

Fluorescence Imaging of Concentration Fields of Dissolved Gases at Water Interfaces

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Abstract Characterization of materials at interfaces includes also transfer processes taking place there. This is an ubiquitous phenomenon in the environment, technical processes, and living species. Because at least one of the two phases at the interface is mobile, these processes are characterized by a complex interplay between molecular diffusion and turbulent transport. In this paper, a new technique is introduced for fluorescence imaging of the mass transfer across the air-water interface.

Keywords Fluorescence Imaging, Interface, Mass Transfer

1 Introduction

The characterization of materials by optical techniques, as it was presented at all previous OCM conferences [1] contains a wide range of material properties, wavelengths from x-rays to thermal infrared, and a remarkable wealth of different optical effects, e. g., the refractive index, reflectance, emission, absorption, fluorescence, elastic and inelastic scattering. With this wealth of techniques quite different material properties can be investigated. This includes the concentration of various chemical species, classification of different materials for sorting, 3-D surface shape and surface contamination, to name just a few.

Dynamic material properties are so far missing. An important class of dynamic processes is the exchange of mass across the interface from one medium into another. Here the question is how fast is this process

and which factors are controlling its mechanisms. At first glance this property might appear quite exotic, but it is actually an ubiquitous process:

Environment In environmental sciences, the exchange of mass between the compartments of the planet earth, i.e., land, oceans, lakes, rivers, and atmosphere is an important process [2]. What controls evaporation from water or land surfaces? How much of the climate relevant gas species emitted by human activities into the atmosphere are transferred into oceans, biosphere and finally into sediments? The most prominent example of this kind is the global carbon cycle.

Engineering In chemical engineering transfer processes are relevant for any gas-liquid, gas-solid, liquid-liquid (immiscible liquids) and liquid-solid reactions. Here the essential question is how to design the corresponding systems in order to maximize the transfer rate and to increase the efficiency [3].

Biology Any living species requires food in order to win energy and to take in the required chemical species to live and grow. Plants transport water and minerals from the soil via roots and xylem to leaves, where they take up carbon dioxide and convert it by photosynthesis into organic material. Animals take up oxygen via lungs or gills. Oxygen carried by blood cells is transported with the blood flow to reach finally each cell, where oxygen is taken as a energy source for metabolism. Waste of the cell metabolism, including carbon dioxide, has to be transported away, and is often chemically converted and finally segregated.

Common to all these processes is that they are of complex nature because of two basic facts. Firstly, the transport is often accompanied by chemical reactions. Secondly, at least one of the two phases at the interface is not solid. Therefore mass is not only transported by molecular diffusion but also by flow. Except for microfluidic systems, the flow is turbulent. This gives rise to viscous boundary layers at the interface, in which molecular diffusion is dominant. Outside of the boundary layer, the transport is controlled by turbulent velocity fluctuations.

In the past, most measuring techniques for mass transfer were non-imaging and non-optical. But already almost forty years ago, it be-

came evident that only contactless imaging techniques can resolve the mechanisms controlling them [4, 5]. From 2005–2015 the joint DFG research unit GRK 1114 “Optical Techniques for Measurement of Interfacial Transport Phenomena” of the Technical University Darmstadt and Heidelberg³ helped to advanced imaging techniques.

In this paper we focus on one of the most complex problem, the gas transfer across air-water interface, which is undulated by wind waves. Under these conditions, the aqueous mass transfer boundary layer, which is the bottleneck for the transfer, is just 10–350 μm thick [6]. Therefore it is obvious that absorption techniques will not work, but fluorescence imaging may work. Nevertheless, serious experimental challenges have to overcome even in laboratory facilities:

1. The concentration of a gas dissolved in water has to be made visible by a suitable fluorescence technique.
2. The fluorescence intensity of the thin layer will be weak and because of the fast movements of the water surface by waves and the shear flow only sub-ms exposure times are possible. Therefore very bright light sources and sensitive cameras are required.
3. Since sub-mm structures have to be resolved, it is impossible to focus over the range of height variations caused by wind waves. Therefore either a wave-following imaging system or permanent refocusing is required.

The paper is organized as follows. After a brief historic description of fluorescence imaging for mass transfer in Section 2, the basic principles of a newly designed and optimized fluorescence technique are explained (Section 3) and first test results from a small linear wind-wave facility are shown (Section 4). The paper closes in Section 5 with an outlook on the planned setup at the large Heidelberg Air-Sea Interaction Facility, the Aeolotron⁴ and 4-D (3 spatial and one time coordinate) imaging of the imaged concentration fields.

