

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE:

On-line Surfactant Monitoring

AUTHOR(S):

Ken I. Mullen, Everett E. Neal, Patrick D. Soran, Barbara F. Smith

SUBMITTED TO:

IFPAC- International Forum Process Analytical Chemistry
Conference Proceeding

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

MASTER

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED DT

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

On-Line Surfactant Monitoring

Ken I. Mullen, Everett E. Neal, Patrick D. Soran, Barbara Smith

Los Alamos National Laboratory, Chemical Science and Technology Division, MS J569, Los Alamos, NM 87545

Abstract

This manuscript describes a novel device for monitoring surfactants or the foaming potential of a solution. This simple, durable device operates on-line and in real-time. The monitor detects surfactants at low ppm levels. Applications include monitoring the concentration of surfactants in a process stream, an alarm for unwanted foaming, or to meter in anti-foaming agent based on the foaming potential of a solution.

Introduction

Our group has developed a process to extract metal ions from dilute aqueous solutions. The process uses water soluble polymers to complex metal ions. The metal/polymer complex is concentrated by ultrafiltration and the metals are recovered by a pH adjustment that frees the metal ions. The metal ions pass through the ultrafiltration membrane and are recovered in a concentrated form suitable for reuse.

Surfactants are present in one of our target waste streams. Surfactants foul the costly ultrafiltration membranes. It was necessary to remove the surfactants before processing the waste stream. This paper discusses an on-line device we fabricated to monitor the process stream to assure that all the surfactant had been removed. The device is inexpensive and sensitive to very low levels of surfactants.

The most commonly used method for measuring surfactants is described in *Standard Methods for the Examination of Water and Wastewater*. This method involves forming an ion pair with methylene blue (a cationic dye) and the anionic surfactant.¹ The ion pair is extracted into an organic phase. The organic phase is interrogated by UV-Vis spectroscopy to determine the concentration of surfactant. There are reports in the literature describing the automation of this, and similar methods, using flow injection analysis.²

Surface tension measurements could also be used to detect surfactants. However, tensiometers require a vibration free environment, are not simple to use by untrained operators, and are far more expensive than was practical for our application. We needed a simple method for detecting low concentrations of surfactant on-line without the use of hazardous chemicals. Our criteria were that the instrument be simple, inexpensive, dependable, sensitive to very low ppm levels of surfactant, and operate continuously on-line.

The device we developed recognizes surfactants due to their surface active properties, specifically their potential to form foam or bubbles.³ Much of the early research on bubbles and foams was performed in the late 1940s.⁴ The foaming properties of surfactants have been used as a characterization tool.⁵ The Ross-Miles test (ASTM method D1173-53) is the standard procedure applied to evaluating the stability of foams.⁶

Experimental

A diagram of the device we developed is presented in Figure 1. The device is a modified gas washing bottle. A slip stream of the process line flows into the inlet at the top of the bottle. An overflow maintains a constant liquid level. Air, from an aquarium pump, is pumped under the glass frit to generate finely divided bubbles. The air bubbles create a foam in the presence of surfactants or other surface active agents.

The inlet is a glass tee that diverts the incoming stream to the walls of the bottle. This serves two purposes. The inflow washes the walls of the vessel and keeps the optical windows clean. The inflow also serves to suppress the foam and carry it out the overflow. Equilibrium is established between the inflow suppressing and washing away the foam and the air generating more foam. Greater concentrations of surfactant, or surface active agent, result in a higher equilibrium level of the foam.

A light beam is directed through the bottle, above the liquid level. Many suitable optical sensors are commercially available to generate and measure the light beam. These sensors are commonly used to detect parts moving down a conveyor belt. In the single beam application we used a PPA14 series Telco sensor. Since the height of the foam is proportional to the concentration of surfactant, the height of the light beam can be adjusted so the beam is interrupted at a predetermined surfactant level.

We have also used a "light curtain" (Banner Photoelectric Controls). This sensor uses an LED to illuminate an optical fiber bundle. At the other end of the fiber bundle the individual fibers are arranged in a line to create a light curtain. A second line of optical fibers collect the light into a fiber bundle and carry the light to a detector. The Banner sensor reports the amount of light passing through the bottle as a 0-10 volt output. This output is proportional to the portion of the light beam that is blocked by foam, thus the analog output is proportional to the height of the foam.

