Generation of Vapor-Phase Hydrogen Peroxide Test Atmospheres for the Evaluation of Respirator Cartridges and Air Samplers

C.R. (Gus) Manning, PhD, CIH
Hydrogen Peroxide

Common substance with unusual properties

– I have a bottle in the bathroom.
– How bad can it be?
Hydrogen Peroxide
(VHP = Vapor Phase Hydrogen Peroxide)

\[ \text{H}_2\text{O}_2 = \text{HO-OH} \]

**Traditional Uses:**

- **Consumer Pharmaceutical**
  - Antimicrobial

- **Industrial**
  - Oxidizing Agent

- **Aerospace**
  - Propellant (rocket fuel)
H$_2$O$_2$ Regulatory Concerns
(formerly)

- Traditional Uses of H$_2$O$_2$
  - Used Low concentrations (3%)
  - Or, were well-contained

- Small number of exposed employees
Medical Sterilizing Agent

Sterilizing Agent with lower risk profile than
Ethylene Oxide
Glutaraldehyde
Formaldehyde
H$_2$O$_2$ Regulatory Concerns
(new)

Medical Sterilization performed in 1000’s of hospitals, surgical centers, and medical mfg facilities

Sterilization generates high vapor levels
(100’s of ppm)
> 25,000 employees exposed

REL = TLV = PEL = 1.0 ppm
Project Needs

- Evaluate Respirator Cartridges
  - Challenge with levels of VHP near IDLH

- Evaluate Personal Monitoring Methods
  - Expose to VHP Levels near PEL
Goals of Study

- Generate VHP (vapor phase H$_2$O$_2$)
  - from PEL to IDLH or higher
    - PEL = 1 ppm
    - IDLH = 75 ppm

- Detect and Measure H$_2$O$_2$
  - Direct Reading & Personal Sampling
    - 0.1 - 75 ppm
Generating H$_2$O$_2$ Vapor for Testing

(issues)

- Not available in gaseous form
- Available as a 3-50% solution in water
  - Strongly attracted to water
Hydrogen Peroxide
Interactions

$\text{H}_2\text{O}_2$ condenses at 150°C

$\text{H}_2\text{O}_2$ \textit{decomposition} $\rightarrow$ $\text{H}_2\text{O}$ + $\frac{1}{2}$ $\text{O}_2$

$\text{H}_2\text{O}$ condenses at 100°C

50% $\text{H}_2\text{O}_2$ Solution in water boils at 114°C

Heating
Vaporization Methods for Liquids
(3 attempted in this study)

- Equilibration with Heated Liquid
  - Air or N2 stream passes over heated liquid

- Liquid Injection through Heated Needle
  - directly into test air stream

- Liquid Injection into Heated Chamber
  - chamber located in test air stream
Test Air Passes Over Heated Liquid

- Highest Concentration Attainment (> 1,000 ppm)
- Liquid components separate by volatility (boiling point)
- Vaporizes 100% of liquid *(does not separates components)*
- Lowest Concentration Attainment *(1-50 ppm)*
Heated Chamber Vaporization

- Higher Concentration Attainment than Heated Syringe (to 500 ppm)
- Does not separate liquid components (if careful)
Evaluating Respirator Cartridges
(Schematic)
VHP Sampling Methods
Hydrogen Peroxide Challenge Sampling Method

OSHA Method ID 006

- Impinger Containing TiOSO$_4$ Solution
  - TiOSO$_4$ Forms Yellow Complex with H$_2$O$_2$
    - Analysis by UV Spectrometer
    - 0.1 – 150 ppm
  - by varying sampling time
Analysis of H2O2 using OSHA ID 006

H2O2 Calibration Curve

\[ y = 0.0089x \]

\[ R^2 = 0.9964 \]
**H₂O₂ Analysis (high levels)**

**OSHA ID 006 Impinger**

Sampling Rate = 1 L/min; Sampling Time = 2 min
Hydrogen Peroxide
Breakthrough Sampling Methods