³ <https://gepris.dfg.de/gepris/projekt/462057?language=en>

⁴ <https://www.youtube.com/watch?v=UN0WLx90w9Q&t=25s>

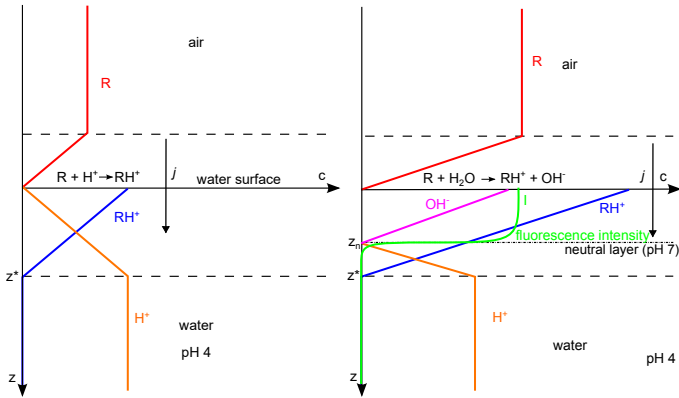


Figure 1: Sketch of the boundary layer thickness imaging technique proposed by Hiby, when an alkaline gas is absorbed by an acid liquid: low flux density with neutral layer at the surface (left) and higher flux with the neutral layer within the mass boundary layer (right).

2 Historical development

To the best knowledge of the authors, the chemical engineer Julius W. Hiby (RWTH Aachen) was the first to use fluorescence imaging for mass transfer studies. He studied absorption of acid or alkaline gases in falling films and reported already in 1966 the usage of fluorescent dyes which are either only fluorescent in the alkaline or acid region [7]. His work was widely overlooked because he published only a few German language papers and just a single late English publication in 1983 [8].

Figure 1 illustrates the fluorescent technique proposed by Hiby. In order to explain the basic idea, it is sufficient to assume that a) the mass boundary layers on both sides of the interface are layers of constant thickness with only molecular diffusion taking place there and b) the process is stationary with a constant flux density j from air to water. Outside of the boundary layer the turbulent mixing should be so strong that the concentrations are constant. This simplification is known as the film model.

The water is slightly acid (pH 4) and a low concentration of an alkaline gas R is put into the air space. At the acid interface it reacts

with the H^+ -ions. Therefore the concentration of the gas $[R]$, is zero at the water surface forcing a constant flux density j , which is given according to Fick's first law for stationary diffusion as

$$j = \frac{D_a}{z_a} \Delta c = k_a [R]. \quad (1)$$

The quantity k has the dimension of a velocity and is known as the *transfer velocity*, D_a the diffusion coefficient of R in air, and z_a the thickness of the mass boundary layer in air. The H^+ -ions are converted at the interface into RH^+ -ions. Therefore a coupled counter diffusion takes place in the aqueous mass boundary layer: H^+ -ions diffuse upwards and RH^+ -ions downwards. The left figure shows the limiting condition, when the H^+ -ions become zero at the interface. Because the flux density j remains constant

$$j = \frac{D_w}{z_w} \Delta c = k_w [RH^+] = k_w [H^+]. \quad (2)$$

If the concentration of R is further increased, no more H^+ -ions are available at the water surface and the alkaline gas now reacts with water to produce OH^- -ions. These ions diffuse downwards and at a neutral layer within the boundary layer react with the H^+ -ions to water again (left part of Figure 1). Assuming that the coupled diffusion coefficients remain the same, half of the boundary layer thickness becomes alkaline, if the concentration of R is the double of the limiting case shown in the left figure. With a pH indicator which fluoresces only in the alkaline region, the total fluorescence intensity is then proportional to the alkaline fraction of the boundary layer thickness.

In this way, the thickness of the mass boundary layer can be measured by the fluorescence intensity. Fluorescence starts, when the H^+ -ion concentration becomes zero at the interface. By comparing Eqn. (1) and (2), the concentration in the air space must reach the following value

$$[R] = \frac{k_w}{k_a} [H^+]. \quad (3)$$

At a pH value of 4 the H^+ -ion concentration is 10^{-4} Mol/L. Because of the much slower diffusion in liquids, k_w is typical three orders of

magnitude lower than k_a . Therefore fluorescence starts already at air concentrations of R higher than about 10^{-7} Mol/L, which corresponds to a partial pressure of only 2.5 ppm (parts per million). Therefore this technique is remarkably sensitive.

However, it has also two significant disadvantages:

1. The transfer process is governed by an interplay between turbulent and molecular transport. Therefore it is not stationary. This means that in regions where k_w is significantly higher than the average, there will be no fluorescence at all and it can not be determined how large the transfer velocity is in this regions.
2. The concentration of the dye must be at least an order of magnitude lower than the H^+ -ion concentration. Otherwise the dye would no longer be an indicator but influence the chemical reactions. The low indicator concentrations hindered so far, to perform measurements at higher wind speeds where the mass boundary layer is correspondingly thin and therefore the fluorescence intensity is too low.