Results and Discussion

It is difficult to accurately measure the foam height manually as the level of the foam fluctuates around an average height. In the case of a single light beam, the beam is intermittently interrupted as the foam height fluctuates. A Newport P6000 frequency meter recorded the total time that the beam was blocked by foam. A calibration curve of dodecyl sulfate is shown in Figure 2. The ordinate of this graph represents the

total number of seconds the beam was blocked in one minute. The height of the light beam was initially set at the lowest point where the light beam was not interrupted when distilled water was flowing through the system. The first curve, labeled "Zero Height," was recorded with this setting. The light beam was then raised 5 mm and the second curve, labeled "5 mm Height," was recorded. These results demonstrate that a single light beam can be used to signal a critical level of surfactant. Time delays will prevent false readings caused by random fluctuations in the foam height.

A light curtain was used to extend the range of surfactant concentration that can be observed without moving the light beam. A Banner model OASBFX Omni-Beam sensor was used as a light source and detector. The sensor was coupled to an optical fiber bundle configured to form a one and one-half inch "line" of fibers. This allowed us to interrogate a one and one-half inch window through the bottle. This sensor was chosen because it provides an analog, 0-10 volt output. The sensor was configured to read 0 volts when only distilled water was flowing through the bottle and 10 volts when the light curtain was completely blocked.

Figure 3 shows a calibration curve for dodecyl sulfate versus the voltage output from the Banner sensor. Clearly, this configuration provides a much larger dynamic range. The break in the curve at 4 ppm dodecyl sulfate is caused by the overflow. When the foam level rises above the overflow, the foam is not swept out as readily.

This configuration would work well for metering anti-foaming agent into a process stream. The anti-foaming agent would be added "upstream" from the surfactant monitor. This device generates foam so efficiently that it will detect foaming well below acceptable levels for most applications. The height of the light curtain would be set so that an acceptable level of foaming would result in a 5-volt output. If the level of foam rises, as indicated by an increasing voltage, more anti-foaming agent would be metered in. If the voltage falls below 5-volts, less anti-foaming agent would be added. If the level is constant at 5-volts the rate of anti-foaming agent addition would be held constant. This provides a way to meter in exactly the correct amount of anti-foaming agent for economical foam control without waste or excessive chemical treatment.

Conclusion

We have demonstrated a device for monitoring surfactant concentration or the foaming potential of a process stream. The device can also be used to continuously meter in the correct amount of anti-foaming agent.

References

1. Greenberg, A.E.; Connors, J.J.; Jenkins, D.; Franson, M.A.H. *Standard Methods For the Examination of Water and Wastewater, 15th Edition*; American Public Health Association, 1980; p 530-532
2. a) Gallego, M.; Silva, M.; Valcarcel, M. *Anal. Chem.* **1986**, *58*, 2265-2269
b) Canete, F.; Rios, A.; Luque de Castro, D.M.; Valcarcel, M. *Anal. Chem.* **1988**, *60*, 2354-2357
c) Motomizu, S.; Kobayashi, M.; *Anal. Chim. Acta* **1992**, *261*, 471-475
3. Soran, P.D.; Neal, E.E.; Smith, B.; Mullen, K.I. *J. Chem. Educ.*, in press.
4. a) Clark, N.O.; Blackman, M. *Trans. Faraday Soc.* **1948**, *44*, 1-7
b) Clark, N.O.; Blackman, M. *Trans. Faraday Soc.* **1948**, *44*, 7-13
c) Clark, N.O. *Trans. Faraday Soc.* **1948**, *44*, 13-15
5. a) Cohen, L.; Moreno, A.; Berna, J.L. *Tenside, Surfactants, Deterg.* **1992**, *29*(2), 131-134
b) Ohsawa, K. *J. Colloid Interface Sci.* **1983**, *94*, 279-283
c) Calus, W.F.; Davies, J.E. *AICHE J.* **1975**, *21*(3), 599-600
d) Rosen, M.J.; Hua, X.Y.; Zhu, Z.H. *Surfactants Solution* **1991**, *11*, 315-327
e) Hart, J.R.; Degeorge, M.T. *J. Soc. Cosmet. Chem.* **1980**, *31*, 223-236
6. a) Ross, J.; Miles, G.D. *Oil and Soap*, **1941**, *18*, 99-102
b) Rosen, M.J.; Solash, J.J. *Amer. Oil Chem. Soc.* **1969**, *46*(8), 399-402

Figure 1.

