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水および有機液体中の溶存酸素（DO）と酸素ウルトラファインバブル（O_2UFB）

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液体中の溶存酸素（DO）と溶存水素（DH）は極めて僅かな量であるが，ヘリウムイオン化検出器付きガスクロマトグラフィーで正確に測定することが出来る．一方，DOが亜硫酸イオンと反応することは良く知られているが，酸素ウルトラファインバブル(UFB)は亜硫酸とは反応しない．液体中のDOとDHは液体を窒素ガスで曝気すると液体中から揮散してなくなる．しかしO_2UFBとH_2UFBは窒素ガスの曝気によって揮散しない．このようなそれぞれの性質を利用して，種々の液体中のDOとO_2UFBおよびDHとH_2UFBをそれぞれ，分別して定量した．水中のDOとDHの濃度は水の温度が高くなると減少した．しかしO_2UFBとH_2UFBの濃度は温度がかなり高くても殆ど変化しなかった．また水中のDOとDHは水が凍結融解すると，殆ど無くなるのに，O_2UFBとH_2UFBの濃度はわずかに減少しただけであった．植物油やバイオ燃料にH2UFBを分散すると，液体の粘度がかなり低くなり，更にバイオ燃料の酸化安定性が著しく増加した．

Dissolved oxygen (DO) and O_2 Ultrafine Bubbles (O_2UFB) in water and organic liquids

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The trace amounts of dissolved oxygen (DO) and dissolved hydrogen (DH) in liquids could be accurately measured using gas chromatography with a helium ionization detector. While sulfite ions react with DO, O_2 ultrafine bubble (UFB) does not react. DO and DH are volatilized from liquids by nitrogen gas bubbling, but O_2 UFB and H_2 UFB do not volatilize. Utilizing these characteristics, DO and O_2 UFB, as well as DH and H_2UFB, were separately quantified in various liquids. In water, DO and DH decreased with rising water temperature, whereas O_2 UFB and H_2 UFB hardly changed even at higher liquid temperatures. Both DO and DH are rapidly reduced by freeze thaw process, on the other hand O_2UFB and H_2UFB concentrations slightly changed. Furthermore, when H_2 UFB was dispersed in vegetable oil or biodiesel fuel, a decrease in liquid viscosity was observed, along with a remarkable increase in the fuel's oxidation stability.

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表1：水および有機溶媒中のH_2およびO_2の溶解度の温度依存性
Table 1: The effect of temperature on the solubilities of H_2 and O_2 in water and organic solvents (From Chemical handbook)

	H_2				O_2			
	Solubilities (mL/mL)			Change at higher temperature	solubilities(mL/mL)			Change at higher temperature
	0 ℃	20 ℃	40 ℃		0℃	20℃	40℃	
Water	0.0214	0.0182	0.0164	decreasing	0.0489	0.0310	0.0231	decreasing
Ethanol	0.0715	0.0769	0.0840	increasing	0.0426	0.0408	0.0398	decreasing
Ethyl acetate	0.0730	0.0825	0.0915	increasing	0.2488	0.2694	0.2877	increasing

1. Introduction:

Dissolved oxygen (DO) in liquids is an important substance closely related to the origin of life, the treatment of polluted water, and the synthesis of chemicals in liquid-phase reactions.

As is well known, the concentration of DO increases or decreases in proportion to the partial pressure of the gas phase. In addition, dissolved oxygen in water decreases as the water temperature rises and increases as the temperature falls. However, as shown in Table 1, the behaviors of DO and dissolved hydrogen (DH) in organic compounds are different from those in water. In ethanol, DH increases while DO decreases with rising temperature.