3 Basic principle of the new pH indicator method

In order to overcome the weaknesses of previous techniques, a new pH indicator method has been developed [9,10]. Its principle is based on a direct chemical reaction with the indicator itself. When an alkaline trace gas R enters the water, it immediately undergoes an acid-base reaction with the pH indicator IH at the water surface



In this way an invisible gas R is replaced at the air-water interface by the alkaline form of the fluorescent dye I^- , which diffuses together with RH^+ across the boundary layer (Figure 2). Two basic prerequisites must be met for the technique to work:

1. The concentration of the fluorescent dye has to be much higher than those of the H^+ and OH^- -ions. This ensures for the alkaline trace gas to predominantly deprotonate the pH indicator according to reaction (4).

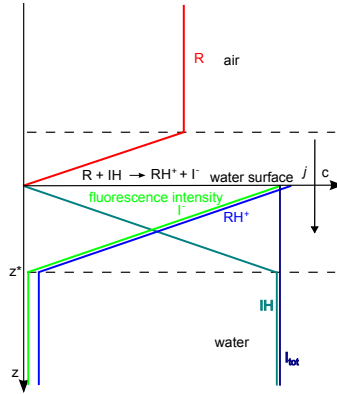


Figure 2: Sketch of the new fluorescence imaging with a sufficient high pH indicator concentration to replace a trace gas via an acid-base reaction at the surface.

2. The pK value of the trace gas should be significantly above the pH value in the water-sided boundary layer to guarantee all gas molecules are protonated when dissolving in the water and the equilibrium of reaction (4) is strongly on the left side.

Both conditions jointly result in a linear relationship between the concentrations of the trace gas dissolving in water and the pH indicator's alkaline form

$$[I^-] \propto [R]_w. \quad (5)$$

For experimental realization of the requirements on the new chemical system, we work with an indicator concentration $[I_{\text{tot}}]$ of about 10^{-4} Mol/L. Then in a pH range from 5 to 9

$$[I_{\text{tot}}] \gg [H^+], [OH^-]. \quad (6)$$

The fluorescent dye pyranine (Trisodium 8-hydroxypyrene-1,3,6-trisulfonate) has proven to be ideal, with a pK value close to the neutral range. We determined the pK value to 7.89 ± 0.01 from absorption measurements of pyranine (Figure 3). Compared to the formerly used ammonia [9] with pK = 9.24, ethylamine and other amines are planned to be used instead, as they have the advantage of a significantly higher alkalinity with a pK value larger than 10.6.

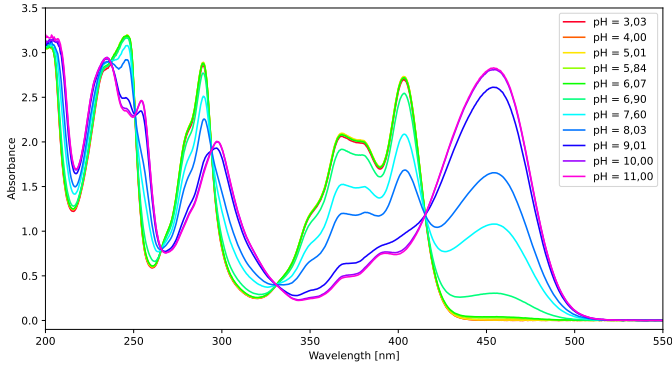


Figure 3: Absorption spectra of a 10^{-4} molar pyranine solution at pH values as indicated. Only the alkaline form of pyranine absorbs in the range of 440–500 nm.

4 First results

In a measurement the pH value of the water is initially adjusted to 5, causing a large proportion of the pyranine to be in its acidic form IH. Subsequently, an alkaline gas is added to the gas space, which increases the alkaline form of pyranine I^- as it invades into water.

Both forms of pyranine are fluorescent, but only the alkaline form absorbs light at wavelengths larger than 440 nm (Figure 3). Therefore the fluorescence will be according to Eq. (5) proportional to the concentration of the dissolved gas, when fluorescence is excited at 450 nm. At the starting pH value of 5 about a permille of pyranine is already existent in its alkaline form, so the water bulk generates a non-negligible background fluorescence. To suppress this, the dye tartrazine is additionally added, which absorbs the excitation light and prevents it from penetrating into deeper water layers. Consequently, the detected fluorescence pattern displays only the concentration fields of the gas in the uppermost centimeter of the water-side boundary layer.

The new method has already been tested in a small linear wind-wave facility and proven to work as expected. With increasing flux density j of the alkaline gas, the patterns just get brighter, but there is no threshold effect as with the Hiby method (Figure 4).