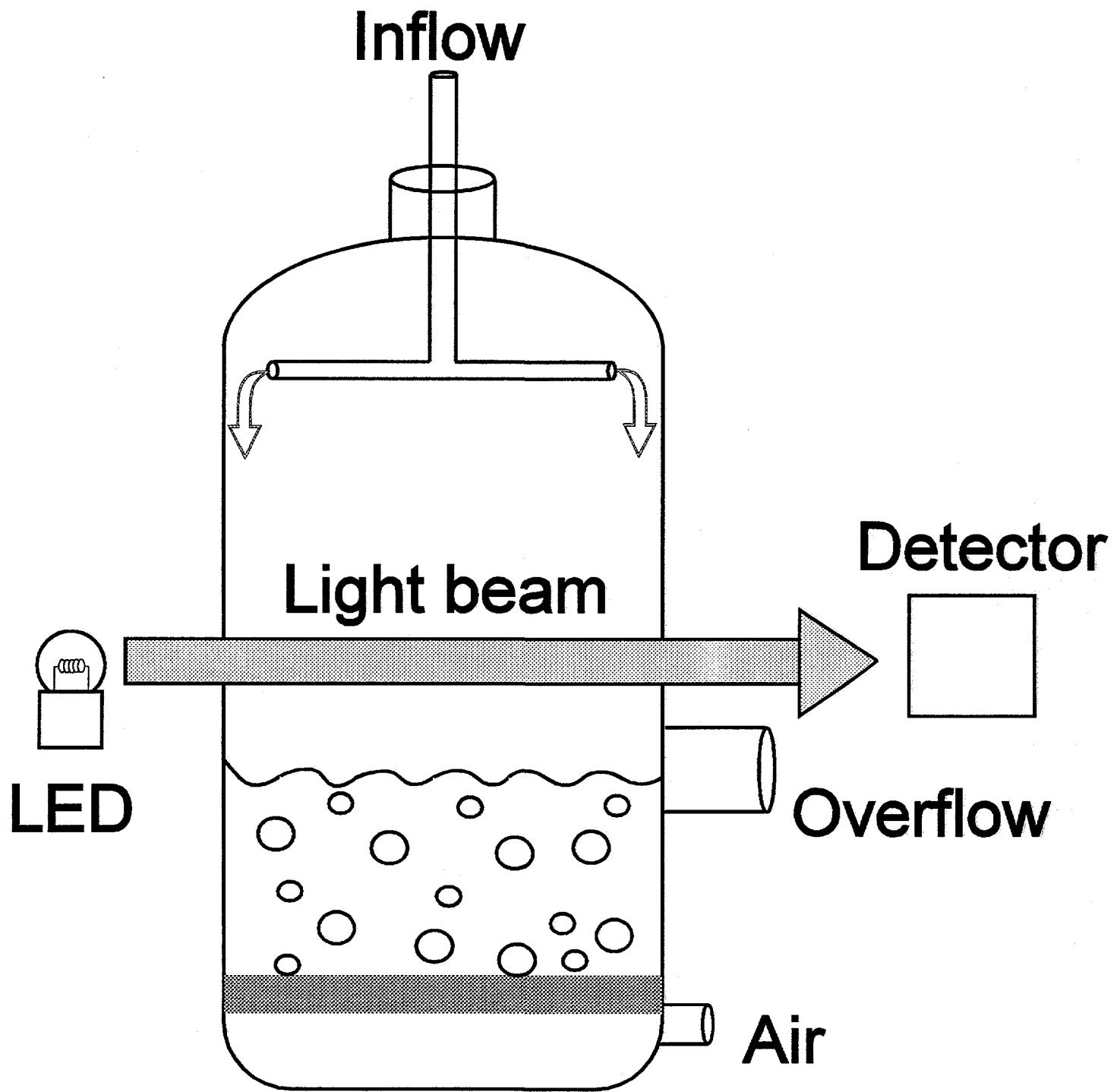


Figure 2.