- Infra Red Spectrometry
  - Interference by Water
  - FTIR can avoid water interference
    - Cost = $65,000

- Honeywell TLD-1 (Chem Key)
  - Paper tape reading device
  - Reagent forms color with $\text{H}_2\text{O}_2$
    - Measures 0.1-3ppm
Evaluating Respirator Cartridges

(Schematic)
H2O2 Generation
Humidity Effects

![Graph showing H2O2 concentration (ppm) vs. H2O2 added (mg/min) across different humidity levels (25%, 85%, 50%, 100%). The graph includes a line indicating 100% efficiency.]
VHP Vapor Pressure is Limited at High Humidity
Hydrogen Peroxide

Interactions

$\text{H}_2\text{O}_2$ condenses at 150°C

$\text{H}_2\text{O}_2 \xrightarrow{\text{decomposition}} \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$

$\text{H}_2\text{O}$ condenses at 100°C

50% $\text{H}_2\text{O}_2$
Solution in water
boils at 114°C

Heating
Evaluating Respirator Cartridges
(Schematic)
Accuracy of VHP Challenge

Challenge Level vs Testing Time

- VHP Challenge Level (ppm)
- Elapsed Time (hr)
Conclusions

- Vapor Phase Hydrogen Peroxide (VHP) can be generated by injecting 50% aqueous H₂O₂ solution into a heated glass chamber with challenge air passing over.
  - Challenge Levels from 50 - 150 ppm
  - Flow Rates from 50 - 175 L/min

- Vaporization Efficiency decreases as %RH increases
  - 75 ppm (IDLH) can be generated at 85% RH
  - 150 ppm can only be generated with difficulty at higher RH

- Challenge Levels of VHP can be monitored using OSHA ID 006 utilizing TiOSO₄ reagent in a glass impinger.
  - Operating range 0.1 – 150 ppm

- Breakthrough Levels of VHP may be monitored using a Honeywell TLD-1 Analyzer.
  - Operating range 0.1 – 3 ppm
Hydrogen Peroxide

Evaluation of Personal Samplers
Concept of Side-by-Side Sampler Comparison

- MNR Atmosphere Generator
- Chemical Vapor Generator
- Air Intake
- Sampling Tubes
- Diffusive Sampler
- Exhaust Fan
- Sampling Pump
- ChemDisk
- Sampling Tube
Comparison of Samplers

(Hydrogen Peroxide)
Evaluating Air Samplers
(schematic)
Hydrogen Peroxide Personal Sampling Methods

- OSHA Method ID 006
  - Impinger Containing TiOSO$_4$ Solution
    - TiOSO$_4$ Forms Yellow Complex with H$_2$O$_2$
      - Analysis by UV Spectrometer

- Diffusive Sampler (from OSHA Method)
  - Personal Monitoring Badge Containing TiOSO$_4$
    - TiOSO$_4$ Forms Yellow Complex with H$_2$O$_2$
      - Analysis by UV Spectrometer
H$_2$O$_2$ Analysis (low levels)

OSHA ID 006 Impinger

Sampling Rate = 1 L/min;  Sampling Time = 40 min
H$_2$O$_2$ Analysis
Personal Monitoring Badge

Sampling Rate = 90 mL/min; Sampling Time = 4 hour
Vapor Phase Hydrogen Peroxide (VHP) can be generated by injecting 50% aqueous \( \text{H}_2\text{O}_2 \) solution into a heated glass chamber with challenge air passing over.

- Challenge Levels from 0.2 - 10 ppm
- Flow Rates from 50 – 150 L/min

Low Levels of Vapor Phase Hydrogen Peroxide (for TWA personal sampling) were monitored side-by-side using OSHA ID 006 and a Personal Monitoring Badge designed using similar chemistry.

- Operating range 0.1 – 10 ppm
Conclusion

Diffusive Samplers (Personal Monitoring Badges) based on TiOSO$_4$ chemistry perform similarly to the OSHA ID 006 method, but with increased convenience.

- Eliminate need for Glass Impingers
- Operating range 0.1 – 10 ppm
Finis