In recent decades, ultrafine bubbles (UFBs) have attracted significant attention due to their unique properties. Ultrafine bubbles are gas bubbles with diameters smaller than 0.1 µm dispersed in a liquid (ISO 20480-1, 2017). By definition, a UFB can consist of any gas in any liquid — for example, hydrogen, air, or oxygen in gasoline, biodiesel, or jet fuel; or air, oxygen, ozone, or nitrogen in ethanol or water. In theory, these bubbles should quickly dissolve and disappear due to the high internal pressure resulting from surface tension. However, they can persist in liquids for hours, days, or even months without the need for any chemical stabilizers (Montazeri et al., 2023).

These mysterious and controversial behaviors have yet to be fully understood. Owing to their extremely large surface area and distinctive physicochemical properties, UFBs have found applications in various fields, such as enhancing mass transfer in bioprocesses (Silva et al., 2024), increasing gas–liquid reaction rates (Joseph et al., 2025)., removing organic pollutants from wastewater (Wu et al., 2023), and cleaning (Susanto et al., 2024), among others.

Although UFBs can theoretically be any gas in any liquid, their behavior and stability differ significantly depending on the system. For example, UFBs possess a surface zeta potential that plays a crucial role in their stability. These electrostatic forces prevent bubble collapse and coalescence; however, changes in solvent properties, such as lower pH, can reduce their lifetime. In addition to water-based systems, UFBs also exist in alcohols and fuels (Yuwen et al., 2021; Yang et al., 2025). Moreover, in the case of oxygen UFBs in water, bubble collapse can generate hydroxyl radicals (Soyluoglu et al., 2021), meaning that chemical reactions may influence UFB stability. Consequently, differences in gas and liquid types can affect the physical properties, behavior, and interactions between the solvent and the UFBs (Karimi et al., 2024). The very existence of ultrafine bubbles is still debated in some cases (Ananda et al., 2020) as no method can clearly and precisely determine what is inside the bubble. Some researchers have proposed simple techniques to identify them—such as freezing–thawing cycles or high-frequency ultrasonic irradiation—to distinguish UFBs from non-UFB particles. These techniques are mainly developed for aqueous systems (Kobayashi et al., 2023; Nirmalkar et al., 2018; Yasuda et al., 2019; Tanaka et al., 2021) and do not conclusively prove that gas bubbles are indeed present.

Kenta Kakiuchi (Kakiuchi et al., 2022, 2023) developed an in-house method to measure oxygen content in UFB-containing liquids, obtaining significant results. They found no mass transfer between UFBs and the surrounding liquid; the observed supersaturated oxygen originated from dissolved oxygen during UFB generation. This finding is controversial because, theoretically, a large surface area should enhance mass transfer, and other studies have reported that UFBs can indeed promote gas–liquid transfer (Montazeri et al., 2023; Kizhisseri et al., 2025).

In contrast, Alheshibr M. *et al*. used Resonant Mass Measurement (RMM) to characterize nanoparticles generated from commercial bubble generators and found their density to be 0.95 g/cm³— inconsistent with that of gas. They concluded that the nanoparticles produced were not nanobubbles, casting doubt

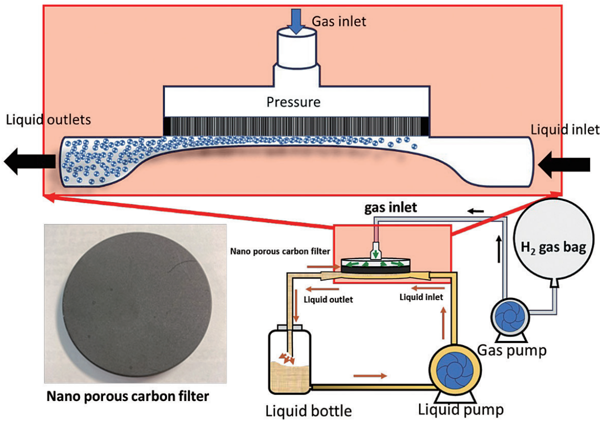

図1：UFBジェネレータ
Figure 1: UFB generator

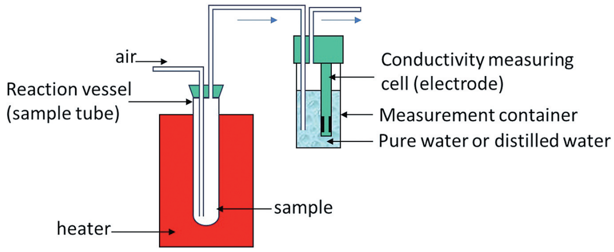

図2：Ransimatシステムによる BDFの酸化速度測定
Figure 2: Oxidation rate measurement of BDF by Ransimat system