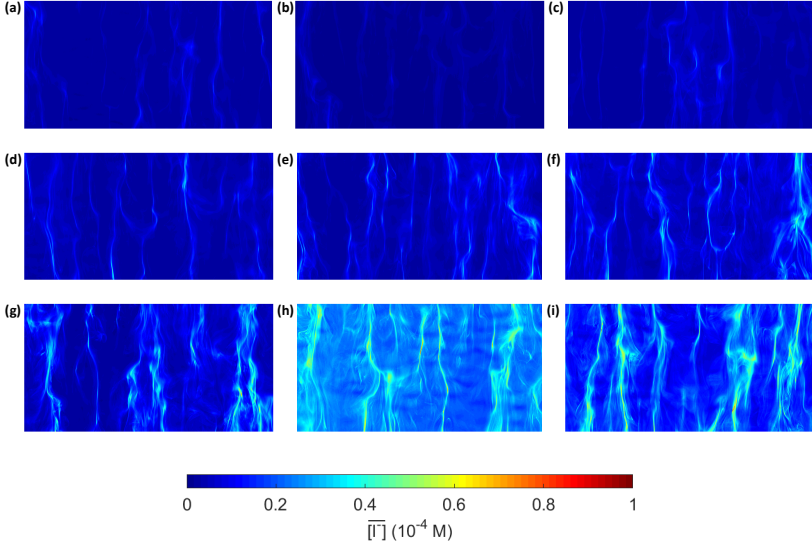


Figure 4: Example images taken in a small linear wind-wave facility with the new pH indicator method [9]. The applied flux of the alkaline gas ammonia increased from images (a) to (h) and started to decrease again at image (i).

5 Outlook

The technique is ready to be used in the Heidelberg Aeolotron, an annular wind-wave-facility 10 m in diameter [11]. The fluorescence is stimulated by four light sources radiating from above through a glass window onto the channel's water surface with a total optical peak power of 250 W irradiating about 0.25 m^2 at the water surface. Seven Lucid Vision Atlas 10GigE ATX051S cameras image the fluorescence patterns at the water surface from underneath through a bottom glass window at 500 fps and a resolution of 1224×1024 pixel.

This arrangement makes 3-D imaging possible to reconstruct the shape of the water surface as well and to distinguish the thin boundary layer at the water surface from structures swept down into the bulk water by surface renewal events. A light field imaging approach, similar to the technique of Wanner and Goldlücke [12] to separate reflective and transparent surfaces, will be used.

References

1. J. Beyerer and T. Längle, Eds., *OCM 2021 - Optical Characterization of Materials: Conference Proceedings*. KIT Scientific Publishing, 2021.
2. P. S. Liss and M. T. Johnson, Eds., *Ocean-Atmosphere Interactions of Gases and Particles*. Springer, 2014.
3. H. D. Baehr and K. Stephan, *Wärme- und Stoffübertragung*, 10th ed. Springer, 2019.
4. B. Jähne, "Transfer processes across the free water interface," Habilitation thesis, Institut für Umweltphysik, Fakultät für Physik und Astronomie, Heidelberg University, 1985.
5. B. Jähne, "Impact of quantitative visualization and image processing on the study of small-scale air-sea interaction," in *Air-Water Gas Transfer, Selected Papers, 3rd Intern. Symp. on Air-Water Gas Transfer*, B. Jähne and E. Monahan, Eds. Hanau: AEON, 1995, pp. 3–12.
6. B. Jähne, "Air-sea gas exchange," in *Encyclopedia of Ocean Sciences*, 3rd ed., J. K. Cochran, H. J. Bokuniewicz, and P. L. Yager, Eds. Academic Press, 2019, vol. 6, pp. 1–13.
7. J. W. Hiby, "Eine Fluoreszenzmethode zur Untersuchung des Transportmechanismus bei der Gasabsorption im Rieselfilm," *Wärme- und Stoffübertragung*, vol. 1, pp. 105–116, 1968.
8. J. W. Hiby, "The chemical indicator: a tool for the investigation of concentration fields in liquid," *Ann. N. Y. Acad. Sci.*, vol. 404, pp. 348–349, 1983.
9. M. Papst, "Development of a method for quantitative imaging of air-water gas exchange," Master's thesis, Institut für Umweltphysik, Universität Heidelberg, Germany, 2019.
10. D. Hofmann and B. Jähne, "Imaging of concentration fields within the mass boundary layer," in *Air-Water Gas Exchange: Cross-linking field measurements, laboratory measurements and modeling*, B. Jähne, K. E. Krall, and C. Marandino, Eds. Heidelberg University Publishing, 2023, in press.
11. K. E. Krall and B. Jähne, "Annular wind-wave tanks," in *Air-Water Gas Exchange: Cross-linking field measurements, laboratory measurements and modeling*, B. Jähne, K. E. Krall, and C. Marandino, Eds. Heidelberg University Publishing, 2023, in press.
12. S. Wanner and B. Goldlücke, "Reconstructing reflective and transparent surfaces from epipolar plane images," in *Pattern Recognition*. Springer, 2013, pp. 1–10.