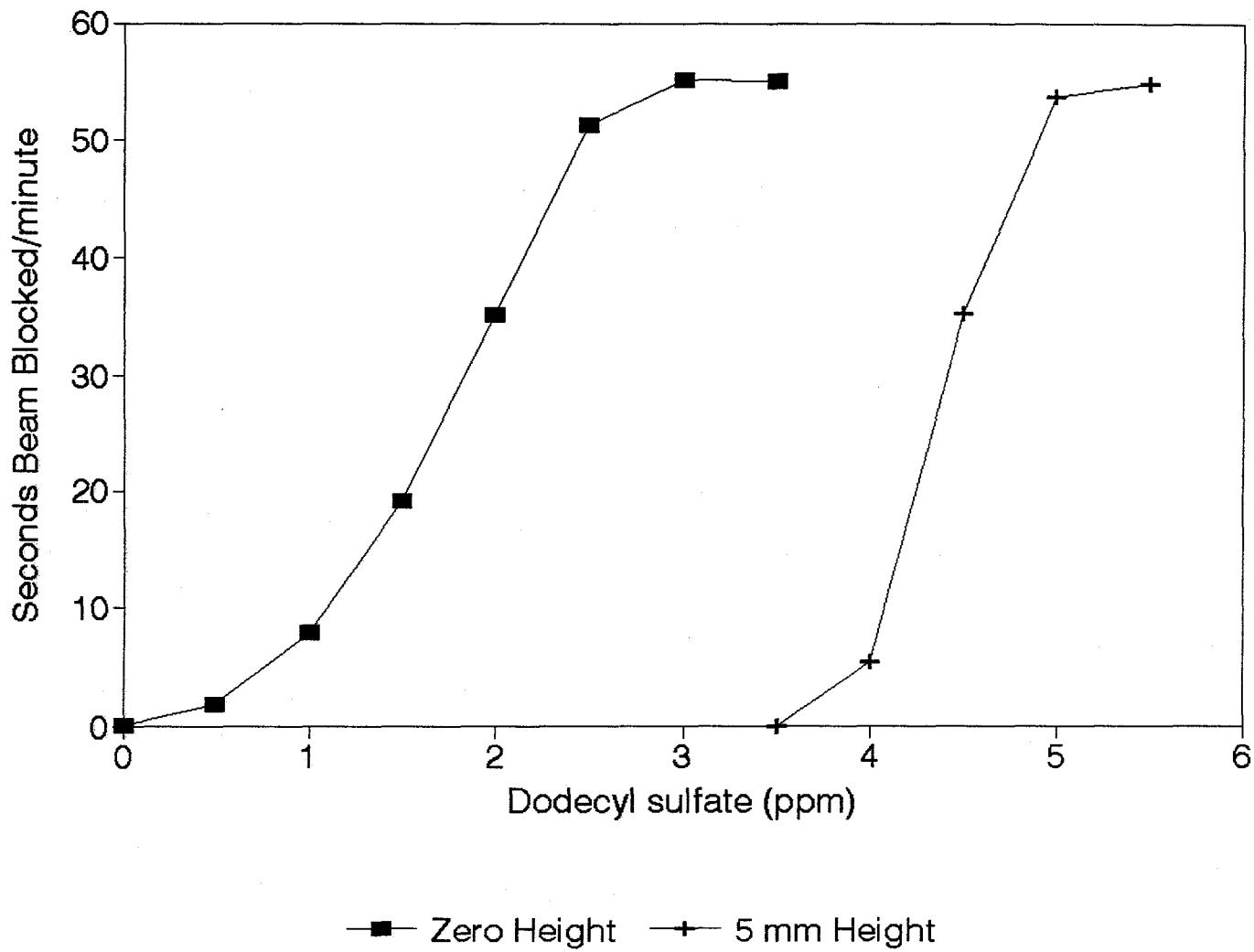


Figure 3.