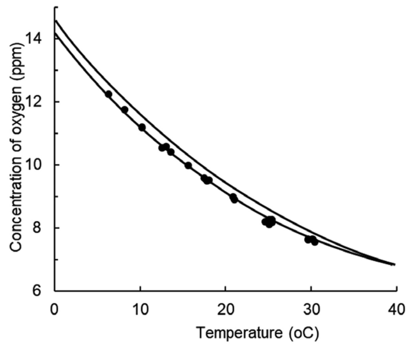

図3：異なる温度における水中のDO測定
A: DOメーター，B: ECD-GC
Figure 3: DO in water measured at different temperature
A: Do meter, B: ECD-GC

on many prior reports concerning UFBs (Alheshibri et al., 2018).

Our research group has conducted studies on UFBs and obtained the following significant findings:

A: The gas within UFBs can be detected using a helium ionization detector, allowing quantitative measurement and confirming that UFBs can persist in liquids for several months.

B: The presence of UFBs in liquids was found to inhibit the dissolution of other gases into the liquid.

In this study, we aim to investigate the differences in the properties and quantities of dissolved gases and gaseous UFBs in various liquids. Furthermore, by dispersing hydrogen UFBs (H_2-UFBs) in biomass fuels, we seek to develop technology that prevents oxidation, fermentation, and spoilage of these liquids. Through these efforts, we aim to enhance the added value of biofuels, whose widespread adoption is being urgently promoted as a measure to mitigate climate change.

2. Experimental

Dissolved oxygen (DO) in water was measured using an optical DO meter (Mettler Toledo Seven2Go Pro). The concentrations of H_2, N_2, and O_2 in liquids were determined by gas chromatography (GC) equipped with a Dielectric Barrier Discharge Ionization Detector (Shimadzu Nexis GC-2030 with GC-BID). Oxygen concentrations in liquids were also measured by GC equipped with an Electron Capture Detector (ECD-GC; Shimadzu GC-2014). Ultrafine bubbles (UFBs) were generated using a Lab-nano-GS-3A-PD51-FA-2109-001 system.

Figure 1 shows the ultrafine bubble (UFB) dispersion apparatus used in this study. UFBs of hydrogen, carbon dioxide (CO_2), and argon, with an average bubble diameter of approximately 100 nm, were introduced into rapeseed oil and biodiesel fuel (BDF, derived from rapeseed oil) using a UFB mixer (model GS-3A73-PD51-FA-2109-001; Nano-Science Laboratory Corporation). The apparatus operates by passing gas through a fine porous carbon filter while the liquid is rotated beneath it.

The concentration of UFBs in the liquids was measured using a light-scattering UFB measurement device (model NBM-L-2020-002; Nano-Science Laboratory Corporation). Polystyrene beads with an average diameter of 100 nm were used for calibration. To ensure accuracy, the same samples were also analyzed using another light-scattering UFB measurement device (model FDLS3000; Otsuka Electronics Co., Ltd.). UFBs were further quantified with a nano-bubble counter (model NBC-2023).

The viscosities of biodiesel fuels were measured using an SV-10 Vibro Viscometer (A&D Company, Japan).

