HORIBA Scientific

Application Note

Nanobubble Size and Concentration Analysis

AN224

NANOBUBBLE SIZE AND CONCENTRATION ANALYSIS WITH MULTI-LASER NANOPARTICLE TRACKING ANALYSIS (NTA)

Introduction

Nanobubbles are submicron gas-filled cavities in an aqueous medium. By virtue of formulation and manufacturing, they remain suspended in liquid for a long time. There are over 18,000 scientific articles on nanobubbles covering an extensive range of applications. From mitigating the excess toxins in lakes to enhancing the health benefit of your everyday beverages, scrub-free cleaning to wellness and health applications [1], nanobubbles are set to disrupt industrial norms with their unique physiochemical characteristics. See Table 1 for some possible applications. With proper understanding and control of nanobubble formation and stability, applications that are traditionally impossible can now be reached.

	Defined size ranges	Characteristics	Example Applications
Larger Conventional Bubbles	>100 µm	Rise rapidly to surfaces and collapse.	Food and beverages, detergents, recycling, mining.
Micro-bubbles	1-100 µm	Rise slowly and undergo shrinking into nanobubbles [2] or collapse.	Cosmetics, wastewater treatment.
Nanobubbles*	<1 µm	Stay suspended for a prolonged period where diffusion overtakes buoyancy.	Drug delivery, non-viral gene therapy, ultrasound imaging, water purification, oil-water separation, cleaning supplies, food and beverages, cosmetics, agricultural.

Table 1. The overall characteristics and behaviors of conventional, micro, and nanobubbles. [4]

**It should be noted that the term "nanoparticles" often refers to particles smaller than 100 nanometers. As reference, ISO 20480-1 defines bubbles under 1 micron as "ultra-fine bubbles" [4]. Today, nanobubbles that are smaller than 100 nanometers are considered a distinct category in the family of "ultra-fine bubbles".*

Background

There are several ways to create nanobubbles and a few are listed below:

1. Acoustic cavitation/ultrasound
2. High shear mechanical agitation [3]
3. Electrolysis
4. Porous ceramic nano-bubbler [6]

Nanobubble stability depends on five main factors [5]:

1. Van der Waals forces
2. Electrostatic forces
3. Hydration forces
4. Hydrophobic interaction
5. Steric forces

In some cases, in order to increase the stability of the nanobubbles in a liquid, suitable surfactants are used to achieve stable suspension conditions.

This note analyzes carbon dioxide (CO_2) and oxygen (O_2) gas nanobubbles used for pain management to demonstrate multi-laser Nanoparticle Tracking Analysis's (NTA) ability to characterize a mixture of nano and microbubbles without sample manipulation. The results of this analysis, specifically bubble mean size and concentration, helped determine the best techniques and formulation to generate stable gas nanobubbles in distilled water.

Materials and Method

Samples were prepared by a company using a proprietary nanobubbler and formulations. Neither the sample composition nor the bubble generating process were disclosed. Samples were analyzed as received with the ViewSizer 3000 multi-laser Nanoparticle Tracking Analyzer (NTA) to determine bubble size and concentration.

Multi-laser NTA is a novel technique incorporating three lasers with different wavelengths and a color camera to visualize the displacement of particles from 10 nm to 15 microns. Displacement is interpreted as Brownian motion, or, for larger particles, settling or creaming and can therefore be readily converted to particle size for each bubble, allowing high-resolution size distribution analysis.

Figure 1. ViewSizer 3000 cuvette includes a black insert that houses a magnetic stir bar to keep larger particles suspended and mix the particles between videos.

Each sample was transferred directly into the system cuvette without further preparation (Figure 1). In this study, we collected 100 videos per sample. Temperature was controlled at 22°C throughout each measurement.

Results and Discussion

The results in Table 2 below confirmed the existence of nanobubbles in the aqueous environment at concentrations well over 3E+07 nanobubble particles/mL. Using ViewSizer 3000 the manufacturer was able to optimize the process in order to increase the particle concentration from 2.77E+06 particles/mL (Sample A) to 2.90E+07 particles/mL (Sample B).

Sample Name	D10 [nm]	D50 [nm]	D90 [nm]	Mean Size [nm]	Concentration [particles/mL]
A	142	483	1382	605	2.768E+06
B	129	332	1382	542	2.898E+07

Table 2. The characterization of samples A and B using the ViewSizer 3000.

