Ozone Water Production without O₃ Gas Emission

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Background

1. Conventional ozone water production systems are dangerous for human body because they emit O₃ gas in a room.

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Gas-phase O₃ concentration at exit of apparatus (ppmv)</th>
<th>O₃ concentration in test room* (ppmv)</th>
<th>Judgment</th>
<th>O₃ concentration in ozone dissolved water (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.2</td>
<td>1.01</td>
<td>Harmful</td>
<td>0.29</td>
</tr>
<tr>
<td>B</td>
<td>5.0</td>
<td>0.51</td>
<td>Harmful</td>
<td>Not detectable</td>
</tr>
<tr>
<td>C</td>
<td>4.3</td>
<td>0.31</td>
<td>Harmful</td>
<td>Not detectable</td>
</tr>
<tr>
<td>D</td>
<td>2.2</td>
<td>0.10</td>
<td>Harmful</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* O₃ concentration after operating each systems for 30 min

2. We have developed a “safe ozone water production system” which does not emit O₃ gas and satisfy the Japanese environmental O₃ gas standards:

- Instantaneous maximum = 0.1 ppmv (0.1 mL/m³)
- 24 h average = 0.05 ppmv (0.05 mL/m³).

Experiment-1

O₃ emission in a closed space

Time dependence of O₃ emission in a 10 cm optical-length cell was measured using ozone water with different dissolved O₃ concentration.

Results: Gas-phase O₃ concentrations exceeded the environmental standards. However, those obtained by adding H₂O₂ showed much lower O₃ concentrations.

Experiment-2

O₃ emission in an open space

Gas-phase O₃ concentrations were measured at 10 or 20 cm above the flow of ozone water with different dissolved O₃ concentration.

Results: Gas-phase O₃ concentrations measured at 10 and 20 cm above the flow of ozone water ranged from 0.1 ppmv, and satisfied the environmental gas-phase O₃ concentration standards. Ozone water with dissolved O₃ concentrations of 1.9 and 2.7 mg/L was found to be safe for use in an open space.

Discussion

1. Safe usage of ozone water

Ozone water is dangerous when it is stored in a closed space, such as polymer-tank and tupperware. Highly concentrated O₃ gas will be formed in the tank. The safest way is to use ozone water with lower concentration than 2.7 mg/L in an open space near a sink.

2. Challenge for higher O₃ concentration in ozone water: Higher concentration of dissolved O₃ than 2.7 mg/L should be possible, if H₂O₂ is added to ozone water (advanced oxidation water).

- H₂O₂ → H⁺ + HO₂⁻ ...(1)
- O₃ + HO₂⁻ → OH⁻ + O₂ + HO₂ ...(2)
- O₃⁻ + H₂O → ·OH + O₂ + OH⁻ ...(3)

3. Reduction mechanism of gas-phase O₃ in advanced oxidation water

Advanced oxidation water with initial dissolved O₃ concentration of 6.8 mg/L and H₂O₂ concentration of 5.8 mg/L showed rapid decrease of dissolved O₃ as shown in Fig. 8. Dissolved O₃ is converted to ·OH radicals in the solution, and the O₃ concentration becomes almost “0” within 100 s.

Conclusion

The safe production and use of ozone water has been studied and 2.7 mg/L ozone water is found to be safe in an open space near a sink. A commercial version of the apparatus has been successfully developed and sold by TOKYO SFR Co. Ltd., as shown in Fig. 9. The IR sensor on the front panel detects human body and ozone water flows for 5 to 10 s.

Reference

Production of Extremely Concentrated O₃ and H₂ Water

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Background

- To replace acidic and alkaline solutions used in semiconductor manufacturing and plastic surface modification processes, ozone water with dissolved O₃ concentration higher than 150 mg/L is required.
- Various methods were investigated to produce such an extremely concentrated O₃ and H₂ water using the water electrolysis cell shown in Fig. 1.
- As a result, "Recycle water electrolysis system" which gradually increases the dissolved O₃ or H₂ concentration in water has been established.

![Fig. 1 Structure of the water electrolysis cell: (a) photograph of the cell having an electrode area of 3 × 6 cm², and (b) inside parts of the cell.](Image)

Experimental

- Flowchart of the apparatus is shown in Fig. 2. All parts were made of Teflon or PFA except for those used in the cathode side.
- 2 L of pure water stored in the recycle water tank was flown at a rate of 1.5 L/min, and water ozonation was repeated in the water electrolysis cell.

![Fig. 2 Flowchart of the recycle water electrolysis system.](Image)

Result-1: Batch operation

Dissolved O₃ concentration of 159 mg/L!

- Extremely concentrated ozone water was obtained in the recycle water tank.
- Time dependence of dissolved O₃ concentration in the batch operation, in which no ozone water was extracted from the apparatus, indicates that the concentration of ozone water reached 159 mg/L as shown in the plots of Fig. 3.
- Absorption spectra of O₃ showed saturation behavior as shown in Fig. 4.

![Fig. 3 Time dependence of dissolved O₃ concentration in the batch operation.](Image)
![Fig. 4 Example of saturated spectra of dissolved O₃ obtained in the batch operation.](Image)

Result-2: Continuous extraction

Ozone water with dissolved O₃ concentration of 112 mg/L was obtained at a flow rate of 0.1 L/min as plotted in Fig. 3.

![Fig. 5 Time dependence of dissolved O₃ concentration in the continuous extraction operation at a flow rate of 0.1 L/min.](Image)

Ozone blue!

Liquid and gas-phases O₃ in the recycle water tank showed ozone blue as shown in Fig. 6, when ozone water with dissolved O₃ of 159 mg/L was produced.

![Fig. 6 Photograph of the recycle water tank. Dissolved O₃ concentration in the tank was 159 mg/L.](Image)

Result-3: Super-saturated H₂ water

Super-saturated H₂ water was produced using the same apparatus as that shown in Fig. 2, when tap water was introduced to the cathode side of the electrolysis cell. Dissolved H₂ concentration of 1.7 mg/L was achieved in the continuous extraction operation of H₂ water at a rate of 0.6 L/min. Moreover, H₂ water with dissolved H₂ concentration of 2.4 mg/L was obtained in the batch operation.

![Fig. 7 Time dependence of dissolved H₂ concentration in continuous extraction operation at 0.6 L/min.](Image)

Discussion

Simulator for recycle water electrolysis

We have developed a simulator to solve O₃ and H₂ mass balance in the recycle water electrolysis system to predict the dissolved O₃ and H₂ concentrations with time. The specifications and operating conditions of the equipment required for increasing O₃ and H₂ concentration in water can be estimated by using this simulator. An example of the experimental and computed dissolved O₃ concentration is shown in Fig. 9.

![Fig. 9 Time dependence of dissolved O₃ concentration estimated from the simulator.](Image)

Conclusion

Extremely high concentrations of dissolved O₃ and H₂ in water were obtained using water electrolysis system: dissolved O₃ concentration reached as high as 159 mg/L in batch operation and super-saturated H₂, 1.7 mg/L, was obtained in continuous extraction operation. Ozone blue indicated that the ozone water was extremely concentrated.

Reference


Acknowledgement

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