The oxidative stability of rapeseed oil and BDF was assessed using the Rancimat method (see Figure 2) in accordance with EN 14112, the standard method widely adopted in Europe, the United States, and Japan. A 3 g sample of oil or BDF was placed in a reaction vessel and subjected to a constant airflow

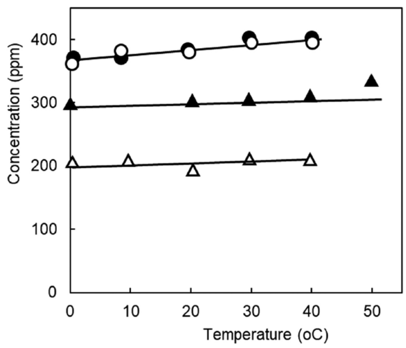

図4：異なる温度におけるアルコール中の溶存酸素（DO）
○）メタノール，●）エタノール，（△）n-プロパノール，
▲）n-ブタノール
Figure 4: DO in alcohols at different temperatures
○) Methanol , ●) Ethanol, (△) n-Propanol , ▲) n-Butanol

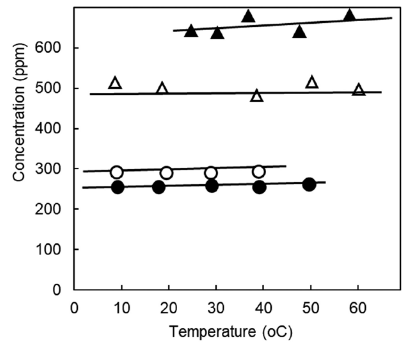

図5：異なる温度における有機溶媒中の溶存酸素（DO）
▲：ヘキサン，△：シクロヘキサン，○：トルエン，
●：ベンゼン
Figure 5: DO in Organic solvents at different temperature
▲：Hexane, △：Cyclohexane, ○：Toluene, ●：Benzene

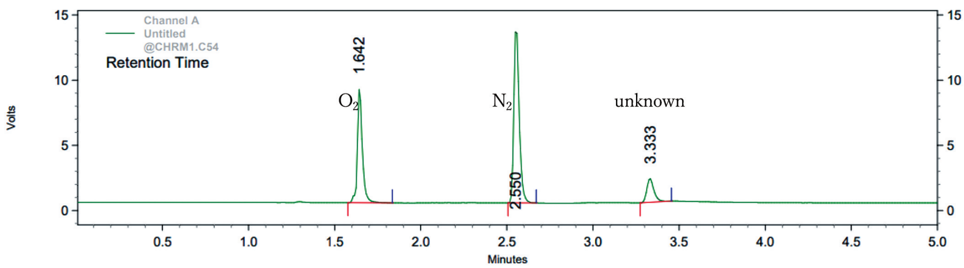

図6：GC-BIDによる純水のクロマトグラム（注入量1μL）
Figure 6: Chromatogram of pure water from GC-BID, 1μL injection volume

of 200 mL·min^{-1} at 110°C. The volatile oxidation products were transported into 50 mL of deionized water, and the increase in water conductivity due to these products was continuously recorded using a conductivity meter (Horiba ES-51, Japan).

3. Results and discussion

3.1 DO measurement by DO meter and GC

As shown in Figure 3, the results of measuring dissolved oxygen (DO) in water using both the DO meter and ECD-GC are in good agreement. In both cases, the DO concentration decreases with increasing water temperature, consistent with predictions based on molecular kinetics. However, as shown in Figure 4 and 5, the DO concentration in various alcohols and organic compounds remains almost constant as the temperature rises, and in some cases, it may even slightly increase. These findings are largely consistent with data reported in chemical handbooks. The magnitude and temperature dependence of DO vary significantly among different types of liquids, following the general order: water < alcohols < hydrocarbons. In contrast, literature data indicate that hydrogen has low solubility in water but dissolves approximately three times more readily in organic substances. Furthermore, the solubility of hydrogen in these organic liquids tends to increase with rising temperature.