For illustration, Sample B is discussed in detail. An image captured from one of the recorded video frames showed that Sample B nanobubbles have a wide range of sizes (Figure 2).

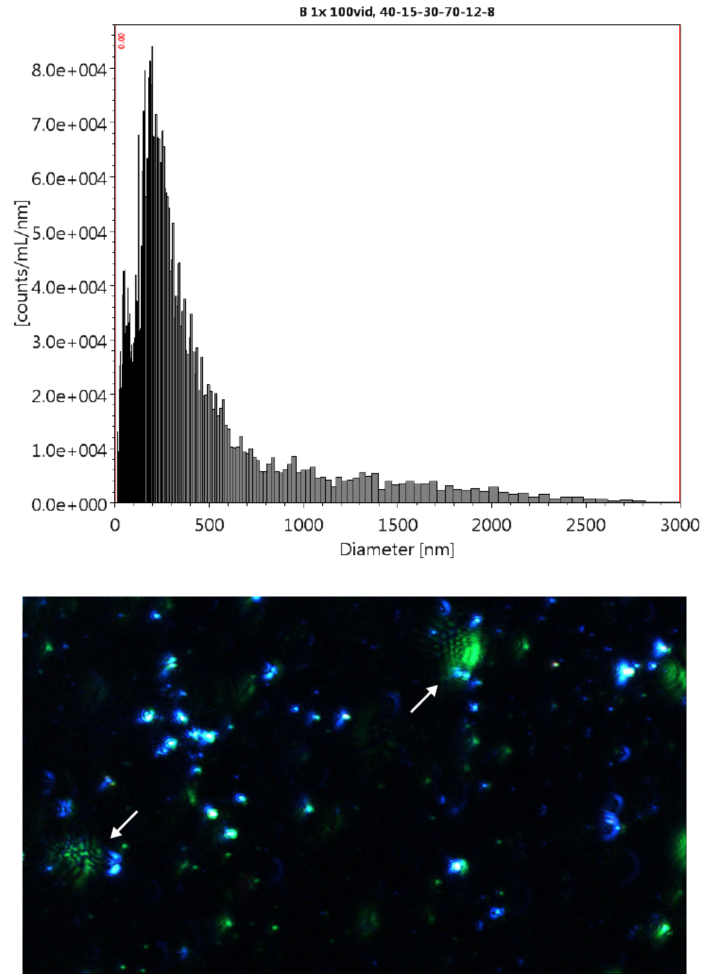

Figure 2. Sample B characterization.

Since NTA is an individual particle-by-particle method, a handful of larger particles did not adversely affect the measurement of the smaller particles like in dynamic light scattering (DLS) measurements. The mean diameter was 542 nm and the total particle concentration was 2.898E+07 particles/mL.

Comparing Sample A with Sample B with respect to the nanobubbles mean size one can observe that the mean size of Sample B is 10% lower than the mean size of Sample A. Larger mean size results in less stable gas nanobubbled aqueous solutions due to the Ostwald ripening effect [7].

Conclusions

The ViewSizer 3000 successfully determined the size, size distribution, and concentration of nanobubbles in suspension. Hence, offering information on nanobubble longevity. The data collected shows that these nanobubbles remain stable in liquid for a long time, from production to shipment to lab analysis. The results from the ViewSizer 3000 also provided insights to improve nanobubbles generation methodology.

References

[1] http://www.periphex.com.

[2] Parmar, Rajeev, and Subrata Kumar Majumder. "Microbubble Generation and Microbubble-Aided Transport Process Intensification—A State-of-the-Art Report." Chemical Engineering and Processing: Process Intensification, vol. 64, 2013, pp. 79–97., doi:10.1016/j.cep.2012.12.002.

[3] Owen, Joshua, et al. "Reducing Tumour Hypoxia via Oral Administration of Oxygen Nanobubbles." Plos One, vol. 11, no. 12, 2016, doi:10.1371/journal.pone.0168088.

[4] ISO 20480-1: 2017 Fine bubble technology — General principles for usage and measurement of fine bubbles — Part 1: Terminology

[5] Nirmalkar, N., et al. "On the Existence and Stability of Bulk Nanobubbles." Langmuir, vol. 34, no. 37, 2018, pp. 10964–10973., doi:10.1021/acs.langmuir.8b01163.

[6] Published Patent US 2019-0060223

[7] https://en.wikipedia.org/wiki/Ostwald_ripening

This document is not contractually binding under any circumstances © 2020 HORIBA Instruments, Inc.