1. Real-Time Micro-Biocontamination Monitor for Ultrapure Water Systems

Jon Sjogren

Center for Microcontamination Control
University of Arizona
2. **International TIE Project:**
*Detection and Control of Microbiocontamination in Ultrapure Water Processes*

I/UCRC The Queen’s University of Belfast
Environmental Science and Technology Research Centre

**NJIT**
New Jersey Institute of Technology
NSF I/UCRC Hazardous Substance Management Research Center

**University at Buffalo**
State University of New York
NSF I/UCRC Center for Biosurfaces

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**The University of Arizona**
Tucson Arizona
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3. Bacterial contamination concerns all high-purity water users.

- Pharmaceutical companies
- Power-generation facilities
- Microelectronics manufacturers
- Others (medical, bio-product, food, etc.)
4. Contamination by surface-attached (sessile) bacteria is significant.

- The advantage of surface attachment, in the harsh ultrapure water (UPW) environment, causes sessile bacteria to far outnumber the planktonic bacteria found suspended in the water.

- Implications of sessile populations:
  1) sloughing events cause product contamination
  2) sessile bacteria that survive biocide application seed microbial repopulation of water system
5. Current methods of detecting biocontamination are inadequate.

- Usually, only planktonic bacteria are sampled.

- Contamination is underestimated, and efficacy of system sterilization is overestimated.

- No real-time instruments are available for industrial detection of sessile bacteria.
6. A real-time micro-biocontamination monitor is needed.

- Monitor would warn of biocontamination before critical levels occur.
- Monitor would enable corrective measures to be taken before contamination is released.
- Monitor will provide early warning by detecting a protein film that forms on wetted surfaces prior to sessile-bacteria attachment.

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7. Various technologies were considered for monitor.

- Surface Plasmon Resonance
- Resonant Wave Modulation
- Optical Fluorescence
- Optical Interference
8. The micro-biocontamination monitor (MBM) being developed uses optical interference.

![Diagram of MBM](image)

- Coherent light ray
- Superstrate (water)
- Adsorbed protein layer
- Substrate (glass)

\[ \triangle = \text{Difference in pathlength} \]

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9. Protein deposition onto thin film modulates reflected-light interference.

- Maximum and minimum interference of reflected waves occurs at wavelengths ($\lambda$) that are quarter multiples of the thin film’s optical thickness ($nd$; $n = \text{refractive index of thin film}$, $d = \text{thickness of thin film}$):

  $$\text{Reflectance} = R = f\{\cos (4\pi)(nd/\lambda)\}$$

- Attachment of bacterial protein to thin film shifts wavelengths of reflectance-spectrum extremes.
10. Reflectance Spectrum of TiO$_2$ Thin-Film
11. Shift in wavelength of spectral extreme can be estimated using basic interference relationship.

- Thin-film’s optical thickness is related to the order \( m \) in an interference spectrum according to:

\[
\frac{2nd}{\lambda} = m
\]

- For small thickness changes (constant \( m \)), where \( i \) and \( f \) denote the initial and final conditions:

\[
m = \frac{(2n_{i}d_{i})}{\lambda_{i}} = \frac{(2n_{f}d_{f})}{\lambda_{f}}; \quad \text{and,} \quad \frac{n_{i}d_{i}}{n_{f}d_{f}} = \frac{\lambda_{i}}{\lambda_{f}}
\]

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12. MBM Experimental Setup

- Excitation Fiber (transmits light from source to thin film)
- Emission Fiber (transmits reflected light from thin film to spectrometer)
- Bifurcated Fiber Cable
- Glass Slide
- TiO$_2$ Thin Film
- Cap Reservoir (filled with test solution)
13. Protein deposition onto thin film was detected with MBM experimental setup.

- MBM detected deposition of, what was assumed to be, a monolayer of fibrinogen protein (used as a bacterial-protein analogue).

- The minimum-reflectance wavelength ($\lambda_{\text{min}}$) near 512 nm, increased by about 1 nm during 4 hrs contact of the thin film with an 8-ppm fibrinogen solution.
14. Wavelength of minimum reflectance increases as fibrinogen protein attaches to thin film.
15. Additional experiments were done to confirm ability of MBM to detect actual monolayer.

- Fibrinogen monolayer is bound to surface by van der Waals forces, and additional layers are attached by hydrogen bonds.

- Control experiments showed that 10, 5-min UPW-elutions of fibrinogen-contacted surfaces should produce fibrinogen monolayer.

- MBM can resolve at least 0.1 nm shift of $\lambda_{\text{min}}$, and a shift of $>0.5$ nm was seen for fibrinogen monolayer.
16. Fibrinogen monolayer caused a $\lambda_{\text{min}}$ increase of more than 0.5 nm.
17. Control experiments were done to validate measurement.

- Thermal variation of $n_{\text{TiO}_2}$ wasn’t significant; no shift in $\lambda_{\text{min}} > 0.1$ nm was seen for 10 °C decrease in thin-film temperature.

- Light-source drift, heating, and photolytic effects caused no change in $\lambda_{\text{min}}$ that was > 0.1 nm.

- $\lambda_{\text{min}}$ decreased significantly during UPW contact (wetting) of TiO$_2$ thin film, and increased during drying period (air contact).
18. The $\lambda_{\text{min}}$ of the TiO$_2$ thin-film changed with UPW-wetting and air-drying.
19. Drift of $\lambda_{\text{min}}$, during UPW contact, probably not caused by redox or hydrolytic reactions.

- Redox conditions, at pH and $E_h$ of UPW, favor TiO$_2$ stability.

- Hydrolysis of thin film was probably negligible.

\[
\text{HTiO}_3^- + H^+ = \text{TiO}_2 + H_2O
\]

\[
\lg[\text{HTiO}_3^-] = \text{pH} - 18.00
\]
20. Drift of \( \lambda_{\text{min}} \) was probably caused by microporosity of the thin film.

- TiO\(_2\) thin film was deposited by e-beam evaporation.

- Possible that \( n_{\text{TiO2}} \) was changed by the hydration of TiO\(_2\) sites as UPW migrated through micropores.

- Reflectance intensity (R) was observed to decrease and increase, with \( \lambda_{\text{min}} \) decrease and increase, respectively. This would be expected for air and water exchange in the micropores; i.e., R would decrease as water displaced air.
21. Drift of UPW-wetted TiO$_2$ thin films can be addressed in various ways.

- Coat thin film with a material (e.g., protein) that will prevent movement of water into the micropores.

- Use CVD to deposit TiO$_2$ onto substrate.

- Use a material such as PVDF for the thin film. The low $n$ of PVDF can be tolerated by using: a thin film of Ta$_2$O$_5$ at the substrate/PVDF interface, to improve reflectivity; and, a photodiode-array detector, to improve signal resolution.
22. Possible Sensors

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23. Design Options

- Various thin-film materials can be used.
- Software aids include signal averaging and polynomial regression.
- Hardware options include optical-grating modification, photodiode use, and source-light referencing.
24. Conclusions

- Monitor shows promise for industrial use.
- Experiments show ability to detect protein deposition onto thin film.
- Design modifications are available to improve performance.