Using ECD-GC in this manner, the amount of oxygen contained in ultrafine bubbles (UFBs) can be measured with sufficient accuracy. However, the concentrations of hydrogen and nitrogen in the solutions were previously too low to be measured accurately. In the present study, by employing gas chromatography equipped with a helium ionization detector, it was found that the minimum detectable concentrations of H_2, O_2, and N_2 are below 0.1 nmol, as shown in Table 2 and Figure 6. This improvement enables the simultaneous and reliable measurement of hydrogen, oxygen, and nitrogen in various liquid samples.

3.2 How to separately determine DO and O_2 UFB?

As shown in Figure 7, dissolved oxygen (DO) reacts rapidly with sulfite ions (SO_3^{2-}) but does not react with thiosulfate ($S_2O_3^{2-}$) or dithionite ($S_2O_4^{2-}$). In contrast, oxygen ultrafine

表2：GC-BIDによる大気中の純水のクロマトグラム（注入量1μL）
Table 2: Chromatogram of pure water under atmosphere by GC-BID, 1μL injection volume.

Peak number	Retention time (min)	Area	Area %	Height	Height %
Peak of O_2	1.642	17322	33.537	8678	36.765
Peak of N_2	2.550	29101	56.343	13113	55.554
Unknown peak	3.333	5227	10.120	1813	7.681
Totals		51650	100.000	23604	100.000

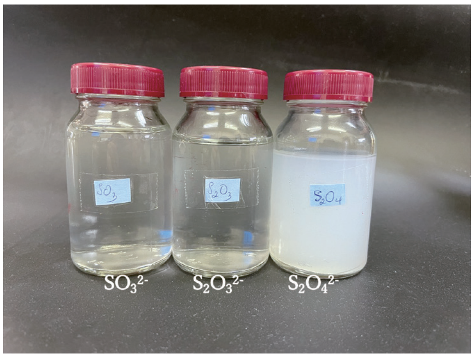

図7：硫黄イオンとDOおよびO_2 UFBの反応
Figure 7: Reaction of Sulfur ions with DO and O_2 UFB

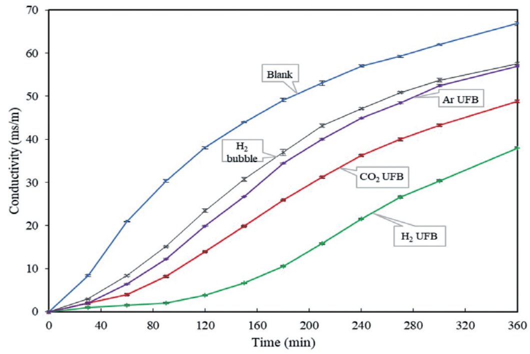

図9：ランシマット法によるBDFの電気伝導率の変化
Figure 9: Variations of electrical conductivity of BDF measured by Rancimat method

