains significant quantities of oxygen (<5 ppm for prepurified grades and <0.5 ppm for oxygen free and ultra high purity grades) and bubbling of  $N_2$  through a solution containing redox sensitive species or minerals represents a constant advection of  $O_2$  through the system. The  $O_2$  in the gas is essentially scrubbed by the solution it passes through and will cause oxidation if bubbling is carried out over extended periods. For example, Pourbaix and Pourbaix<sup>16</sup> have shown, with reference to corrosion and aqueous sulphide systems, that occasional exposure to limited amounts of

oxygen is not necessarily corrosive, but that continuous exposure of  $H_2S$  solutions to traces of oxygen can produce a significant  $pH$  drop possibly leading to corrosion. A better method to preserve such solutions would be to maintain them under a nitrogen or methane atmosphere, so allowing a minimum of exchange with oxygen impurities in the gas.

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