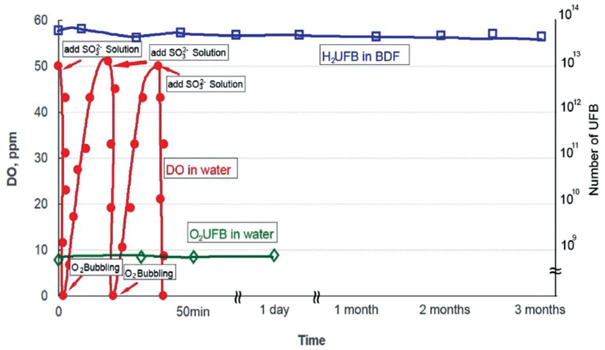

図8：亜硫酸塩はDOおよびO_2 UFBと反応する
Figure 8: Sulfite reaction with DO and O_2 UFB

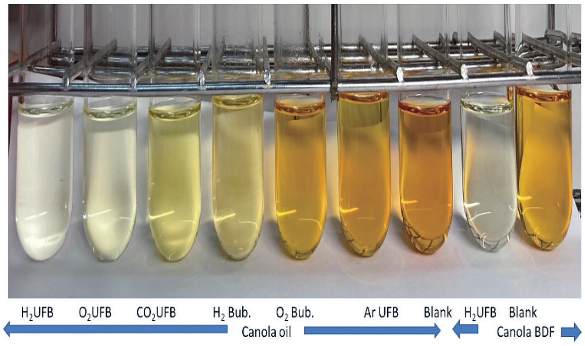

図10：UFB添加油と添加なし油の色変化
Figure 10: Color change of oils with UFB and without UFB

bubbles (O_2-UFBs) do not react with SO_3^{2-} or $S_2O_3^{2-}$ but react only with $S_2O_4^{2-}$. During this reaction, small white solid particles presumably elemental sulfur produced by disproportionation—were observed. As shown in Figure 8, when O_2 gas was bubbled into water, the DO concentration measured by the DO meter increased to approximately 50 ppm. Upon the addition of sulfite ions, the DO concentration immediately decreased to zero, and this phenomenon could be repeatedly reproduced.

On the other hand, the number of O_2-UFBs (8×10^8) remained unchanged throughout the process. From these results, it can be concluded that only dissolved oxygen reacts with sulfite ions (SO_3^{2-}), whereas oxygen ultrafine bubbles (O_2-UFBs) do not.

3.3 UFB in organic compounds

Hydrogen (H_2), oxygen (O_2), carbon dioxide (CO_2), and argon (Ar) ultrafine bubbles (UFBs) were dispersed in vegetable oil and biodiesel fuel (BDF). As shown in Figure 9, the oxidation stability, measured using the Rancimat method, was improved by the dispersion of H_2-UFBs into both vegetable oil and BDF. Furthermore, as shown in Figure 10, the color of the oil did not change after H_2-UFB dispersion, and Figure 11 the viscosity of corn oil became lower compared to that without dispersion. These results indicate that the dispersion of UFBs has the potential to improve the quality and stability of oils and biofuels. This figure demonstrates that the dispersion of ultrafine bubbles (UFBs) affects the viscosity of oils. The addition of hydrogen

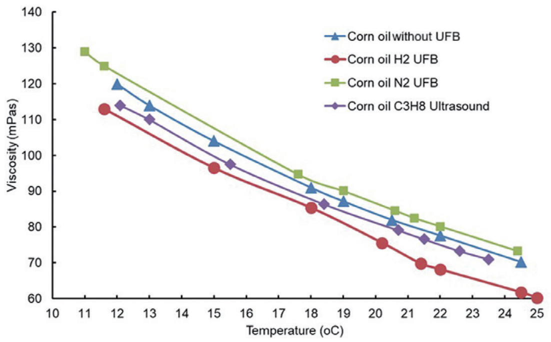

図11：UFB添加によるキャノーラ油の粘度変化
Figure 11: Viscosities of canola oil dispersed by UFB

UFBs (H_2-UFBs) decreases the viscosity, whereas the addition of nitrogen UFBs (N_2-UFBs) results in an increase. The reason for these contrasting effects of H_2-UFBs and N_2-UFBs on viscosity is currently under investigation.

4. Conclusion

In this study, the behaviors of dissolved gases and gaseous ultrafine bubbles (UFBs) in water and various organic compounds were investigated using highly sensitive gas chromatography equipped with a helium ionization detector, as well as through reaction analyses with different sulfur compounds. The results revealed distinct differences between dissolved oxygen and oxygen UFBs, indicating that gaseous UFBs exhibit unique physicochemical properties compared with conventional dissolved gases. Furthermore, when hydrogen, oxygen, argon, and carbon dioxide UFBs were dispersed into vegetable oils and biofuels, a marked reduction in viscosity and a significant improvement in oxidative stability were observed. These findings demonstrate the potential of UFB dispersion as a promising technique for enhancing the quality and durability of oils and biofuels, contributing to future developments in clean and sustainable energy materials.

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